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Position Paper on Gas Generation in the Waste Isolation Pilot Plant

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ABSTRACT

Gas generation by transuranic (TRU) waste is a significant issue because gas will, if produced in significant quantities, affect the performance of the Waste Isolation Pilot Plant (WIPP) with respect to Environmental Protection Agency (EPA) regulations for the long-term isolation of radioactive and chemically hazardous waste. If significant gas production occurs, it will also affect, and will be affected by, other processes and parameters in WIPP disposal rooms. The processes that will produce gas in WIPP disposal rooms are corrosion, microbial activity and radiolysis. This position paper describes these processes and the models, assumptions and data used to predict gas generation in WIPP disposal rooms.

MASTER

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1.0 EXECUTIVE SUMMARY

Gas generation by transuranic (TRU) waste is a significant issue because gas will, if produced in significant quantities, affect the performance of the Waste Isolation Pilot Plant (WIPP) with respect to Environmental Protection Agency (EPA) regulations for the long-term isolation of radioactive and chemically hazardous waste (see 2.1). (In this report, "gas generation" refers to both production and consumption of gas.)

If significant gas production occurs, it will also affect, and will be affected by, other processes and parameters in WIPP disposal rooms (see 2.2). These include: (1) the H_2O content of the repository; (2) room closure; (3) the chemical conditions that affect the actinide source term; (4) transport and, perhaps, generation of VOCs.

The processes that will produce gas in WIPP disposal rooms are: (1) corrosion (see 2.3.1 and B.1); (2) microbial activity (see 2.3.2 and B.2); (3) radiolysis (see 2.3.3 and B.3). From the standpoint of expected gas-production rates, the most important processes are corrosion and microbial activity. Radiolysis will not produce gas at rates comparable to those expected for corrosion and microbial activity. Gas-consuming processes include reaction with cementitious materials and dissolution in brine (see 2.3.4).

Oxic corrosion (oxidation of metals by molecular O_2) of steels and other Fe-base alloys will significantly affect the O_2 content of WIPP disposal rooms but not the overall gas content of the repository or its H_2O content (see 2.3.1 and B.1.1). After depletion of the O_2 initially present and in the absence of radiolytically produced O_2, anoxic corrosion (oxidation of metals by H_2O or H_2S) of steels and other Fe-base alloys will produce significant quantities of H_2 and consume significant quantities of H_2O if: (1) sufficient H_2O is present; (2) significant microbial activity (resulting in passivation by microbially produced CO_2 or H_2S) does not occur; (3) in the event of microbial activity, consumption of CO_2 by reaction with cementitious materials or other processes depassivates steels and other Fe-base alloys. Anoxic corrosion of Al and Al-base alloys will produce significant quantities of H_2 and consume significant quantities of H_2O if sufficient H_2O is present. Subsubsection 2.3.1 and B.1.2 describe anoxic corrosion in detail.

Microbial consumption of substrates such as cellulosics and, perhaps, plastics and rubbers will produce significant quantities of gas in WIPP disposal rooms if: (1) microorganisms survive for a significant fraction of the 10,000-year period of performance of the repository; (2) sufficient H_2O is present; (3) sufficient electron acceptors (oxidants) are available; (4) sufficient nutrients, especially P, are present and available. Because of these and other uncertainties (see 2.3.2 and B.2.1), significant microbial gas production is possible but by no means certain. Aerobic microbial activity (respiration using molecular O_2 as the electron acceptor) will significantly affect the O_2 content of the repository but not its gas or its H_2O content (see 2.3.2 and B.2.3). After depletion of the O_2 initially present and in the absence of radiolytic O_2, anaerobic microbial activity (respiration using NO_3^-, Mn(IV) and Fe(III) oxides and hydroxides, SO_4^{2-}, or CO_2 as the electron acceptor) will produce various gases and, perhaps, consume CO_2 and H_2 (see B.2.4). If significant microbial activity occurs in WIPP disposal rooms (see 2.3.2 and B.2.1) anaerobic microbial activity will be much more important than aerobic respiration from the standpoint of the gas and H_2O contents of the repository.

Radiolysis (the chemical dissociation of molecules by radiation) of H_2O in the waste and brine will significantly affect the O_2 content of WIPP disposal rooms but not the overall gas content of the repository or its H_2O content (see 2.3.3 and B.3.1). Radiolysis of cellulosics, plastics, and rubbers in the waste will produce a variety of gases, but at rates much lower than radiolysis of H_2O in the waste and brine (see 2.3.3 and B.3.2).

Consumption of gases (especially CO_2) by various reactions with constituents of cementitious materials or proposed backfill additives, or dissolution of gases (especially CO_2 and H_2S) in brine will remove gas from WIPP disposal rooms

The reaction-path gas-generation model (see C.3) is the most defensible WIPP gas-generation model. This model is more defensible than the average-stoichiometry model (see C.2), the gas-generation model used in the hydrologic code BRAGFLO for the 1992 PA calculations.

Several assumptions are necessary to predict gas generation in WIPP disposal rooms. These include: (1) which corrosion product will form during anoxic corrosion of steels and other Fe-base alloys in the absence of CO_2 and H_2S (see B.1.2); (2) whether microorganisms capable of carrying out each potentially significant respiratory pathway will be present when the repository is filled and sealed and survive for a significant fraction of its 10,000-year period of performance (see B.2.1.3); (3) whether microbes will consume significant quantities of plastics and rubbers (see B.2.1.5); (4) whether sufficient electron acceptors (oxidants) are available (see B.2.1.6); (5) whether sufficient nutrients, especially P, are present and available (see B.2.1.7); (6) the stoichiometry of the overall reactions for each potentially significant microbial process that occurs, especially methanogenesis (see B.2.4).

Appendix D describes the gas-generation rates used in the average-stoichiometry gas-generation model for the 1992 PA calculations. However, the most defensible gas-generation rates currently available are those provided for use in the average-stoichiometry model for the planned 1993 PA calculations (see Appendix E). (Although PA personnel used these rates for preliminary calculations pertaining to undisturbed conditions, they did not carry out a complete set of calculations in 1993.)

2.0 OVERVIEW OF GAS GENERATION UNDER EXPECTED WIPP CONDITIONS

2.1 Significance of Gas Generation in the WIPP

Gas generation by TRU waste is a significant issue because gas will, if produced in significant quantities, affect the performance of the WIPP with respect to EPA regulations for the long-term isolation of radioactive and chemically hazardous waste. (In this report, "gas generation" refers to both "production" and "consumption" of gas.) For example, several of the processes that produce gas will consume H_2O present in the waste at the time of emplacement or in any brine that enters the repository after filling and sealing. This will in turn decrease the H_2O content of the repository and retard or even completely eliminate additional gas production by reactions that consume H_2O. Furthermore, the pressure increase caused by this gas production will retard or prevent additional brine inflow and gas production. Therefore, gas production will decrease the quantity of H_2O present in the repository, or even remove it entirely. Because most plausible scenarios for radionuclide release from the repository involve dissolution or suspension of these radionuclides in brines, decreasing the quantity of H_2O present will improve the performance of the repository with respect to the EPA regulations for radioactive waste constituents and other contaminants transported by brine.

On the other hand, gas will, if present in sufficient quantities, enhance the permeability of the rock surrounding WIPP disposal rooms and serve as a carrier for the small quantities of VOCs present in the waste at the time of emplacement. Therefore, the rates at which major gases are produced will affect the performance of the repository with respect to the EPA regulations for chemically hazardous waste.

2.2 Interactions between Gas Generation and Other Processes Expected in the WIPP

If significant gas generation occurs, it will affect, and will be affected by, other processes and parameters in WIPP disposal rooms. These include: (1) the H_2O content of the repository; (2) room closure; (3) the chemical conditions that affect the actinide source term; (4) transport and, perhaps, generation of VOCs. Gas generation is significant from the standpoint of its effects on these processes and parameters to the extent that they affect compliance with EPA regulations for radioactive and chemically hazardous waste.

Gas generation will significantly affect, and will be significantly affected by, the H_2O content of the waste at the time of emplacement, brine inflow and outflow and, hence, the H_2O content of WIPP disposal rooms. PA personnel concluded that the H_2O content of the waste at the time of emplacement will significantly affect gas-production rates. Brush and Anderson (1989) demonstrated that processes such as anoxic corrosion of steels, microbial degradation of cellulosics, and radiolysis (the chemical dissociation of molecules by radiation) of H_2O in the waste and brine will affect the H_2O content of the repository as significantly as inflow of intergranular brines from the surrounding Salado Formation. Subsequently, results obtained from laboratory studies of gas generation have shown that the H_2O content of the repository will affect gas-production rates, or even whether gas production occurs at all (see 2.3.1, 2.3.2, B.1.2, and B.2.4).

Gas production will retard room closure by pressurizing WIPP disposal rooms. It will thus reduce the rate at which and the extent to which room closure decreases the porosity and permeability of the waste and backfill and the susceptibility of these materials to erosion and spalling during human intrusion. However, gas production, H_2O consumption and concomitant precipitation of salts from brine will decrease the porosity and permeability of these materials and increase their strength. Room closure will affect gas generation by rupturing drums and exposing their contents to materials and conditions different from those within the drums (brine, gas with a different composition or humidity, crushed salt and, perhaps, bentonite and other backfill additives, the microorganisms in the backfill, electron acceptors and nutrients in other drums, etc.). Furthermore, room closure will also affect gas generation by decreasing the connected porosity available for brine inflow and outflow and the permeability of the waste and backfill.

Finally, gas generation will affect chemical conditions such as the O_2 content of the repository[1] and the pH of any brine present. These parameters will in turn affect the solubilities of the actinide elements, their sorptive properties, the extent to which they form colloids and, hence, the actinide source term.

The O_2 content of the gaseous phase in WIPP disposal rooms at the time of filling and sealing will be similar to that of an equivalent volume of air. Subsequently, however, oxic corrosion (see 2.3.1 and B.1.1) and aerobic microbial activity (see 2.3.2 and B.2.3) will consume O_2. Radiolysis of H_2O in the waste and brine will produce O_2 (see 2.3.3), but not as fast as oxic corrosion and microbial activity will consume it. Therefore, the repository will become anoxic after filling and sealing.

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[1] In general, the concept of Eh as an intrinsic thermodynamic parameter is invalid in aqueous, geochemical systems at a temperature of 30°C, the expected temperature of WIPP disposal rooms after filling and sealing. This is because the kinetics of most oxidation-reduction (redox) reactions are so slow at this temperature that they rarely reach equilibrium, and the Eh calculated from the activity ratio of one redox couple rarely agrees with the values calculated from other couples, or with the value measured with an Eh electrode (see, for example, Lindberg and Runnells, 1984). Microbial activity, however, is known to catalyze redox reactions such as reduction of NO_3^-, Mn(IV) and Fe(III) oxides and hydroxides, and SO_4^{2-} in natural systems (see B.2.4). If significant microbial activity occurs in WIPP disposal rooms (see 2.3.2 and B.2.1), it will catalyze at least some of these redox reactions and, at least to some extent, render Eh a meaningful parameter. Nevertheless, this report uses words such as "O_2 content of the repository" instead of the term "Eh" to avoid giving the impression that the WIPP Project assumes that significant microbial activity will occur and catalyze redox reactions in the repository.

Reactions between brine and the contents of WIPP disposal rooms will increase or decrease the pH significantly from the mildly acidic values reported for intergranular brines from the Salado Formation at or near the stratigraphic horizon of the repository by Deal and Case (1987) and Deal et al. (1989a, 1989b, 1991a, 1991b). Microbial production of CO_2 or H_2S will decrease the pH of the brine to acidic values. Reactions between brine and $Ca(OH)_2$ in hydrated cementitious materials used to remove liquids from sludges, grouts used in seals, or grouts proposed to reduce the permeability of WIPP disposal rooms (see Butcher, 1990) will increase the pH to basic values. Reactions between brine and CaO, a backfill additive proposed to remove CO_2, will also increase the pH to basic values. Brush (1993) (see E) estimated that, because of these reactions, the pH in the repository will vary between about 3 and 12.

2.3 Summary of Current Understanding of WIPP Gas-Generation Mechanisms

The processes that will produce gas in WIPP disposal rooms are: (1) corrosion (see 2.3.1 and B.1); (2) microbial activity (see 2.3.2 and B.2); (3) radiolysis (see 2.3.3 and B.3). From the standpoint of the gas-production rates expected in WIPP disposal rooms, the most important processes are anoxic corrosion and anaerobic microbial activity. Brush (1993) (see E) concluded that radiolysis will not produce gas at rates comparable to those expected for corrosion and microbial activity. However, radiolysis will be important from the standpoint of the O_2 content of the repository. This parameter will in turn affect the actinide source term (see 2.2). Gas-consuming processes include reaction with cementitious materials and dissolution in brine.

Subsubsections 2.3.1, 2.3.2 and 2.3.3 summarize the results of studies of corrosion, microbial activity and radiolysis carried out for the WIPP Project by Telander and Westerman (1993), Francis and Gillow (1994) and Reed et al. (1993), respectively, and the results of studies conducted for applications other than the WIPP Project. Appendix B reviews these results in detail.

2.3.1 Corrosion

Oxic corrosion (oxidation of metals by molecular O_2) will consume O_2 and H_2O in WIPP disposal rooms (see B.1.1). Oxic corrosion of steel waste containers (drums and boxes), Fe-base alloys in the waste, and other metals in the waste such as Al and Al-base alloys will significantly affect the O_2 content of the repository. Oxic corrosion of these metals will be significant from this standpoint because this process is, along with aerobic microbial activity, one of the two major processes that will consume O_2 in the repository. (Radiolytically induced uptake by plastics and, perhaps, rubbers, and oxidation of dissolved, reduced species such as Fe^{2+} produced by dissolution of Fe(II)-bearing corrosion products will also consume O_2, but these processes will be less significant than oxic corrosion and aerobic microbial activity.) The O_2 content of the repository will, in turn, affect other important processes and parameters. These include: (1) how soon the repository becomes anoxic after filling and sealing; (2) whether gas is produced or consumed by corrosion of metals; (3) which gases are produced or consumed by microbial degradation of cellulosics and, perhaps, plastics and rubbers; (4) the actinide source term (see 2.2).

However, oxic corrosion will not affect the overall gas content of the repository or its H_2O content significantly because the quantity of O_2 in the repository at the time of filling and sealing, and that produced thereafter by brine radiolysis will be small (see B.1.1), thus limiting the extent of oxic corrosion relative to that of anoxic corrosion (see below).

After depletion of the O_2 initially present in WIPP disposal rooms and in the absence of radiolytically produced O_2, anoxic corrosion (oxidation of metals by H_2O or H_2S) will produce H_2 and consume H_2O, CO_2, and H_2S (see B.1.2). Anoxic corrosion of steels and other Fe-base alloys will produce significant quantities of H_2 and consume significant quantities of H_2O if: (1) sufficient H_2O is present in the waste at the time of emplacement (either as aqueous phase or as an interlayer constituent of clay minerals such as vermiculite), or sufficient brine enters the repository after filling and sealing; (2) significant microbial activity (see 2.3.2 and B.2.1) (and concomitant passivation) does not occur (microbial activity will produce CO_2 or CO_2 and H_2S, which will passivate steels and other Fe-base alloys and thus prevent additional H_2 production and H_2O consumption from anoxic corrosion of these metals); (3) in the event of microbial activity and passivation, consumption of CO_2 or H_2S depassivates steels and other Fe-base alloys. Anoxic corrosion of Al and Al-base alloys will produce significant quantities of H_2 and consume significant quantities of H_2O if sufficient H_2O is present in the waste or brine (neither CO_2 nor H_2S passivates Al and Al-base alloys). Other metals subject to oxic or anoxic corrosion might include (but are not necessarily limited to) Pb, Pu, and U.

In the absence of CO_2 and H_2S, anoxic corrosion of steels and other Fe-base alloys by intergranular Salado-Formation brines with a neutral or nearly neutral pH will produce H_2 at a rate of about 0.10 mole per m^2 of steel per year, equivalent to an H_2-production rate of 0.60 mole per drum of CH TRU waste per year and a corrosion rate of 0.99 μm of steel per year (see B.1.2). Acidic conditions, high N_2 partial pressure and, presumably, high total pressure will increase these rates significantly; basic conditions and high H_2 partial pressures will decrease them significantly (see B.1.2 and E for discussions of the effects of pressure and pH, respectively). How much H_2 will be produced will depend on: (1) the quantity of steels and other Fe-base alloys in the repository; (2) the quantity of aqueous H_2O present; (3) which corrosion product forms (see B.1.2). If sufficient steels, other Fe-base alloys, and H_2O are available, CO_2 and H_2S are absent, and $Fe(OH)_2$ is the corrosion product, anoxic corrosion of steels and other Fe-base alloys and concomitant H_2 production will continue until the H_2 fugacity (roughly equivalent to the partial pressure) increases to its equilibrium value of about 60 atm. (When a chemical reaction reaches equilibrium, the forward and backward rates of that reaction are equal and the reaction "stops.") However, the equilibrium H_2 fugacity for Fe_3O_4, the other possible corrosion product in the absence of O_2, CO_2, and H_2S, is about 400 atm. Therefore, if Fe_3O_4 forms, anoxic corrosion and H_2 production will continue even if the H_2 fugacity increases to its highest possible value of roughly 150 atm (lithostatic pressure at the depth of the WIPP underground workings).

If sufficient CO_2 or H_2S is present, anoxic corrosion of steels and other Fe-base alloys will stop prior to producing significant quantities of H_2 and consuming significant quantities of

H_2O, even if brine is present, because of passivation by the adherent corrosion product $FeCO_3$, FeS, or, perhaps, FeS_2 (see B.1.2). Because microbial activity in WIPP disposal rooms will produce CO_2 and/or H_2S (in addition to other gases such as H_2, N_2, and CH_4), significant microbial activity will, if it occurs (see 2.3.2 and B.2.1), passivate steels and other Fe-base alloys and thus prevent additional H_2 production and H_2O consumption from anoxic corrosion of these metals. High CO_2 partial pressures will not depassivate steels and other Fe-base alloys.

Under humid conditions (gaseous, but not aqueous, H_2O present), anoxic corrosion of steels and other Fe-base alloys will not occur, even if the gaseous phase is O_2-, CO_2-, and H_2S-free (see B.1.2). Therefore, anoxic corrosion in WIPP disposal rooms will be self-limiting. Small quantities of brine in the repository will initiate anoxic corrosion, which will produce H_2, consume H_2O, increase the pressure, prevent additional brine inflow or even cause brine outflow, and thus prevent additional anoxic corrosion.

2.3.2 Microbial Activity

Microbial activity in WIPP disposal rooms will produce gases such as CO_2, N_2, NH_3, H_2S, H_2, and, perhaps, CH_4, and consume O_2 and, perhaps, CO_2 and H_2 (see B.2). It is not known how microbial activity will affect the H_2O content of the repository. Microbial consumption of substrates such as cellulosics and, perhaps, plastics and rubbers will produce significant quantities of gas if: (1) microorganisms survive for a significant fraction of the 10,000-year period of performance of the repository; (2) sufficient H_2O is present in the waste or brine; (3) sufficient electron acceptors (oxidants) are available; (4) sufficient nutrients, especially P, are present and available. High pressure will not preclude microbial activity or even inhibit it significantly, even when it increases to 150 atm (lithostatic pressure at the depth of the repository). Subsubsection B.2.1 considers these and other issues in detail and concludes that, although significant microbial gas production is possible, it is by no means certain.

If significant microbial activity occurs in WIPP disposal rooms (see above and B.2.1), there are additional uncertainties as to its effects on the gas and H_2O contents of the repository. The most important issues are: (1) whether microorganisms will consume significant quantities of plastics and rubbers during the 10,000-year period of performance of the repository (see B.2.1.5); (2) the stoichiometry of the overall reaction for each microbial process that occurs, especially methanogenesis (see B.2.4); (3) whether microbial activity will produce or consume H_2O (see below and B.2.4.1).

Brush and Anderson (1989) and Brush (1990) used the conceptual model of sequential consumption of electron acceptors by microorganisms in natural environments (see B.2.2) and estimates of which electron acceptors will be present in significant quantities in the repository after filling and sealing to determine which microbial processes will be significant if microbial activity occurs (see above and B.2.1), which will be insignificant, and to predict the overall equation for each microbial process (see B.2.3 and B.2.4).

Aerobic microbial activity (respiration using molecular O_2 as the electron acceptor) will produce CO_2 and consume O_2 in WIPP disposal rooms (see B.2.3). Aerobic microbial consumption of cellulosics and, perhaps, plastics and rubbers will significantly affect the O_2 content of the repository. Aerobic microbial activity will be significant from this standpoint because this process is, along with oxic corrosion of metals, one of the two major processes that will consume O_2 in the repository. The O_2 content of the repository will, in turn, affect the actinide source term (see 2.2). However, aerobic microbial activity will not affect the overall gas content of the repository or its H_2O content significantly because the quantity of O_2 in the repository at the time of filling and sealing, and that produced thereafter by brine radiolysis will be small, thus limiting the extent of aerobic microbial activity relative to that of anaerobic microbial activity (see below and B.2.4).

After depletion of the O_2 initially present and in the absence of radiolytic O_2, anaerobic microbial activity (respiration using NO_3^-, Mn(IV) and Fe(III) oxides and hydroxides, SO_4^{2-}, or CO_2 as the electron acceptor) will produce CO_2, N_2, NH_3, H_2S, H_2, and, perhaps, CH_4, and, perhaps, consume CO_2 and H_2 (see B.2.4). If significant microbial activity occurs in WIPP disposal rooms (see above and B.2.1) anaerobic microbial activity will be much more important than aerobic respiration from the standpoint of the gas and H_2O contents of the repository because there will be much more NO_3^-, SO_4^{2-}, and CO_2 present than O_2. The most important anaerobic processes will be denitrification or NO_3^- reduction, which will use NO_3^- as the electron acceptor and produce CO_2 and N_2 or CO_2 and NH_3; SO_4^{2-} reduction, which will use SO_4^{2-} as the electron acceptor and produce CO_2 and H_2S; and methanogenesis, which will use CO_2 as the electron acceptor and produce CH_4 or, perhaps, consume CO_2 and H_2 and produce CH_4. Whether denitrification, SO_4^{2-} reduction, fermentation and methanogenesis will be significant will depend on whether the microorganisms responsible for a processes survive long enough for conditions to become conducive to that process and the relative quantities of electron acceptors present. The rates at which these processes will produce or, perhaps, consume gas will depend on whether conditions are humid or inundated, the concentrations of nutrients such as P, the dissolved Pu concentration (Pu inhibits microbial activity), and other factors. Microbial reduction of Mn(IV) and Fe(III) oxides and hydroxides will be insignificant relative to denitrification, SO_4^{2-} reduction, fermentation and methanogenesis because there will be very limited quantities of Mn(IV) and Fe(III) oxides and hydroxides present. It is not known whether anaerobic microbial consumption of cellulosics will produce or consume significant quantities of H_2O in WIPP disposal rooms (see B.2.4.1). It is also not known whether microbial consumption of plastics and rubbers will produce or consume significant H_2O. Quantification of the effects of microbial activity on the H_2O content of the repository is essential to predict the extent of gas production from anoxic corrosion (see 2.3.1 and B.1.2) and brine radiolysis (see 2.3.3 and B.3.1), both of which consume H_2O, and the quantity of brine available for the transport of radioactive waste constituents and other contaminants subject to aqueous-phase transport (see 2.1).

2.3.3 Radiolysis

In this position paper, "radiolysis" refers to "α radiolysis," the chemical dissociation of molecules by α particles emitted during the radioactive decay of the actinide elements in TRU waste. Because molecular dissociation caused by other types of radiation will be insignificant in a TRU-waste repository such as the WIPP, this report considers only α radiolysis.

Radiolysis of H_2O in the waste and brine in WIPP disposal rooms will produce H_2 and O_2 and consume H_2O (see B.3.1). Radiolysis of H_2O will significantly affect the O_2 content of the repository. Brine radiolysis will be significant from this standpoint because this process is the only major process that will produce O_2 in the repository. The O_2 content of the repository will, in turn, affect the actinide source term (see 2.2). However, based on calculations using the results of laboratory studies of brine radiolysis, estimates of the quantities of brine that could be present in the repository after filling and sealing, and estimates of the actinide source term (see B.3.1), radiolysis of H_2O will not affect the overall gas or H_2O contents of the repository significantly.

Radiolysis of cellulosics, plastics, and rubbers in the waste will produce a variety of gases. However, radiolysis of these materials will produce gas at rates much lower than radiolysis of H_2O in the waste and brine (see B.3.2).

2.3.4 Gas-Consuming Processes

Consumption of gases (especially CO_2) by various reactions with constituents of cementitious materials or proposed backfill additives, or dissolution of gases (especially CO_2 and H_2S) in brine will remove gas from WIPP disposal rooms..

Although the WIPP Project has carried out fewer studies of gas-consuming processes, reaction of CO_2 with $Ca(OH)_2$ in hydrated cementitious materials or with proposed backfill additives such as CaO will consume significantly more gas than dissolution in brine. This is because the gases produced by corrosion, microbial activity, and radiolysis will not dissolve to a significant extent in WIPP brines (see Cygan, 1991) and because there will not be enough brine present to consume significant quantities of these relatively insoluble gases.

3.0 WIPP COMPLIANCE-RELATED GAS-GENERATION ISSUES

This section describes the gas-generation models and assumptions required for PA calculations. It also discusses the gas-generation and related data required for these calculations. A description of the interactions between gas generation and other processes appears in 2.2.

3.1 Interactions between Gas Generation and Other Processes

Subsection 2.2 explains how gas generation will affect, and be affected by, other processes and parameters in WIPP disposal rooms.

3.2 Gas-Generation Models and Assumptions

The reaction-path model currently being developed by Brush et al. (1994) is the most defensible WIPP gas-generation model. Although still incomplete (see C.3), this model is more defensible than the average-stoichiometry model (see C.2), the gas-generation model used in the hydrologic code BRAGFLO for the 1992 PA calculations. The reaction-path model is more defensible because it includes: (1) additional gas-generation mechanisms; (2) additional reactions simulating these mechanisms; (3) interactions among gas-generation mechanisms. Because of these additional features, the reaction-path model predicts gas-generation in WIPP disposal rooms more realistically than the average-stoichiometry model. For example, the reaction-path model includes several gas-consuming mechanisms and reactions not included in the average-stoichiometry model. These include consumption of CO_2 by $Ca(OH)_2$ (in cementitious materials) and by CaO (a potential backfill additive) and consumption of CO_2 and H_2 by microbial methanogenesis (see B.2.4). Therefore, if there are sufficient quantities of cementitious materials in the TRU waste to be emplaced in the repository, if CaO is added to the backfill, or if laboratory studies of microbial activity imply that methanogenic consumption of CO_2 and H_2 is significant under expected repository conditions, the reaction-path model will predict that significantly less gas will be present. Furthermore, the reaction-path model includes passivation of steels and Fe-base alloys by microbially produced CO_2 and H_2S, the most important interaction among gas-generation mechanisms observed in laboratory studies of gas generation since the development of the average-stoichiometry model. Consequently, the reaction-path model will predict that anoxic corrosion will stop prior to producing significant quantities of H_2 and consuming significant quantities of H_2O, even if brine is present. Moreover, because the reaction-path model includes oxic corrosion, aerobic microbial activity and radiolysis (three gas-generation reactions or mechanisms not included in the average-stoichiometry model), it can predict the O_2 content of the repository as a function of time. The O_2 content of the repository will, in turn, affect the actinide source term.

Because it contains the additional features described above, incorporation of the reaction-path model in BRAGFLO will also result in more realistic predictions of the interactions among gas generation, brine inflow and outflow and room closure. (The hydrologic code BRAGFLO also includes a room-closure model.)

Several assumptions are necessary to predict gas generation in WIPP disposal rooms. These include: (1) which corrosion product will form during anoxic corrosion of steels and other Fe-base alloys in the absence of CO_2 and H_2S (see B.1.2); (2) whether microorganisms capable of carrying out each potentially significant respiratory pathway will be present when the repository is filled and sealed and survive for a significant fraction of its 10,000-year period of performance (see B.2.1.3); (3) whether microbes will consume significant quantities of plastics and rubbers (see B.2.1.5); (4) whether sufficient electron acceptors (oxidants) are available (see B.2.1.6); (5) whether sufficient nutrients, especially P, are present and available (see B.2.1.7); (6) the stoichiometry of the overall reactions for each potentially significant microbial process that occurs, especially methanogenesis (see B.2.4).

Ongoing laboratory studies of gas generation will not eliminate the need for these assumptions. Although it might be possible to determine which corrosion product will form during anoxic corrosion of steels and other Fe-base alloys in the absence of CO_2 and H_2S, it will not be possible to eliminate the need for these assumptions about microbial gas generation (see B.2.1.3, B.2.1.5, B.2.1.6, B.2.1.7, and B.2.4). Furthermore, it will be difficult to defend any of the possible outcomes, condition, or reactions listed above to the exclusion of the other. Therefore, it will be necessary to carry out probabilistic calculations based on all possible combinations of these outcomes, condition, or reactions.

WIPP Performance Assessment Division (1991) and Sandia WIPP Project (1992) described the average-stoichiometry gas-generation model in detail. However, they did not describe the reaction-path model at all. Brush et al. (1994) provided a preliminary description of the reaction-path model.

WIPP Performance Assessment Division (1991) and Sandia WIPP Project (1992) described some, but not all, of the assumptions listed above.

3.3 Gas-Generation and Related Data

This subsection describes the gas-generation and related data used on the 1991 and 1992 PA calculations, data obtained since the 1992 PA calculations, the sources of these data, and the interpretation of these data.

3.3.1 Gas-Generation and Related Data Used in the 1992 Performance-Assessment Calculations

Brush (1991) (see D) provided the gas-generation rates used in the average-stoichiometry gas-generation model (see C.2) for the 1992 PA calculations. (Actually, Brush (1991) provided these data for the 1991 PA calculations, but PA personnel used them for both their 1991 and

1992 calculations because experimental data obtained between 1991 and 1992 did not justify any changes.) These are the most recent gas-production rates used in a complete set of PA calculations. They are also the most recent rates described in PA reports (WIPP Performance Assessment Division, 1991; Sandia WIPP Project, 1992). Although Brush (1991) recommended best estimates and ranges of gas-production rates, he did not specify how these rates are distributed within these ranges. WIPP Performance Assessment Division (1991) described the distributions that PA personnel assumed for these parameters. WIPP Performance Assessment Division (1991) also discussed how PA personnel converted these rates from the units given below to those used in the average stoichiometry model.

3.3.2 Gas-Generation and Related Data Obtained since the 1992 Performance-Assessment Calculations

The most defensible gas-generation rates currently available are the data provided by Brush (1993) (see E) for use in the average-stoichiometry model for the planned 1993 PA calculations. (Although PA personnel used these rates for preliminary calculations pertaining to undisturbed conditions, they did not carry out a complete set of calculations in 1993 and hence have not described these rates in any of their reports to date.)

The gas generation rates provided by Brush (1993) (see E) are significantly different from those provided by Brush (1991) (see D). These differences, described in detail below, arose mainly because: (1) Brush (1993) estimated rates of oxic corrosion of steels and other Fe-base alloys and concomitant O_2 consumption, not just anoxic corrosion and H_2 production; (2) Brush (1993) used data from 12- and 24-month, low-pressure, anoxic-corrosion experiments with steels (Telander and Westerman, 1993), not just 3- and 6-month results; (3) Brush (1993) estimated the effects of more factors on the ranges of H_2-production and anoxic-corrosion rates of steels and other Fe-base alloys than did Brush (1991); (4) Brush (1993) used data from Reed et al. (1993) and estimates of actinide solubilities summarized by Trauth et al. (1992) to estimate H_2- and O_2-production rates from α radiolysis of WIPP brines. Brush (1993) reviewed data on microbial gas-production from Francis and Gillow (1994), not just the results summarized by Molecke (1979), Sandia Laboratories (1979), and Brush (1991). However, the gas-production rates reported by Francis and Gillow (1994) have all fallen within the range estimated by Brush (1991) for the 1991 and 1992 PA calculations. There is probably no justification, at least on the basis of the results obtained from BNL to date, for reducing the previously-estimated range. On the other hand, there is certainly no justification for extending it. Therefore, Brush (1993) recommend using the previously-provided microbial gas-production rates again.

3.3.3 Sources of Gas-Generation and Related Data

Brush (1993) (see E) used several primary sources of gas-generation and related data obtained by the WIPP Project. (The list of primary sources from the late 1970s is not necessarily complete.) Molecke (1979) provided very limited data on oxic and anoxic corrosion of steel and no description of the experiments that yielded them. Telander and Westerman (1993) described laboratory studies of anoxic corrosion of steels and other metals carried out at PNL since November 1989. They emphasized the effects of factors such as inundated and humid conditions, the compositon of the gaseous phase and pressure on corrosion of ASTM A 360 and ASTM A 570 steels, the low-C steels that simulate the CH TRU waste drums and boxes, respectively, and concomitant H_2 production. Caldwell et al. (1987) described laboratory studies of microbial activity carried out at the University of New Mexico during the late 1970s. Francis and Gillow (1994) discussed laboratory studies of microbial activity conducted at BNL since May 1991. They emphasized the effects of factors such as inoculation, amendment with nutrients and/or NO_3^- (an electron acceptor), and addition of bentonite (a proposed backfill additive) on gas production from microbial degradation of papers under inundated conditions. Kosiewicz et al. (1979), Zerwekh (1979) and Kosiewicz (1981) described laboratory studies of radiolysis performed at Los Alamos National Laboratory. Reed et al. (1993) described laboratory studies of brine radiolysis at ANL, especially the effects of brine composition and dissolved Pu concentration on the G values for α radiolysis. Stein and Krumhansl (1986), Deal and Case (1987), Stein and Krumhansl (1988), and Deal et al. (1989a, 1989b, 1991a, 1991b) studied intergranular Salado-Formation brines at or near the stratigraphic horizon of WIPP disposal rooms. Popielak et al. (1983) studied fluids from brine reservoirs in the Castile Formation, which could enter the repository in the event of human intrusion. Although Brush (1993) did not use these data directly, Brush (1990) used the results of these studies to plan laboratory studies of gas generation.

Brush (1993) (see E) also used several primary sources of gas-generation and related data obtained for applications other than the WIPP Project. Uhlig and Revie (1963) provided data used to estimate the effects of pH on the O_2-consumption, H_2-production, and corrosion rates for oxic and anoxic corrosion of steels and other Fe-base alloys. Wikjord et al. (1980), Haberman and Frydrych (1988), and Simpson and Schenk (1989) studied the effects of various factors on anoxic corrosion of steels and other Fe-base alloys. Although Brush (1993) did not use their results directly, their studies led to a greater understanding of anoxic corrosion of these materials under conditions expected in WIPP disposal rooms. Grauer et al. (1991) provided additional data used to estimate the effects of pH on the H_2-production and corrosion rates for anoxic corrosion of steels and other Fe-base alloys. and Froelich et al. (1979) and Berner (1980) provided the conceptual model of sequential usage of electron acceptors applied by Brush and Anderson (1989) and Brush (1990) to determine which microbial respiratory processes are potentially significant under expected WIPP conditions. Brush (1990) used these results to plan laboratory studies of microbial gas generation. Brush et al. (1994) also incorporated this conceptual model and the overall reactions for the microbial respiratory processes of Berner (1980) in the reaction path gas-generation model.

3.3.4 Interpretations of Gas-Generation and Related Data

Several secondary sources summarized, reviewed, or interpreted the "raw" data obtained by the WIPP Project (see 3.3.3). Molecke (1979) summarized and interpreted data from studies of corrosion, microbial activity, radiolysis, and "thermal degradation" carried out for the WIPP

Project and other applications during the 1970s. Sandia Laboratories (1979) briefly reviewed gas generation by these mechanisms from the standpoint of the WIPP waste-acceptance criteria. Brush et al. (1991a) reviewed and interpreted preliminary data from laboratory studies of gas generation carried out for the WIPP Project after these studies were restarted in 1989. These included studies of: (1) anoxic corrosion of steels and other Fe-base alloys conducted by Westerman and his colleagues at PNL; (2) halophilic microorganisms from the WIPP Site and vicinity performed by Vreeland and his students at West Chester University; (3) microbial consumption of cellulose carried out by Grbic-Galic and her students at Stanford University; (3) radiolysis of brine and plastics conducted by Reed and his colleagues at ANL. (The study at Stanford University did not yield any useful results.) Brush et al. (1991b) also reviewed and interpreted preliminary data from these studies. Brush (1991) (see D) provided gas-production rates for anoxic corrosion, microbial activity, and radiolysis for the (1991 and) 1992 PA calculations. WIPP Performance Assessment Division (1991) described the distributions that PA personnel assumed for the ranges of corrosion and microbial gas-production rates provided by Brush (1991) and discussed how PA personnel converted these rates from the units given by Brush (1991) to those used in the average stoichiometry model. (Sandia WIPP Project, 1992, used the same rates and distributions for the 1992 PA calculations.) Brush et al. (1993) reviewed and interpreted data from the following laboratory studies carried out for the WIPP Project: (1) anoxic corrosion of steels and other Fe-base alloys at PNL; (2) microbial consumption of papers conducted by Francis and his colleagues at BNL; (3) brine radiolysis at ANL. Brush (1993) (see E) provided gas-production rates for anoxic corrosion, microbial activity and radiolysis for the planned 1993 PA calculations. PA personnel have not described these data in any of their reports.

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APPENDIX A: HISTORY OF WIPP STUDIES OF GAS GENERATION

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The WIPP Project carried out laboratory studies of gas generation during the late 1970s to support the development of TRU waste-acceptance criteria. Molecke (1979) summarized the results of these studies. For the most part, they comprised single-mechanism experiments on microbial activity, and radiolysis, with nonradioactive and some radioactive simulated waste. There was very little work on anoxic corrosion. Based on laboratory measurements carried out on samples obtained by drilling from the surface, the permeability of the Salado Formation appeared to be high enough for rapid migration of gas from the repository, even given the highest gas-production rates summarized by Molecke (1979). Furthermore, EPA regulations for chemically hazardous waste constituents did not apply at the time these studies were conducted. Therefore, the WIPP Project terminated studies of gas generation in 1979.

In 1987, PA personnel carrying out preliminary calculations on the effects of human intrusion identified inflow of intergranular brine from the Salado Formation as a concern for the long-term performance of the repository. In early 1988, L. H. Brush and D. R. Anderson examined the possible effects of processes such as anoxic corrosion of steels, microbial degradation of cellulosics, and brine radiolysis on the H_2O content of the repository (Brush and Anderson, 1989). They concluded that these processes could affect its H_2O content as significantly as brine inflow. Furthermore, they concluded that these processes may also produce significant quantities of gas. Meanwhile, in situ measurements in the WIPP underground workings had revealed by this time that the permeability of the Salado Formation was much lower than believed in the late 1970s.

Systems analysis carried out by Lappin et al. (1989), which used these new permeabilities, assumptions on gas-generation from Brush and Anderson (1989a, 1989b, and 1989c), and the rates-and-potentials gas-generation model of Lappin et al. (1989) (see C.1), demonstrated that gas, if present in significant quantities, will affect the overall performance of the repository.

Therefore, the WIPP Project restarted laboratory studies of gas generation in February 1989. These studies have comprised mainly single-mechanism experiments on anoxic corrosion, microbial activity, and radiolysis, mostly with nonradioactive, simulated CH TRU waste (see B). Brush (1990) presented detailed plans for these studies. Brush et al. (1991a, 1991b, and 1993), Reed et al. (1993), Telander and Westerman (1993), and Francis and Gillow (1994) have described most of the results obtained to date from these ongoing studies.

The WIPP Project also started to plan large-scale, multi-mechanism tests with CH TRU waste at about the same time it restarted laboratory studies with simulated waste. Molecke (1990a, 1990b) and Molecke and Lappin (1990) provided detailed plans for these bin-scale and alcove tests. Lappin et al. (1991) provided additional justification for these tests.

The WIPP Project has also developed and used models to predict gas-generation by TRU waste (see C). For their 1989 systems analysis, which demonstrated that significant quantities of gas will affect repository performance, Lappin et al. (1989) used the rates-and-potentials gas-generation model (see C.1). WIPP Performance Assessment Division (1991) developed the average-stoichiometry gas-generation model (see C.2) and incorporated it in the two-phase (brine and gas) hydrologic model BRAGFLO, which also simulates room closure. Incorporation of the average-stoichiometry model in BRAGFLO thus coupled this gas-generation model with the hydrologic and geomechanical models used for PA. Brush (1991) (see D) reviewed laboratory studies of gas generation carried out for the WIPP Project during the late 1970s, laboratory studies conducted for the WIPP Project since 1989, and similar studies for other applications (see D.3.1). WIPP Performance Assessment Division (1991) and Sandia WIPP Project (1992) used these data and estimates from Brush (1991) in the average-stoichiometry model for their 1991 and 1992 calculations, respectively. In 1992, work began on the reaction-path gas-generation model (see C.3), which includes more gas-generation mechanisms than the average-stoichiometry model and the interactions among these mechanisms. Brush et al. (1994) provided a brief description of this model, which will replace the average stoichiometry model in BRAGFLO.

On October 21, 1993, the US Department of Energy (DOE) canceled the bin and alcove tests prior to their initiation in the WIPP underground workings. This decision was based, at least in part, on the results of the Independent Technical (Red Team) Review of these tests (US DOE Office of Environmental Restoration and Waste Management, 1993). The DOE also announced that an Enhanced Laboratory Program (ELP) will replace the bin and alcove tests.

In mid 1994, the WIPP Project began planning the ELP. This program will comprise multi-mechanism experiments with radioactive (Pu-doped) simulated waste and multi-mechanism tests with actual CH TRU waste. Once started, both the simulated and actual-waste testing will continue for about two years.

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APPENDIX B: REVIEW OF WIPP-RELATED LABORATORY STUDIES OF GAS GENERATION

Contents of Appendix B

APPENDIX B: REVIEW OF WIPP-RELATED LABORATORY STUDIES OF GAS GENERATION

This section reviews WIPP-related studies of gas generation. It emphasizes laboratory studies carried out by the WIPP Project since 1989. However, it includes some theoretical calculations conducted by the WIPP Project during that period and results from studies performed for applications other than the WIPP Project. Molecke (1979) summarized the results of laboratory studies of gas generation carried out during the late 1970s to support the development of waste-acceptance criteria.

Subsubsections 2.3.1, 2.3.2, and 2.3.3 summarize the results of these studies.

B.1 Corrosion

B.1.1 Oxic corrosion of Steels and Other Iron-Base Alloys

Brush and Anderson (1989a) concluded that oxic corrosion of steels, other Fe-base alloys, and, perhaps, other metals will not have a significant, direct effect on the gas and H_2O contents of WIPP disposal rooms. They concluded, based on their 1988 estimate of the quantity of steel in the CH TRU waste drums to be emplaced in the repository, that the O_2 in mine air trapped in the repository at the time of filling and sealing would only be sufficient to oxidize about 0.4 to 1.1% of the drums, depending on the initial void volume assumed. Inclusion of the Fe-base alloys in the CH TRU waste, the steels or other Fe-base alloys used for RH TRU waste canisters and plugs, and the Fe-base alloys contained in RH TRU waste would, of course, decrease the estimated range given above. Whether oxic corrosion will be important also depends on the rate of O_2 production from radiolysis of H_2O in the waste and brine. The radiolytic O_2-production rate depends in turn on the quantity of H_2O in the waste and the quantity of brine in the repository (both of which will probably vary with time), and the dissolved and suspended concentrations of the important actinide elements in TRU waste. Assuming the estimates of actinide solubilities presented by Trauth et al. (1992) and estimates of the quantities of brine from Brush (1993) (see E), brine radiolysis will produce O_2 at such low rates that oxic corrosion will continue to be an insignificant process throughout the 10,000-year period of performance of the repository.

The most likely oxic-corrosion reaction in WIPP disposal rooms is:

$$4Fe + 2H_2O + 3O_2 = 4\gamma FeO(OH) \quad (B.1)$$

In this reaction, "Fe" represents the Fe in steels and other Fe-base materials and $\gamma FeO(OH)$ is lepidocrocite. This reaction is the most likely of many possible reactions because $\gamma FeO(OH)$ was the most abundant corrosion product observed in oxic, inundated, corrosion experiments carried out for the Strategic Petroleum Reserve Project. Fe_3O_4 (magnetite) was also a major corrosion product and βFeO(OH) was a minor product. (The identity of the polymorph of FeO(OH), or even whether FeO(OH) or Fe_3O_4 is the dominant composition of oxic corrosion products will not affect predictions of gas generation significantly because oxic corrosion is a minor process.)

B.1.2 Anoxic Corrosion of Steels and Other Iron-Base Alloys

Because the WIPP Project had carried out very little work on anoxic corrosion during the 1970s, Brush (1990) used thermodynamic calculations and kinetic results from laboratory studies carried out for applications other than the WIPP Project to determine the possible behavior of steels and other Fe-base alloys under expected WIPP conditions. He concluded that, from the standpoint of the gas and H_2O contents of the repository, the most important issues were: (1) whether anoxic corrosion of these materials will produce H_2 and consume H_2O at the same rates under humid conditions as expected for inundated conditions; (2) how gases produced by microbial activity (the other major gas-production mechanism) will affect anoxic corrosion; (3) the effects of pressure on anoxic corrosion; (4) the effects of pH. Brush (1990) also recognized that these issue also apply to anoxic corrosion of other metals, especially Al and Al-base alloys.

Telander and Westerman (1993) reported the results of laboratory studies of anoxic corrosion carried out for the WIPP Project at Pacific Northwest Laboratory (PNL) since November 1989. So far, they have observed three anoxic-corrosion reactions in their experiments (see Reactions B.2, B.4, and B.5 below). In addition, thermodynamic calculations by Brush (1990) and results from studies carried out for applications other than the WIPP Project suggest that at least two other reactions are possible (Reactions B.3 and B.5, respectively).

Telander and Westerman (1993) conducted most of their studies with two heats each of the low-C steels ASTM A 366 and ASTM A 570 under inundated conditions (specimens immersed in Brine A) or humid conditions (specimens suspended above Brine A) with initially pure N_2, CO_2, and H_2S at low pressures (about 10 to 15 atm) at 30 ± 5°C. Cold-rolled ASTM A 366 steel simulates the CH TRU waste drums to be emplaced in the repository; hot-rolled ASTM A 570 steel simulates the CH TRU waste boxes. Brine A is a synthetic brine that, although developed to simulate fluids equilibrated with K^+- and Mg^{2+}-bearing minerals in the overlying potash-rich zones of the Salado Formation prior to entering the repository (Molecke, 1983), is coincidentally similar in composition to intergranular brines from the Salado Formation at or near the stratigraphic horizon of the WIPP underground workings (Stein and Krumhansl, 1986; Deal and Case, 1987; Stein and Krumhansl, 1988; Deal et al., 1989a, 1989b; Brush, 1990; Deal et al., 1991a, 1991b). PNL personnel have also conducted experiments with these steels under inundated conditions with initially pure N_2, CO_2, or H_2 at high pressures (about 35 or 70 atm). Finally, they have performed a few experiments with these steels in simulated backfill materials (crushed salt and a mixture of 70 wt % crushed salt and 30% bentonite) at low pressures.

In low-pressure, inundated experiments started with initially pure N_2 in the headspace above Brine A, Telander and Westerman (1993) reported that the pressures increased at a nearly constant rate due to H_2 production, probably from the reaction:

$$Fe + (x + 2)H_2O = Fe(OH)_2 \cdot xH_2O + H_2. \quad (B.2)$$

The results from separate, duplicate 3-, 6-, 12-, and 24-month runs were very similar at any given time, but the H_2-production and corrosion rates decreased somewhat with time. Posttest analysis of the headspace gases from the 3-, 6-, 12-, and 24-month runs yielded average H_2-production rates of 0.19, 0.21, 0.16, and 0.10 mole per m^2 of steel per year, respectively. Assuming 6 m^2 of steel and other Fe-base alloys per drum of CH TRU waste (4 m^2 for the containers and 2 m^2 for the Fe-base alloys in the waste) (see 3.3.1), these rates are equivalent to 1.14, 1.26, 0.96, and 0.60 moles of H_2 per drum per year. The average corrosion rates, determined independently by gravimetric (weight-loss) analysis of replicate steel specimens from the 3-, 6-, 12-, and 24-month runs were 1.97, 1.72, 1.23, and 0.99 μm of steel per year. Telander and Westerman (1993) could not explain why the H_2-production and corrosion rates decreased by about a factor of two from the 3- to the 24-month runs. Possible explanations include: (1) pretest preparation of the specimens resulted in initially rapid rates, which decreased as surficial material was removed by corrosion; (2) some inhibition of Reaction B.2 occurred due to accumulation of a thin film of the corrosion product on the surfaces of the steel specimens (however, PNL personnel have observed no such film); (3) depletion of a reactant, perhaps in Brine A (posttest analysis of the Brine A used for these runs, however, revealed no changes in the concentrations of its major constituents).

The ratios of moles of H_2 produced to moles of metal consumed were 0.65, 0.83, 0.90, and 1.0. Telander and Westerman (1993) could not explain why these ratios were less than the expected value of unity in the 3-, 6-, and 12-month runs, or why they increased and eventually attained unity in the 24-month runs.

The unidentifiable corrosion product, probably with the composition $Fe(OH)_2 \cdot xH_2O$, $(Fe,Mg)(OH)_2 \cdot xH_2O$, or $(Fe,Mg,Mn)(OH)_2 \cdot xH_2O$, did not adhere to the specimens in these experiments. Therefore, H_2 production and corrosion may continue at these rates under inundated conditions unless the backfill prevents this corrosion product from sloughing off or salts precipitated from brine during corrosion isolate the steels.

Brush (1990) calculated that $Fe(OH)_2$, the apparent corrosion product of the inundated experiments with initially pure N_2, is unstable with respect to Fe_3O_4 below an H_2 fugacity of about 100,000 atm. Therefore, significant quantities of steels and other Fe-base alloys might corrode via the reaction

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2 \quad (B.3)$$

if Fe_3O_4 eventually nucleates and replaces $Fe(OH)_2$. Telander and Westerman (1993) did not observe Fe_3O_4 in experiments that lasted for up to 24 months. However, Sorensen observed Fe_3O_4 among the corrosion products in oxic, inundated, corrosion experiments carried out for the SPR Project. Therefore, oxic corrosion may produce Fe_3O_4, which may then serve as nuclei for Reaction B.3.

Which of these reactions is predominant at low fugacities of CO_2 and H_2S may be an important issue if sufficient H_2O is available to corrode enough steel to produce high H_2 fugacities in WIPP disposal rooms. Brush (1990) calculated that, if sufficient steels, other Fe-base alloys, and H_2O are available, Reaction 2 will reach equilibrium at an H_2 fugacity of about 60 atm, but that Reaction B.3 will continue until the H_2 fugacity is 400 atm. Simpson and Schenk (1989) calculated similar equilibrium H_2 fugacities for these reactions (about 100 and 500 atm, respectively) under conditions expected for a Swiss high-level-waste repository in granite. In both cases, the equilibrium H_2 fugacity for Reaction B.2 is well below lithostatic pressure at the depth of WIPP disposal rooms (about 150 atm), but that of Reaction B.3 is well above lithostatic pressure.

No detectable corrosion occurred in the 3-, 6-, 12-, and 24-month humid experiments with initially pure N_2 except for very limited corrosion of the bottom 10% of the specimens splashed with brine during pretest preparation procedures. These results suggest that anoxic corrosion in the repository will be self-limiting. Small quantities of brine in the repository will initiate anoxic corrosion, which will produce H_2, consume H_2O, increase the pressure, prevent additional brine inflow or even cause brine outflow, and thus prevent additional anoxic corrosion.

In low-pressure, inundated experiments started with initially pure CO_2 in the headspace above Brine A, the pressures decreased initially because of continuing dissolution of CO_2 in Brine A. (The pretest preparation procedures used by Telander and Westerman (1993) apparently did not saturate Brine A with CO_2 prior to the start of these runs). The pressures then increased rapidly, probably because of acceleration of anoxic corrosion and H_2 production by acidic conditions caused by CO_2 dissolution in the brine. After about 3 or 4 months, however, the pressures stopped increasing due to passivation of the steel specimens. Posttest analysis demonstrated that passivation resulted from formation of the adherent corrosion product $FeCO_3$ (siderite), probably by the reaction

$$Fe + H_2O + CO_2 = FeCO_3 + H_2. \quad (B.4)$$

In these low-pressure experiments, passivation by $FeCO_3$ consumed 0.33 moles of CO_2 per m^2 of steel, equivalent to 2 moles of CO_2 per drum. (The results of other experiments, described below, imply that the CO_2 passivation requirement depends on the CO_2 fugacity and pH, and varies from 0.33 to at least 2.2 moles of CO_2 per m^2 of steel.) These are small quantities relative to the amount of CO_2 that could be produced by microbial activity (tens, hundreds, or even a few thousand moles per drum). Even if room closure results in mechanical removal of the passivating layer of $FeCO_3$, the quantities of CO_2 required for passivation would still be relatively small.

As in the case of the low-pressure, humid experiments with initially pure N_2, no detectable corrosion occurred in the 3-, 6-, 12-, and 24-month humid runs with initially pure CO_2 except for very limited corrosion of the bottom 10% of the specimens splashed with brine during pretest preparation procedures.

In low-pressure, inundated experiments started with initially pure H_2S in the headspace above Brine A, anoxic corrosion produced some H_2 initially. However, H_2S rapidly passivated these steels by the reaction:

$$Fe + H_2S = FeS + H_2. \quad (B.5)$$

Posttest x-ray-diffraction revealed that FeS_{1-x} (mackinawite) passivated the steels in these runs. This was surprising in view of results from studies for applications other than the WIPP Project (see, for example, Wikjord et al., 1980), which have identified Fe sulfides with higher S/Fe ratios, such as $Fe_{1-x}S$ (pyrrhotite) and FeS_2 (pyrite) as the passivating phases in H_2S-bearing systems, but have found that mackinawite is nonprotective. In these low-pressure runs, the passivation requirement was 0.056 moles of H_2S per m^2 of steel, equivalent to 0.336 moles of H_2S per drum. In view of these published results, there is at least one more potentially significant anoxic-corrosion reaction:

$$Fe + 2H_2S = FeS_2 + 2H_2. \quad (B.6)$$

Of course, it is not known, absent experimental confirmation, whether this reaction (or any other reaction that produces a sulfide with a higher S/Fe ratio than mackinawite) will result in passivation of steels under expected WIPP conditions. However, it is clear that passivation of steels and other Fe-base alloys by $FeCO_3$ and FeS is a real phenomenon under at least some combinations of conditions expected in WIPP disposal rooms. On the other hand, results obtained during the development of the reaction-path gas-generation model (see C.3) suggest that depassivation is also possible, especially if consumption of CO_2 by $Ca(OH)_2$ (in hydrated cementitious materials) and CaO (a proposed backfill additive) decrease the fugacity of CO_2 below values required to stabilize $FeCO_3$.

Although it has not been observed yet, at least one other passivation mechanism might occur in WIPP disposal rooms. Precipitation of salts on the surfaces of corroding metals due to the consumption of H_2O during anoxic (or oxic) corrosion might isolate steels, other Fe-base alloys, and other metals from further contact with brine.

B.1.2.1 EFFECTS OF ANOXIC CORROSION ON THE WATER CONTENT OF WIPP DISPOSAL ROOMS

Oxic corrosion of steels and other Fe-base alloys in WIPP disposal rooms will probably not consume significant quantities of H_2O, despite the stoichiometry of Reaction B.1 (see B.1.1), because this process will probably be insignificant relative to other gas-generation mechanisms. (There will probably not be enough O_2 trapped in the repository at the time of filling and sealing, and radiolysis will probably not produce O_2 at sufficient rates thereafter for oxic corrosion to consume significant quantities of H_2O.)

However, anoxic corrosion of steels and other Fe-base alloys by Reactions B.2 and B.3 will consume significant quantities of H_2O. These reactions will consume at least 2 and 1.33 moles of H_2O per mole of Fe consumed, respectively. Furthermore, these reactions did not result in passivation of steels in experiments carried out by Telander and Westerman (1993). Therefore, as long as conditions remain conducive to formation of $Fe(OH)_2$ or Fe_3O_4, these reactions will continue to consume H_2O until one or both of the reactants are consumed or until equilibrium is attained.

Although anoxic corrosion of steels and other Fe-base alloys by Reaction B.4 will consume 1 mole of H_2O per mole of Fe consumed, this reaction will probably result in passivation of these metals prior to consumption of significant quantities of H_2O. Reaction B.5, which will also passivate steels and other Fe-base alloys, and Reaction B.6 will not consume any H_2O.

B.2 Microbial Activity

B.2.1 Significant Issues Pertaining to Microbial Activity in WIPP Disposal Rooms

Whether microbial gas production will be significant in WIPP disposal rooms has been a controversial topic since the WIPP Project first began to study gas generation during the late 1970s. The most significant issues pertaining to microbial activity were or have been whether: (1) microorganisms will be present in the repository when it is filled and sealed; (2) sterilization of the waste and other contents of the repository will prevent microbial activity; (3) microbes will survive for a significant fraction of the 10,000-year period of performance of the repository; (4) sufficient H_2O will be present; (5) sufficient quantities of biodegradable substrates will be present; (6) sufficient electron acceptors will be available; (7) sufficient nutrients, especially P, will be present and available This subsubsection considers these issues and concludes that, although significant microbial gas generation is possible, it is by no means certain (see B.2.1.1 through B.2.1.7).

B.2.1.1 AVAILABILITY OF MICROORGANISMS IN WIPP DISPOSAL ROOMS

Microorganisms will be present in WIPP disposal rooms when they are filled and sealed. Although the WIPP Project has carried out little, if any, characterization of the microbes present in TRU waste, they are no doubt present when the waste is generated. Because most of these microbes probably have been or will be introduced to the waste by processes related to its generation, packaging, and storage prior to emplacement in the repository, most of these microbes are probably nonhalophilic. (Halophilic microbes can survive only in highly saline environments such as such as salt lakes and salt marshes.) However, some of the microbes in the waste, especially those that lived on human skin in the presence of salt from perspiration, might be halotolerant or develop halotolerance when exposed to saline conditions. (Halotolerant microbes prefer asaline environments, but can tolerate saline conditions.) At least some of the microbes in the waste will probably survive the period of storage, the period of emplacement, and the interval between filling and sealing of the repository and rupture of containers caused by room closure. (Container rupture will probably occur on the order of years or tens of years after emplacement.) The microbes in the waste could include numerous species capable of fermentation and methanogenesis once anaerobic conditions develop in the containers (see B.2.4). (In fact, fermentation and methanogenesis, as well as other microbial processes, have probably occurred or will occur to some extent in many containers during storage, especially in those containers in which the humidity is high.) Exposure of the mainly nonhalophilic, nonhalotolerant microbes in the waste to the highly saline conditions expected after container rupture, however, will probably cause most of them to lyse. Although a few halotolerant microbes may survive and a few others may develop halotolerance when exposed to saline conditions, the most potentially significant microbes during most of the 10,000-year period of performance of the repository will be halophilic microbes present in WIPP disposal rooms when they are filled and sealed.

Halophilic microorganisms capable of carrying out the microbial processes described below (see B.2.3 and B.2.4) currently exist throughout the WIPP underground workings. However, the source of these microbes is not known. They have probably entered the WIPP underground workings since excavation on dust particles transported from the salt lakes in Nash Draw, nearby soils, and the WIPP tailings pile by wind and the mine ventilation system, or by various human vectors. The salt lakes in Nash Draw contain an abundance of halophilic and, perhaps, halotolerant microbes, which occur both in the waters in these lakes and in the underlying sediments. These lacustrine waters and sedimentary pore waters are concentrated brines with salinities similar to those of brines that could enter the repository after filling and sealing. It is also possible, although highly unlikely, that the halophilic microbes that currently exist in the WIPP underground workings were present in the Salado Formation prior to excavation. Because these halophilic microbes have evolved under saline conditions, they are probably better adapted to expected repository conditions than halotolerant or potentially halotolerant microbes in TRU waste, and would probably affect the behavior of the repository more than halotolerant species. At least some of the halophilic microbes in the WIPP underground workings will probably survive until waste is emplaced, during emplacement, and throughout the interval between filling and sealing and container rupture. In fact, unless these microbes were present in the Salado Formation prior to excavation of the WIPP underground workings, waste emplacement will probably increase the number of microbes present.

The WIPP Project has not carried out a systematic survey to determine the numbers and types of microorganisms in the underground workings, nor has it attempted to determine the source of these microbes. Instead, investigators such as Francis and Gillow (1994) at Brookhaven National Laboratory (BNL) have collected halophilic and nonhalophilic microbes from a variety of sources, including the WIPP underground workings and the salt lakes in Nash Draw, and enriched them in the laboratory. They then subjected the microbial communities thus obtained to various combinations of the conditions expected in the repository after filling and sealing to quantify microbial gas-production rates (see 4.2.3 and 4.2.4).

B.2.1.2 STERILIZATION OF WIPP DISPOSAL ROOMS AND THEIR CONTENTS

Some reviewers of the WIPP Project have proposed sterilization of the waste and other contents of WIPP disposal rooms, or addition of a biocide or biocides to prevent microbial activity after filling and sealing of the repository. Because of the uncertainties inherent in predicting microbial gas production, these suggestions do have some appeal, at least at first glance. Although these solutions might delay the start of microbial gas production, reduce microbial gas-production rates, or reduce the quantity of microbial gas produced somewhat, it would be very difficult to defend the efficacy of these remedies. Therefore, they would probably not reduce the uncertainties in predictions of microbial gas production significantly.

B.2.1.3 LONG-TERM SURVIVAL OF MICROORGANISMS IN WIPP DISPOSAL ROOMS

Although microorganisms will be present in WIPP disposal rooms when they are filled and sealed, it is by no means certain that they will survive long enough to affect the behavior of the repository significantly if, as expected, sealing the shafts and boreholes around the repository effectively isolates its contents from the surficial environment. Microbes occur in deep, subsurface environments (see, for example, DOE Subsurface Science Program's Taylorsville Working Group, 1994). However, it is generally not known how and when they arrived in these environments. Therefore, it is also unknown how long microbes can survive n such environments, especially under suboptimal conditions. Furthermore, it is difficult, if not impossible, to carry out microbial survival experiments for periods long enough to be relevant to the long-term performance of the WIPP. Therefore, it will be very difficult to determine whether the halophilic or halotolerant microbes that carry out any given microbial process (see B.2.3 and B.2.4) will survive until containers rupture, brine enters the repository, the electron acceptors and nutrients in other types of waste diffuse to the waste containing cellulosics and other potential substrates, and the microbes that conduct preceding processes render conditions conducive to that process.

It is still not known whether there will be sufficient nutrients in WIPP disposal rooms for microbial activity, which potentially significant microbial processes (see B.2.4) will occur, at what rates they will produce gas and produce or consume H_2O under realistic repository conditions, and whether or not the H_2O content and pressure of the repository will affect these rates. The extent to which any of these potentially significant processes will affect the chemical behavior of radionuclides under realistic conditions is also unknown. Finally, it is unclear 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.

B.2.1.4 AVAILABILITY OF WATER IN WIPP DISPOSAL ROOMS

Some reviewers of the WIPP Project have also maintained that the H_2O contnent of the repository will be insufficient for significant microbial gas production to occur. Give more details!!!

Humid conditions will retard, but will not eliminate, microbial gas production

B.2.1.5 AVAILABILITY OF SUBSTRATES IN WIPP DISPOSAL ROOMS

Brush and Anderson (1989a) and Brush (1990) concluded that, for all of these processes, microorganisms in WIPP disposal rooms will probably use cellulosics as the substrate in preference to plastics and rubbers. However, microbes might use plastics and rubbers after the depletion of cellulosics, especially if slow (on the human time scale) inorganic degradation reactions or α radiolysis render these materials more biodegradable.

B.2.1.6 AVAILABILITY OF ELECTRON ACCEPTORS IN WIPP DISPOSAL ROOMS

There will be sufficient quantities of electron acceptors for significant microbial gas production in WIPP disposal rooms. Give more details!!!

Electron acceptors will be present in the repository, but will, for the most part, require the presence of aqueous H_2O for transport from drums containing sludges, from brine, from the crushed-salt backfill, or from the disturbed rock zone to drums containing cellulosics and, perhaps, plastics and rubbers);

B.2.1.7 AVAILABILITY OF NUTRIENTS IN WIPP DISPOSAL ROOMS

It is unclear whether there will be enough nutrients, especially P, for significant microbial gas production to occur in WIPP disposal rooms. Give more details!!!

It is not known whether sufficient nutrients, especially P, will be present but, if so, they will also, at least to some extent, require the presence of aqueous H_2O for transport from drums containing sludges to drums containing cellulosics, plastics and rubbers)..

B.2.2 Sequential Consumption of Electron Acceptors

Brush and Anderson (1989a) and Brush (1990) applied the conceptual model of sequential consumption of electron acceptors by microorganisms in natural environments (see, for example, Froelich et al., 1979; Berner, 1980) to WIPP disposal rooms. Brush (1990) used this model and estimates of which potential electron acceptors will be present in significant quantities in the repository after filling and sealing to determine which microbial processes may be significant, which will probably be insignificant, and to predict the overall equations for the potentially significant processes (see B.2.4). Furthermore, Brush (1990) planned laboratory studies to quantify the effects of various factors on the rates at which halophilic microbes from the WIPP Site and vicinity produce gas by carrying out these processes. Recently, Brush et al. (1994) used some of these equations, slightly modified, and microbial gas-production rates from Molecke (1979) and Francis and Gillow (1994) (see B.2.3 and B.2.4) to simulate microbial gas generation in the reaction-path gas-generation model (see C.3).

In the natural environment, microorganisms oxidize organic matter by consuming the electron acceptor that yields the most free energy per mole of organic C consumed (see, for example, Froelich et al., 1979; Berner, 1980). After the depletion of this electron acceptor, other microorganisms consume the next most efficient electron acceptor present. (However, facultative anaerobes consume O_2 as long as it is available, but can use other electron acceptors, such as NO_3^-, after the depletion of O_2.) If the environment remains conducive to microbial activity, sequential consumption of electron acceptors continues until microorganisms have consumed all of the substrate or substrates, all available electron acceptors, or all essential nutrients. In natural systems, the order of consumption of electron acceptors is O_2, NO_3^-, Mn(IV) oxides and hydroxides, Fe(III) oxides and hydroxides, SO_4^{2-}, and CO_2. (In some systems, consumption of Mn(IV) oxides and hydroxides occurs prior to that of NO_3^-.) Microbiologists refer to microbes that consume O_2 as "aerobic" and to those that use any of the other electron acceptors listed above as "anaerobic." They refer to consumption of NO_3^- as "denitrification" or "NO_3^- reduction," depending on whether the N-bearing, gaseous product is N_2 or NH_3. They refer to consumption of Mn(IV) oxides and hydroxides, Fe(III) oxides and hydroxides, SO_4^{2-}, and CO_2 as "Mn(IV) reduction," "Fe(III) reduction," and "SO_4^{2-} reduction," and "methanogenesis," respectively.

For the sake of simplicity, Brush and Anderson (1989a) and Brush (1990) described these microbial processes as though they will occur sequentially in WIPP disposal rooms. This is generally the case in natural systems such as lacustrine, estuarine, and marine sediments. The processes described below may occur sequentially in many locations in the repository, but may also occur simultaneously because of the heterogeneous nature of the TRU waste to be emplaced in the repository. Aerobic microbial activity, for example, could continue for lengthy periods near large, radionuclide-bearing particles because of continuous production of O_2 from radiolytic consumption of H_2O in the waste or brine. Simultaneously, anaerobic microbial activity may occur in waste with low concentrations of radionuclides but with large quantities of steels and other Fe-base alloys, Al and Al-base alloys, organic materials, or other reductants.

During any of these microbial processes, the degradation of organic matter is complex and involves several intermediate steps usually mediated by different microorganisms. Geochemists have described microbial activity by writing overall equations representative of each process (see, for example; Froelich et al., 1979; Berner, 1980; and Brush and Anderson, 1989a). They use various formulas such as CH_2O (a simplified formula for glucose) or $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$ (the Redfield ratio) to represent the substrate, but do not include microbial synthesis of cellular material (biomass) by in their equations. Microbiologists, on the other hand, include synthesis of biomass by adding formulae such as $C_5H_7O_2N$ to the right-hand side of their equations. To illustrate this difference, Brush (1990) used equations with and without biomass. Furthermore, both types of equations appear in the discussion below (see B.2.3 and B.2.4).

As written, these overall reactions suggest that all of the microbially produced CO_2, N_2, H_2S, and CH_4 remain in the gaseous phase. However, it is also possible to write these reactions such that all or most of the CO_2 and H_2S dissolve in the aqueous phase, if any. Significant quantities of CO_2 and H_2S would dissolve if enough brine were present and the pH of the brine were basic. Furthermore, it is possible to write these equations such that all or most of the CO_2 reacts with $Ca(OH)_2$ (in hydrated cementitious materials) or CaO (a proposed backfill additive). The quantity of CO_2 consumed would depend, of course, on the quantities of $Ca(OH)_2$ and CaO present, the permeability of the waste and backfill, and the extent to which the carbonation product (probably $CaCO_3$) isolate $Ca(OH)_2$ or CaO from additional reaction with CO_2.

Despite these uncertainties, it is possible to determine, based on estimates of which potential electron acceptors will be present in significant quantities in WIPP disposal rooms after filling and sealing, which of these microbial processes would, if their rates were high enough, be significant in the repository.

B.2.3 Aerobic Microbial Activity

Aerobic microorganisms use O_2 as the electron acceptor and produce CO_2 and, perhaps, H_2O (see B.2.2).

Brush and Anderson (1989a) concluded that aerobic microbial consumption of cellulosics will not have a significant, direct effect on the gas and H_2O contents of WIPP disposal rooms. (They assumed that neither aerobic nor anaerobic microorganisms would consume plastics and rubbers.) Brush and Anderson (1989a) calculated, based on their 1988 estimate of the quantity of cellulosics in the CH TRU waste to be emplaced in the repository, that the O_2 in mine air trapped in the repository at the time of filling and sealing would only be sufficient to oxidize about 1.1 to 1.7% of the cellulosics, depending on the initial void volume assumed. Inclusion of the cellulosics in CH TRU waste boxes and in RH TRU waste would decrease this estimated range. Furthermore, the estimates of actinide solubilities presented by Trauth et al. (1992) and estimates of the quantities of brine from Brush (1993) (see E), suggest that brine radiolysis would produce O_2 at such low rates that aerobic microbial activity would continue to be an insignificant process throughout the 10,000-year period of performance of the repository.

The overall reactions for aerobic microbial activity as written by Berner (1980) and Brush (1990), respectively, are:

$$CH_2O + O_2 = H_2O + CO_2; \quad \text{(B.7a)}$$

$$CH_2O + 0.11H^+ + 0.11NO_3^- + 0.21O_2 = 0.11C_5H_7O_2N + 0.67H_2O + 0.44CO_2. \quad \text{(B.7b)}$$

In these reactions and the reactions for other potentially significant microbial processes (see B.2.4), CH_2O represents the substrate. In Reaction B.7b and the second equation for each of the other processes, $C_5H_7O_2N$ represents biomass.

Discuss aerobic results from Francis et al. (1994) here!!!

B.2.4 Anaerobic Microbial Activity

After the depletion of O_2, anaerobic respiration begins. During denitrification, microorganisms use NO_3^- as the electron acceptor and produce CO_2 and N_2. During NO_3^- reduction, microorganisms also use NO_3^- as the electron acceptor, but produce CO_2, various oxides of nitrogen (NO_x), and eventually NH_3. These processes could be significant in the repository because: (1) sludges in the WIPP inventory contain copious amounts of NO_3^- which, because of its high solubility, could dissolve in any brine present and diffuse to drums or boxes containing cellulosic materials; (2) N_2 might diffuse into the surrounding Salado Formation even less readily than other gases because the concentration of N_2 in intergranular brines may already be at or close to its solubility limit; (3) although there is no known backfill additive to remove or prevent the production of N_2 or NH_3 at a reasonable cost, emplacement of containers with sludges in different rooms or panels than containers with cellulosics might prevent denitrification and NO_3^- reduction if these processes affect the long-term performance of the repository adversely.

Because cellulosics and sludges will be emplaced in separate containers, it is unlikely that cellulosics and NO_3^- will come into contact prior to rupture of drums and boxes, resaturation of the repository with brine, and diffusion of NO_3^- through the brine. Therefore, denitrification and NO_3^- reduction could be significant in WIPP disposal rooms under saline, but not asaline, conditions.

The overall reactions for microbial denitrification from Berner (1980) and Brush (1990), respectively, are:

$$CH_2O + 0.8NO_3^- = 0.6H_2O + 0.8OH^- + 1.0CO_2 + 0.4N_2; \quad \text{(B.8a)}$$

$$CH_2O + 0.46H^+ + 0.46NO_3^- = 0.076C_5H_7O_2N + 0.96H_2O + 0.624CO_2 + 0.192N_2. \quad (B.8b)$$

Reaction B.8a and some of the reactions below are modified slightly from Berner 1980) and Brush 1990) so that all of the microbially produced CO_2, N_2, H_2S, and CH_4 remain in the gaseous phase. This facilitates comparison of the ratio of the number of moles of gas produced per mole of organic C consumed. The equations for NO_3^- reduction are similar to those for denitrification.

Once denitrification or NO_3^- reduction deplete all available NO_3^-, some microorganisms may use Mn(IV) oxides and hydroxides as electron acceptors, thereby reducing them to soluble Mn(II) phases (Lovley and Phillips, 1988).[1] Although this mode of microbial respiration has received only limited study to date, Mn(IV) reduction would probably be insignificant in the repository because of the expected lack of significant quantities of this element in the CH and RH TRU waste to be emplaced in WIPP disposal rooms, in the surrounding Salado Formation, or in likely WIPP brines (Deal and Case, 1987; Deal et al., 1989a, 1989b, 1991a, 1991b).

Brush and Anderson (1989a) proposed the addition of MnO_2 to the backfill to prevent SO_4^{2-} reduction (see Reactions B.11a and B.11b), the concomitant production of H_2S, the reaction of H_2S with steels and other Fe-base alloys, or their corrosion products to form FeS_2, and the concomitant production of H_2. However, Brush (1990) maintained that MnO_2 would probably not prevent SO_4^{2-} reduction effectively. Therefore, Mn(IV) reduction will probably be insignificant in the repository.

The overall reactions for microbial Mn(IV) reduction from Berner (1980) and Brush (1990) are:

$$CH_2O + 2MnO_2 + H_2O = 2Mn^{2+} + 4OH^- + CO_2; \quad (B.9a)$$

$$CH_2O + 1.08MnO_2 + 2.2243H^+ + 0.0657NO_3^- =$$

$$0.0657C_5H_7O_2N + 1.8843H_2O + 1.08Mn^{2+} + 0.6713CO_2. \quad (B.9b)$$

---

[1] Because Mn(II)-bearing solids are significantly more soluble than Mn(IV)-bearing solids, an increase in the concentration of dissolved Mn in the pore waters of lacustrine, estuarine, or marine sediments implies that microbial Mn(IV) reduction is occurring in that section of the sediments.

Subsequent to the depletion of Mn(IV) oxides and hydroxides, some microorganisms may also use Fe(III) oxides and hydroxides as electron acceptors, reducing them to Fe(II)-bearing solids and aqueous species in the process (Lovley and Phillips, 1986; 1988).[1]

Brush and Anderson 1989a) calculated that the quantity of O_2 present in the air trapped in WIPP disposal rooms at the time they are filled and sealed will only be sufficient to oxidize about 0.4 to 1.1% of the drums in a room to $\gamma FeO(OH)$, an Fe(III) oxide and the most likely oxic corrosion product (see B.1.1). Furthermore, radiolysis of H_2O in the waste and brine will probably not produce much O_2 thereafter (see B.3.1) or, thus, promote much oxic corrosion thereafter. Haberman and Frydrych (1988) identified $Fe(OH)_2$ (amakinite), an Fe(II) hydroxide, as their anoxic corrosion product, but the Fe(II, III) phase Fe_3O_4 (magnetite) is also a possible anoxic corrosion product under expected WIPP conditions (see B.1.2). Reaction of steels and other Fe-base alloys with CO_2 in the absence of H_2S would produce $FeCO_3$ (siderite), an Fe(II) carbonate, at least prior to passivation. Reaction of $Fe(OH)_2$ and Fe_3O_4 with CO_2 in the absence of H_2S would also produce $FeCO_3$. Reaction of H_2S with steels and other Fe-base alloys or their corrosion products would form various polymorphs of FeS or FeS_2. Although it is unclear which Fe phase or phases will be produced as a result of these processes, microorganisms would probably not use the Fe(II) phases $Fe(OH)_2$, $FeCO_3$, FeS, and FeS_2 as electron acceptors, but could use $\gamma FeO(OH)$ or other polymorphs of FeO(OH) and, perhaps, Fe_3O_4. Therefore, Fe(III) reduction would be a potentially significant microbial process only in the event of significant formation of FeO(OH) or, perhaps, Fe_3O_4.

According to Berner 1980) and Brush 1990), the overall reactions for microbial Fe(III) reduction are:

$$CH_2O + 4Fe(OH)_3 = 3H_2O + 4Fe^{2+} + 8OH^- + CO_2; \quad (B.10.a)$$

$$CH_2O + 1.79Fe(OH)_3 + 0.08NO_3^- =$$

$$0.08C_5H_7O_2N + 1.58H_2O + 1.79Fe^{2+} + 3.66OH^- + 0.60CO_2. \quad (B.10.b)$$

After the depletion of NO_3^- and any Mn(IV) and/or Fe(III) oxides and hydroxides, obligately anaerobic microorganisms use SO_4^{2-} as the electron acceptor. These microorganisms reduce SO_4^{2-} to H_2S.

---

[1] Because Fe(II)-bearing solids are significantly more soluble than Fe(III)-bearing solids, an increase in the dissolved Fe concentration in sedimentary pore waters implies that microbial Fe(III) reduction is under way.

Because the dissolved SO_4^{2-} concentration of Salado- and Castile-Formation brines is on the order of a few hundred millimolar (Stein and Krumhansl, 986; Deal and Case, 987; Stein and Krumhansl, 988; Deal et al., 1989a, 1989b; Brush, 1990; Deal et al., 1991a, 1991b), microbial SO_4^{2-} reduction could be a significant process if brine were present in WIPP disposal rooms. It is unknown whether or not microorganisms could use SO_4^{2-} from evaporite minerals as an electron acceptor under humid conditions. However, significant quantities of SO_4^{2-} may also occur in sludges.

Reaction of steels and other Fe-base alloys with H_2S in the absence of CO_2 would produce FeS or FeS_2, at least prior to passivation. Reaction of $Fe(OH)_2$ and Fe_3O_4 with H_2S in the absence of CO_2 would also form FeS and FeS_2.

The overall equations for microbial SO_4^{2-} reduction form Berner (1980) and Brush (1990) are:

$$CH_2O + 0.5SO_4^{2-} = OH^- + CO_2 + 0.5H_2S; \quad \text{(B.11a)}$$

$$CH_2O + 0.58H^+ + 0.04NO_3^- + 0.34SO_4^{2-} =$$

$$0.04C_5H_7O_2N + 0.88H_2O + 0.18HS^- + 0.18H_2S + 0.4CO_2. \quad \text{(B.11b)}$$

Fermentative microorganisms convert various substrates to acetic acid, butyric acid, ethyl alcohol, methyl alcohol, propyl alcohol, propionic acid, valeric acid, etc., and CO_2 and H_2. Next, some microorganisms convert these acids and alcohols, along with H^+, to acetic acid, CO_2 and H_2. This step, H^+-reducing acetogenesis, only occurs if SO_4^{2-}-reducing or methanogenic microorganisms are present to scavenge H_2. Methanogenic microorganisms then convert CO_2 and H_2 to CH_4 and H_2O. Methanogens can also convert acetic acid to CH_4 and CO_2. Although acetic acid could be produced by fermentation and H^+-reducing acetogenesis, it will also be present in the waste and could dissolve in any brine present in WIPP disposal rooms.

Because fermentation and methanogenesis could occur without electron acceptors from sludges (NO_3^- and SO_4^{2-}) or brines (SO_4^{2-}), it is the most likely microbial process in drums or boxes containing cellulosics prior to rupture of containers caused by room closure. Furthermore, these are the most likely microbial processes to be carried out to a significant extent by nonhalophilic or nonhalotolerant microorganisms, which will be present in the waste prior to emplacement. Of course, any microbial activity that occurs in unbreached containers would necessarily have to occur under humid conditions. Fermentation and methanogenesis may also be significant after the containers rupture and brine enters the repository, especially as the electron acceptors discussed above are depleted.

The overall equations for microbial methanogenesis form Berner (1980) and Brush (1990) are

$$2CH_2O = CH_4 + CO_2; \quad \text{(B.12a)}$$

$$CH_2O + 0.04H^+ + 0.04NO_3^- =$$

$$0.04C_5H_7O_2N + 0.16H_2O + 0.36CH_4 + 0.44CO_2. \quad \text{(B.12b)}$$

These reactions will, if they occur, produce significant quantities of gas.

Another possible methanogenic reaction is:

$$CO_2 + 4H_2 = CH_4 + 2H_2O. \quad \text{(B.13)}$$

If both CO_2 (from microbial activity) and H_2 (from anoxic corrosion or microbial activity) are present, this reaction will consume significant quantities of gas. Clearly, Reactions B.12a, B.12b, and B.13 will have significantly different effects on the gas and H_2O contents of the repository.

Discuss anaerobic results from Francis et al. (1994) here!!!

B.2.4.1 EFFECTS OF ANAEROBIC MICROBIAL ACTIVITY ON THE WATER CONTENT OF WIPP DISPOSAL ROOMS

It is not known whether anaerobic microbial consumption of cellulosics will produce or consume significant quantities of H_2O in WIPP disposal rooms. Reactions B.8a through B.12b imply that microbial consumption of simple sugars would produce H_2O in most cases (see B.2.4), but hydrolysis of cellulosics, the most important potential substrate in the WIPP inventory, will consume H_2O prior to the start of these reactions. Therefore, the net effect of microbial activity on the H_2O content of the repository is unclear. For the reaction-path gas-generation model (see C.3), Brush et al. (1994) used $C_6H_{10}O_5$, a simplified formula for cellulosics, to represent the substrate in Reactions B.8a through B.12b. These equations suggest that, even after inclusion of hydrolysis, anaerobic microbial activity will produce H_2O. However, laboratory studies under expected WIPP conditions have not confirmed this yet.

It is also not known whether microbial consumption of plastics and rubbers will produce or consume H_2O.

Quantification of the effects of anaerobic microbial activity on the H_2O content of the repository is essential to predict the extent of gas production from anoxic corrosion (see 2.3.1 and B.1.2) and brine radiolysis (see 2.3.3 and B.3.1), both of which require H_2O, and the quantity of brine available for the transport of radioactive waste constituents and other contaminants subject to aqueous-phase transport (see 2.1).

B.3 Radiolysis

Radiolysis of H_2O in the waste and brine in WIPP disposal rooms will produce H_2 and O_2 and consume H_2O. Radiolysis of cellulosics, plastics, and rubbers in the waste will produce a variety of gases.

B.3.1 Radiolysis of Water in the Waste and Brine

Brush (1993) concluded that radiolysis of H_2O in brine that will enter WIPP disposal rooms after filling and sealing will not produce gas at rates comparable to those expected for anoxic corrosion and microbial activity. He based this conclusion on calculations using the results of Reed et al. (1993) (see below), estimates of the quantities of brine that could be present in the repository after filling and sealing, and estimates of the concentrations of Pu, Am, Np, U, and Th in WIPP brines from Trauth et al. (1992). (Laboratory and modeling studies of the chemical behavior of Pu, Am, Np, U, and Th under expected WIPP conditions are currently under way to replace the estimates of Trauth et al. (1992) with actual data.)

Radiolysis of H_2O in the waste and brine in WIPP disposal rooms will probably not consume significant quantities of H_2O, despite the stoichiometry of Reaction B.14, because this process will probably be insignificant relative to other gas-generation mechanisms.

However, radiolysis of H_2O in the waste and brine may be significant from the standpoint of the O_2 content of WIPP disposal rooms. This is because brine radiolysis is the only important process that will produce O_2 in the repository.

Describe the results of Reed et al. (1993) here!!!

B.3.2 Radiolysis of Cellulosics, Plastics, and Rubbers

The data summarized by Molecke (1979) imply that radiolysis of cellulosics, plastics, and rubbers would not be a significant, long-term gas-generation mechanism in WIPP disposal rooms.

B.4 Gas-Consuming Processes

$Ca(OH)_2$ (in hydrated cementitious materials) and CaO (a potential backfill additive) may consume CO_2 and H_2S and produce H_2O. Brush (1990) described these processes in detail.

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APPENDIX C: REVIEW OF WIPP GAS-GENERATION MODELS

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APPENDIX C: REVIEW OF WIPP GAS-GENERATION MODELS

This section describes three gas-generation models used or developed by the WIPP Project to date: (1) the rates-and-potentials model, used by Lappin et al. (1989) for systems analysis; (2) the average-stoichiometry model currently in BRAGFLO, used by WIPP Performance Assessment Division (1991) and Sandia WIPP Project (1992) for the 1991 and 1992 PA calculations; (3) the reaction-path model of Brush et al. (1994), currently under development for eventual incorporation in BRAGFLO.

C.1 The Rates-and-Potentials Model

The rates-and-potentials gas-generation model of Lappin et al. (1989) included two processes: (1) anoxic corrosion of steels and other Fe-base alloys; (2) microbial degradation of cellulosics and rubbers. Although Lappin et al. (1989) realized that α radiolysis of H_2O present in the waste at the time of emplacement, of H_2O in brine that may flow into WIPP disposal rooms from the surrounding Salado Formation, or of combustibles (cellulosics, plastics, and rubbers) could produce a variety of gases, they assumed that this process would be insignificant relative to anoxic corrosion and microbial activity. They based this assumption on the data summarized by Molecke (1979), which showed that, in general, radiolysis of TRU waste produced gas at rates significantly lower than corrosion and microbial activity.

The rates-and-potentials model also does not include interactions between anoxic corrosion and microbial activity, such as passivation of steels and other Fe-base alloys by microbially produced CO_2 or H_2S.

For their gas-generation model, Lappin et al. (1989) simply estimated gas-production rates and potentials for anoxic corrosion and microbial activity, and divided the potentials by the rates to calculate gas generation in WIPP disposal rooms. They did not specify which corrosion or microbial reactions would occur, only that these processes would occur and produce gas. Although they realized that anoxic corrosion will produce H_2 and that microbial activity will produce CO_2, CH_4, H_2, H_2S, and N_2, they did not predict the composition of the gaseous phase because of uncertainties as to which microbial respiratory process or processes would be significant in the repository.

Lappin et al. (1989) estimated an H_2-production rate of 1.70 moles per equivalent drum of waste per year for anoxic corrosion of steels and other Fe-base alloys. Laboratory studies of anoxic corrosion at PNL had not yet yielded any H_2-production or corrosion rates. Therefore, they based this estimate on a previous study for the WIPP Project (Molecke, 1979) and a more recent study for the Salt Repository Project for commercial spent fuel and HLW (Haberman and Frydrych, 1988). Based on estimates by Brush and Anderson (1989) and Drez (1989) of the numbers of steel CH TRU drums and boxes to be emplaced in WIPP disposal rooms, the quantities of steel in these containers, and the quantities of Fe-base alloys in CH TRU waste), Lappin et al. (1989) also estimated an H_2-production potential of 894 moles per drum. These estimates of the H_2-production rate and the H_2-production potential did not include the steels or other Fe-base alloys used for RH TRU waste canisters and plugs, or the Fe-base alloys contained in RH TRU waste. Although Lappin et al. (1989) realized that corrosion would consume significant quantities of H_2O, they assumed that sufficient brine would be available to produce 894 moles of H_2 per drum. Furthermore, laboratory studies at PNL had not yet demonstrated that CO_2 and H_2S can, if available in sufficient quantities, passivate steels, or that anoxic corrosion and H_2 production do not occur under humid conditions. Therefore, they calculated that corrosion would produce H_2 at a constant rate of 1.70 moles per drum per year for 526 years.[1]

Lappin et al. (1989) estimated a microbial gas-production rate of 0.85 moles per drum per year for their gas-generation model. Because laboratory studies of microbial activity had not yet yielded any gas-production rates since they were restarted by the WIPP Project in 1989 they used the arithmetic mean of the range of "the most probable overall average" gas-production rate from Molecke (1979) for this estimate. For their estimate of the microbial gas-production potential, Lappin et al. (1989) used the same assumptions made by M. A. Molecke for Sandia Laboratories (1979) and estimates by Drez (1989) of the quantities of cellulosics and rubbers in CH TRU waste to calculate a value of 606 moles of various gases per drum.[2] The most important of these assumptions was that microorganisms would consume all of the cellulosics and half of the rubbers, but none of the plastics in CH TRU waste. The other assumptions comprised the yields of various gases expected from microbial degradation of cellulosics and rubbers. Lappin et al. (1989) did not know whether microbial activity would produce or consume H_2O, but they believed, based on data summarized by Molecke (1979), that microbial gas production was likely even under humid conditions. Therefore, they calculated that microbial activity would produce gas at a constant rate of 0.85 moles per drum per year for 713 years.

Based on the estimates described above, Lappin et al. (1989) calculated that anoxic corrosion and microbial activity would produce various gases at a combined rate of 2.55 moles per drum per year for 526 years after filling and sealing WIPP disposal rooms. Because laboratory studies at PNL had not yet revealed that CO_2 and H_2S can passivate steels, they did not include this process during the 526-year period during which corrosion and microbial activity produce gas simultaneously. From 526 to 713 years, microbial activity would produce gases at a rate of 0.85 moles per drum per year.

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[1] Lappin et al. (1989) did not believe that the use of three significant figures for these estimates was defensible. However, they reported them to three significant figures to facilitate verification of their calculations.

[2] Because Sandia Laboratories (1979) did not describe the assumptions used for its estimate of the microbial gas-production potential, Lappin et al. (1989) described them based on information provided by M. A. Molecke.

C.2 The Average-Stoichiometry Model

The average-stoichiometry gas-generation model (WIPP Performance Assessment Division, 1991; Sandia WIPP Project, 1992) includes: (1) anoxic corrosion of steels and other Fe-base alloys; (2) microbial degradation of cellulosics and rubbers. This model is similar to the rates-and-potentials model of Lappin et al. (1989) in that it does not include radiolysis or interactions between anoxic corrosion and microbial activity.

Perhaps the most significant difference between these two models is that, because the average-stoichiometry model is part of the two-phase (brine and gas) hydrologic model BRAGFLO, gas generation is coupled with brine and gas inflow and outflow. Moreover, because BRAGFLO uses a porosity surface to simulate room closure (see Butcher and Mendenhall, 1993), it also couples gas generation to the geomechanical behavior of WIPP disposal rooms. From this point on, the term "average-stoichiometry model" refers to a component of BRAGFLO, not a stand-alone gas-generation model.

Another significant difference between the rates-and-potentials model and the average-stoichiometry model is that the latter does not use gas-production potentials as input parameters. Instead, the average-stoichiometry model produces gas by corrosion or microbial activity until a reactant is consumed. Because BRAGFLO couples gas generation with brine inflow and outflow, anoxic corrosion can consume all available H_2O prior to attaining its gas-production potential. Thus, availability of H_2O, not steels and other Fe-base alloys, may limit anoxic corrosion and H_2 production. Therefore, other input parameters, not predetermined gas-production potentials, determine how much gas is produced in a given calculation. Input parameters that affect gas-generation calculations by the average stoichiometry model include, in addition to gas-production rates, the initial quantities of steels and other Fe-base alloys, cellulosics, and H_2O in the waste, and the calculated quantity of brine that may seep into WIPP disposal rooms from the surrounding Salado Formation. For their 1991 and 1992 calculations, PA personnel used gas-production rates provided by Brush (1991) (see D).

The average-stoichiometry model includes two anoxic-corrosion reactions, a simplified form of Reaction B.2 in which x = 0 and Reaction B.3 (see B.1.2). WIPP Performance Assessment Division (1991) defined the average stoichiometry of Reactions B.2 and B.3 as:

$$Fe + ((4 + 2x)/3)H_2O = ((4 - x)/3)H_2 + (3x)Fe(OH)_2 + ((1 - x)/3)Fe_3O_4. \quad (C.1)$$

In Reaction C.1, x is the mole fraction of Fe consumed by Reaction B.2. PA personnel then sampled the parameter x from a uniform distribution between 0 and 1, hence the name "average-stoichiometry" for this model.

During a calculation, the average-stoichiometry model uses an effective corrosion rate consisting of a weighted average of the inundated and humid corrosion rates sampled for that calculation. The weighting depends on the quantities of steels and other Fe-base alloys in a waste panel in contact with brine, gas, and other materials such as non-Fe-base waste constituents, backfill, or rock,. The model assumes that the steels and other Fe-base alloys in contact with brine corrode and produce H_2 at the inundated rate, that those in contact with the gas react at the humid rate, and that those in contact with other materials do not react at all. The model calculates the volume fractions of steels and other Fe-base alloys in contact with brine, gas, and other materials from the initial quantities of these materials in a panel and the computed, time-dependent porosity and saturation.

For their 1991 and 1992 calculations, PA personnel assumed that the inundated or humid corrosion rate is constant as long as these conditions persist in a given volume of the waste. Thus, they assumed that the sampled corrosion rates are independent of the "concentrations" of steels and other Fe-base alloys in the waste, the surface area of these materials, the total pressure, the composition of the aqueous phase (including pH and salinity), or the composition of the gaseous phase (including the humidity). The effects of some of these factors, such as the "concentration" of corroding metals, pressure, salinity, or humidity, may indeed be modest. However, pH, CO_2, and H_2S may affect corrosion of steels and other Fe-base alloys significantly (see B.1.2. and 3.3.2). Therefore, Brush (1991) (see D) attempted to take some of these factors into account by estimating ranges for the rates of anoxic corrosion and H_2 production (see 3.3.1).

Although BRAGFLO does quantify the effects of Reaction C.1 on the H_2O content of the repository, it does not calculate the reduction in porosity, or other geomechanical effects, caused by the precipitation of salts accompanying corrosion-induced consumption of H_2O from brine.

The average-stoichiometry model uses a generalized form of an overall reaction for microbial consumption of the potentially significant substrates in TRU waste (cellulosics, plastics, and rubbers) and concomitant gas production (WIPP Performance Assessment Division, 1991):

$$CH_2O + \text{unknowns} + \text{microorganisms} = (5/3)\text{gas} + \text{unknowns}. \qquad \text{(C.2)}$$

In Reaction C.2, CH_2O (a simplified formula for glucose) represents potentially significant microbial substrates. For their 1991 and 1992 calculations, WIPP PA personnel assumed that microorganisms may, depending on the rate of Equation 20, consume all of the cellulosics, half of the rubbers, and none of the plastics in the repository. WIPP Performance Assessment Division (1991) obtained Reaction C.2 from Brush and Anderson (1989), who listed overall reactions for a number of microbial processes that could occur in WIPP disposal rooms to determine the range of the ratio of moles of gas produced per mole of organic C consumed. Brush and Anderson (1989) concluded that this ratio could vary from -1 in the case of aerobic respiration with complete consumption of CO_2 by dissolution in basic brine (their Reaction 17) to 5/3 in the case of microbial Fe_3O_4 reduction (their Reaction 20e*). Although microbial reduction of Fe(III) oxides and hydroxides occurs in natural environment, it is unknown whether microbes can use Fe_3O_4 as the electron acceptor. Brush and Anderson (1989) chose this reaction to bound the range of the ratio of moles of gas produced per mole of organic C consumed.

Although Reaction C.2 produces the maximum number of moles of gas per mole of organic C consumed, PA personnel actually sampled this parameter x from a uniform distribution between 0 and 1 for their 1991 and 1992 calculations. They chose a lower limit of 0 instead of -1 because they assumed that aerobic respiration with complete consumption of CO_2 is unlikely to be a significant reaction in WIPP disposal rooms, a reasonable assumption in view of the conclusion by Brush and Anderson (1989) that aerobic microbial activity would not have a significant, direct effect on the gas and H_2O contents of WIPP disposal rooms (see B.2.3). Although that assumption was reasonable, their range of 0 to 5/3 neglects Reaction B.13, which will, if it occurs in WIPP disposal rooms, consume significant quantities of CO_2 and H_2 (see B.2.4). (Neither Brush and Anderson (1989) nor Brush (1990) included Reaction B.13 in their lists of potentially significant microbial gas-generation reactions.)

The average-stoichiometry model uses an effective microbial gas-production rate comprising a weighted average of the inundated and humid rates in a manner identical to that for anoxic corrosion. For microbial activity, the weighting depends on the quantities of cellulosics and rubbers in a waste panel in contact with brine, gas, waste constituents such as other combustibles, steels and other Fe-base alloys, backfill, or rock. The model assumes that microbes consume cellulosics and rubbers in contact with brine at the inundated rate, that they consume cellulosics and rubbers in contact with gas at the humid rate, and that they do not consume cellulosics and rubbers in contact with other materials at all.

PA personnel assumed for their 1991 and 1992 calculations that the inundated or humid microbial gas-production rate is constant in those volumes of the waste that remain subject to these conditions. Thus, they assumed that the sampled microbial gas-production rates are independent of the concentrations, types, or the surface areas of cellulosics and rubbers in the waste, the numbers and types of microorganisms present, the concentrations of nutrients and electron acceptors, pressure, the composition of the aqueous phase, or the composition of the gaseous phase (including the concentrations or partial pressures of byproduct gases such as CO_2, N_2, and H_2S). Although the effects of some of these factors, such as the concentrations of cellulosics and rubbers, pressure, salinity, or humidity, may indeed be modest, other factors could affect microbial activity significantly. These include the numbers and types of microbes, the concentrations of nutrients and electron acceptors, pH, and the concentrations or partial pressures of byproduct gases. Brush (1991) tried to take some of these factors into account by estimating ranges for the rates of anoxic corrosion and H_2 production (see 3.3.1).

Because it was unknown at the time (and is still unknown) whether microbial degradation of the potentially significant substrates to be emplaced in the WIPP will result in a net production or consumption of H_2O (see B.2.4.1)), PA personnel assumed for their 1991 and 1992 calculations that microbial activity will have no net effect on the H_2O content of the repository.

WIPP Performance Assessment Division (1991) and Sandia WIPP Project (1992) used gas-production rates from Brush (1991) in the average-stoichiometry gas-generation model for the 1991 and 1992 PA calculations. Subsubsection 3.3.1 describes these data in detail.

C.3 The Reaction-Path Model

The reaction-path gas-generation model (Brush et al., 1994) includes: (1) oxic and anoxic corrosion of steels and other Fe-base alloys, including passivation by the adherent corrosion products $FeCO_3$ and FeS and depassivation caused by destabilization of these phases due to changes in the composition of the gaseous phase; (2) microbial degradation of cellulosics with sequential or concurrent use of O_2, NO_3^-, FeO(OH), SO_4^{2-}, or CO_2 as the electron acceptor; (3) α radiolysis of brine; (4) consumption of CO_2 by $Ca(OH)_2$ (in hydrated cementitious materials) or CaO (a proposed backfill additive).

The reaction-path model is similar to the average stoichiometry model (WIPP Performance Assessment Division, 1991; Sandia WIPP Project, 1992) in that it uses input parameters such as the initial quantities of steels and other Fe-base alloys, cellulosics, and H_2O in the waste or brine, and gas-generation rates, but not gas-production potentials, to calculate gas generation in WIPP disposal rooms. The most significant differences between these models are that the reaction path model includes more gas-generation processes (and therefore, requires more input parameters) than the average-stoichiometry model. Furthermore, the reaction-path model includes interactions among these processes. Finally, because it has not been incorporated in BRAGFLO yet, the reaction-path model does not simulate interactions among gas generation, brine inflow and outflow, and room closure.

The reaction-path model includes one oxic-corrosion reaction (see Reaction B.1 in B.1.1) and five anoxic-corrosion reactions (Reactions B.2 through B.6 in B.1.2). (In the reaction-path model, the value of x in Reaction B.2 is 0.) It also includes the following reactions among Fe-bearing corrosion products:

$$Fe(OH)_2 + CO_2 = FeCO_3 + H_2O; \quad (C.3)$$

$$Fe(OH)_2 + H_2S = FeS + 2H_2O; \quad (C.4)$$

$$Fe(OH)_2 + 2H_2S = FeS_2 + 2H_2O + H_2; \quad (C.5)$$

$$FeCO_3 + H_2S = FeS + H_2O + CO_2; \quad (C.6)$$

$$FeCO_3 + 2H_2S = FeS_2 + H_2O + CO_2 + H_2; \quad (C.7)$$

$$3Fe(OH)_2 = Fe_3O_4 + 2H_2O + H_2; \quad (C.8)$$

$$Fe_3O_4 + 3CO_2 + H_2 = 3FeCO_3 + H_2O \quad (C.9)$$

$$Fe_3O_4 + H_2 + 3H_2S = 3FeS + 4H_2O; \quad (C.10)$$

$$Fe_3O_4 + 6H_2S = 3FeS_2 + 4H_2O + 2H_2. \quad (C.11)$$

The reaction-path model uses the following reactions to simulate gas production from microbial consumption of cellulosics:

$$C_6H_{10}O_5 + 6O_2 = 5H_2O + 6CO_2; \quad (C.12)$$

$$C_6H_{10}O_5 + 4.8H^+ + 4.8NO_3^- = 7.4\ H_2O + 6CO_2 + 2.4N_2; \quad (C.13)$$

$$C_6H_{10}O_5 + 24FeO(OH) + 7H_2O = 24Fe(OH)_2 + 6CO_2; \quad (C.14)$$

$$C_6H_{10}O_5 + 24FeO(OH) + 18CO_2 = 24FeCO_3 + 17H_2O; \quad (C.15)$$

$$C_6H_{10}O_5 + 24FeO(OH) + 24H_2S = 24FeS + 41H_2O + 6CO_2; \quad (C.16)$$

$$C_6H_{10}O_5 + 24FeO(OH) + 48H_2S = 24FeS_2 + 41H_2O + 6CO_2 + 24H_2; \quad (C.17)$$

$$C_6H_{10}O_5 + 24FeO(OH) = 8Fe_3O_4 + 9H_2O + 6CO_2 + 8H_2; \quad (C.18)$$

$$C_6H_{10}O_5 + 6H^+ + 3SO_4^{2-} = 5H_2O + 6CO_2 + 3H_2S. \quad (C.19)$$

In Reactions C.12 through C.19, $C_6H_{10}O_5$ is a simplified formula for cellulosics. These reactions are analogous to Reactions B.7a through B.12b (see B.2.3 and B.2.4), except that they use $C_6H_{10}O_5$ instead of CH_2O (a simplified formula for glucose) to represent the microbial substrate. Currently, the reaction-path model includes only gas production from microbial consumption of cellulosics, not plastics and rubbers. To simulate microbial consumption of plastics and rubbers, one would simply replace $C_6H_{10}O_5$ with formulae for various plastics and rubbers and add the resulting reactions to the model.

The reaction-path model uses Reaction B.14 to simulate α radiolysis of H_2O in brine (or H_2O present in the waste at the time of emplacement). The model does not include radiolysis of combustibles at this time.

For consumption of CO_2 by $Ca(OH)_2$ or CaO the reaction-path model includes the reactions:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O; \quad (C.20)$$

$$CaO + CO_2 = CaCO_3. \quad (C.21)$$

The reaction-path model simulates corrosion, microbial activity, brine radiolysis, and CO_2 consumption, and the interactions among these processes, by converting the reactants in Reactions B.1 through B.6 (see B.1.1 and B.1.2) and C.12 through C.21 (see above) to the products at the rates observed in laboratory studies of gas generation (see B.1.2, B.2.3, B.2.4, and B.3) or at rates estimated from studies carried out for applications other than the WIPP Project (see 3.3.2). At the start of each time step, the model uses the fugacities of CO_2, H_2, and H_2S in the gaseous phase and thermodynamically calculated, three-dimensional phase diagrams for the solid phases in the Fe-H_2O-CO_2-H_2-H_2S system to determine the solid corrosion product(s) stable at the start of that time step. Currently, the solid phases used to calculate these phase diagrams include Fe, $Fe(OH)_2$, Fe_3O_4, $FeCO_3$, FeS, and FeS_2. It then simulates corrosion, microbial activity, brine radiolysis, and CO_2 consumption by converting reactants (steels and other Fe-base alloys, cellulosics, H_2O, CO_2, etc.) to products (gases, corrosion products, H_2O, etc.) at experimentally observed or estimated rates. The fugacities of the gases produced and consumed by Reactions B.2 through B.6 and C.3 through C.21 in turn determine the fugacities of CO_2, H_2, and H_2S and the corrosion product(s) stable at the start of the next time step. In addition to these gases, the model calculates the quantities of several other materials produced and consumed during each time step. These include other gases (O_2, N_2, and CH_4), H_2O, steels and other Fe-base alloys, corrosion products ($Fe(OH)_2$, Fe_3O_4, $FeCO_3$, FeS, and FeS_2), microbial substrate ($C_6H_{10}O_5$), electron acceptors (O_2, NO_3^-, FeO(OH), SO_4^{2-}, and CO_2), and materials that consume CO_2 ($Ca(OH)_2$ and CaO). (Some of these components appear more than once in this list because they are reactants or products of more than one type of reaction. However, the model does not distinguish between these multiple functions except in two cases described below.) It uses the ideal gas law to calculate individual gas fugacities and the total pressure. The model continues to convert reactants to gases, H_2O, and other products (or, in the case of gas- or H_2O-consuming reactions, it continues to convert gases or H_2O to condensed products) until a reactant is completely consumed or until that reaction is in equilibrium with the products. The model calculates reaction paths by plotting points simultaneously depicting the common logarithms of the fugacities of CO_2, H_2, and H_2S (the gases that determine the stabilities of observed or possible corrosion products) in the three-dimensional phase diagrams for Fe-H_2O-CO_2-H_2-H_2S system after each time step.

In general, the current version of the reaction-path model assumes that equilibrium is attained after the incremental conversion of reactants to products in each time step. For example, the model uses one or more of Reactions B.2 through B.6 to convert steels and other Fe-base alloys to the solid corrosion product(s) stable (or, in the case of $Fe(OH)_2$, metastable) at the start of that time step. If one or more corrosion products are present at the end of a time step, the model then uses one or more of Reactions C.3 through C.11 to adjusts the fugacities of CO_2, H_2, and H_2S to values that simultaneously satisfy the equilibrium relationship(s) for these corrosion products. By adjusting the fugacities of CO_2, H_2, and H_2S to their equilibrium values, these corrosion products are in a sense, buffering the fugacities of these gases. Only after one of these corrosion products is completely consumed are the fugacities of CO_2, H_2, and H_2S free to deviate from values characteristic of equilibrium with that phase.

However, the reaction-path model does include disequilibrium behavior observed in laboratory studies of gas generation. For example, at low fugacities of CO_2 and H_2S, the model can, at the user's discretion, convert steels and other Fe-base alloys to $Fe(OH)_2$, the experimentally observed anoxic-corrosion product, despite the fact that $Fe(OH)_2$ is thermodynamically unstable with respect to Fe_3O_4 under these conditions (see B1.2). On the other hand, formation of Fe_3O_4 at low fugacities of CO_2 and H_2S is also an option in the model to determine the effects of possible long-term conversion of $Fe(OH)_2$ to Fe_3O_4.

Furthermore, the model simulates experimentally observed passivation of steels and other Fe-base alloys (see B.1.2) by "removing" these materials from the system once the experimentally observed passivation requirements are met (formation of enough $FeCO_3$ or FeS on the surfaces of the steels and other Fe-base materials to isolate them from additional corrosion). To determine whether the passivation requirements are met, the model distinguishes between the $FeCO_3$ or FeS that forms by corrosion of Fe and thus adheres to corroding surfaces, and the $FeCO_3$ or FeS that, for example, replaces $Fe(OH)_2$, which sloughs off the corroding surfaces.

It is, of course, possible to include other disequilibrium phenomena in the reaction-path model if necessitated by results form additional laboratory studies of gas generation.

The reaction-path model is not a system-wide model.. Therefore, it is necessary to use other models, such as the EQ3/6 geochemical software package (Daveler and Wolery, 1992; Wolery, 1992a; 1992b; Wolery and Daveler, 1992), to address issues other than gas generation, such as the effects of high CO_2 partial pressures on brine pH or the effects of H_2O consumption on salinity.

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APPENDIX D: BRUSH (1991)

Sandia National Laboratories

Albuquerque, New Mexico 87185

date: July 8, 1991

to: D. R. Anderson, 6342

from: L. H. Brush, 6345

subject: Current Estimates of Gas Production Rates, Gas Production Potentials, and Expected Chemical Conditions Relevant to Radionuclide Chemistry for the Long-Term WIPP Performance Assessment

This memorandum justifies the estimates of gas production rates, gas production potentials, and expected chemical conditions relevant to radionuclide chemistry in WIPP disposal rooms for design-basis transuranic (TRU) waste provided to R. P. Rechard last month (Table 1). Many of these estimates are new; some are based on recently obtained data from laboratory studies of anoxic corrosion.

I will provide similar estimates for the Engineered Alternatives Task Force's (in prep.) Alternatives 2 and 6 by August 1, 1991.

ANOXIC CORROSION

R. E. Westerman (1990, 1991a) of Pacific Northwest Laboratory (PNL) has observed significant H_2 production from anoxic corrosion of two heats each of ASTM A 366 and ASTM A 570 steels by WIPP Brine A under inundated conditions when N_2 is present at low pressures (about 150 psig) in the headspace above the brine. The low-C, cold-rolled steel alloy ASTM A 366 simulates the drums to be emplaced in the repository; the medium-C, hot-rolled steel alloy ASTM A 570 simulates the boxes. The H_2 production rate was essentially constant during 3- and 6-month experiments; the average value for all four heats obtained from the 6-month experiments is 0.21 moles per m^2 of steel per year. Based on my estimate of 6 m^2 of steels per equivalent drum of waste, which includes steels used to fabricate waste containers (drums and boxes) and steels contained in the waste, this is equivalent to 1.26 mole of H_2 per drum per year. Westerman also reported an average corrosion rate of 1.72 μm of steel per year for the 6-month runs. The H_2 production rates of 0.2 moles per m^2 per year or 1 mole per drum per year and the corrosion rate of 2 μm per year are my best estimates for inundated conditions, rounded to one significant figure (Table 1).

Strictly speaking, the H_2 production rates and the corrosion rate are not equivalent. Although he obtained both rates from each experiment, Westerman used independent techniques to obtain them (pressure measurements and posttest analysis of the headspace gases for the H_2 production rate and gravimetric, or weight-loss, analysis for the corrosion rate). These techniques agreed well, but not exactly, when applied to the 6-month experiments, but not as well for the 3-month experiments. (The best estimates described above are from the 6-month runs.) The discrepancies between these techniques probably result from uncertainties as to the identity and composition of the corrosion product or products formed during these experiments.

(Characterization of the corrosion product is necessary to write the chemical reactions used to convert corrosion rates to H_2 production rates.) We are still attempting to characterize the corrosion product from these runs.

Although the H_2 production rate has been constant for 6 months when N_2 is present at low-pressures, the results of high-pressure experiments at PNL imply that the build-up of H_2 pressure would eventually reduce this rate significantly (Westerman, 1991b). After 6 months, the corrosion rate of two heats of ASTM A 366 steel under inundated conditions with H_2 at a pressure of 1,000 psig was 0.356 μm per year, 21.8% of the rate of 1.63 μm per year observed for the same two heats of ASTM A 366 steel under low-pressure, inundated conditions with N_2. Multiplying 1.72 μm per year, the average rate for all four heats, by 0.218 gives 0.375 μm per year, my estimate of the average corrosion rate for all four heats of steel at 1,000 psig H_2. However, at an N_2 pressure of 1,000 psig the corrosion rate of two heats of ASTM A 366 steel was 2.96 μm per year, 81.6% higher than the low-pressure, inundated rate of 1.63 μm per year observed for the same two heats of ASTM A 366 steel. The product of 1.72 μm per year and 1.82 is 3.13 μm per year, my estimated average corrosion rate for all four heats of steel at 1,000 psig N_2. Westerman did not report H_2 production rates for the high-pressure experiments. Furthermore, we have still not identified the corrosion product or products yet. However, the corrosion product appears to be the same phase that formed in the 6-month, low pressure experiments. It is thus possible to estimate an H_2 production rate by multiplying the 6-month, low-pressure rates of 0.21 moles per m^2 or 1.26 moles per drum of waste by 0.218 (1,000 psig H_2) and 1.82 (1,000 psig N_2) to obtain 0.046 moles per m^2 per year or 0.275 moles per drum per year (1,000 psig H_2) and 0.38 moles per m^2 per year or 2.29 moles per drum per year (1,000 psig N_2). At present, we do not have corrosion rates for any pressures other than 150 and 1,000 psig. Westerman will, however, report 12-month data for 500 psig H_2 and 1,000 psig H_2 in November or December 1991. The adjusted, measured corrosion rate of 3 μm per year and the estimated H_2 production rate of 0.4 mole per m^2 per year or 2 moles per drum per year with N_2 at 1,000 psig are my maximum estimates for inundated conditions, rounded to one significant figure (Table 1).

Under low-pressure, inundated conditions with CO_2, H_2 production occurred for about 3 months, then virtually stopped after 3 or 4 months due to formation of a passivating layer of $FeCO_3$, or siderite (Westerman, 1991a). This suggests that, if microbially produced CO_2 were present, passivation of steel surfaces by $FeCO_3$ could stop H_2 production before the generation of significant quantities of this gas. However, we do not know the partial pressure of CO_2 required to form $FeCO_3$. Furthermore, crushing of drums and boxes during room closure could disrupt the layer of $FeCO_3$ and lead to some additional H_2 production. Nevertheless, the passivation observed after 3 or 4 months is the basis for my minimum estimates of 0 moles of H_2 per m^2 per year or 0 moles of H_2 per drum per year and 0 μm of steel per year for inundated conditions (Table 1).

Because we have still not identified the corrosion product or products, we cannot calculate the number moles of H_2O consumed per mole of Fe consumed or the number moles of H_2O consumed per mole of H_2 produced from anoxic corrosion of steels. However, the corrosion reaction that produces $Fe(OH)_2$ (amakinite) a possible corrosion product identified by Brush and Anderson (1988) and Brush (1990), would consume 2 moles of H_2O per mole of Fe consumed, or consume 2 moles of H_2O per mole of H_2 produced. The corrosion reaction that produces Fe_3O_4 (magnetite), another possible corrosion product, would consume 1.33 mole of H_2O per mole of Fe consumed, or consume 1 mole of H_2O per mole of H_2 produced. These values are probably typical of other corrosion reactions.

In 3- and 6-month, low-pressure, humid experiments with either CO_2 or N_2, Westerman (1990, 1991a) observed no H_2 production except for very limited quantities from corrosion of the bottom 10% of the specimens splashed with brine during pretest preparation of the containers. These results and modeling studies conducted by Davies (personal communication) suggested to me that anoxic corrosion could be self-limiting; small quantities of brine in the repository could produce H_2, increase the pressure, prevent additional brine inflow or even cause brine outflow, and thus prevent additional H_2 production. However, the thin film of brine introduced by capillary rise or condensation followed by dissolution of salts from the backfill, or H_2O absorbed by crushed salt or bentonite in the backfill, which will be in contact with drums and boxes, could cause additional anoxic corrosion of steels and H_2 production after brine is driven away from corroding steels.

Westerman (1991c) has just started a study to quantify H_2 production from anoxic corrosion of steels in contact with noninundated backfill materials and will report preliminary results by the end of September 1991. Until then, I propose the following arbitrarily estimated rates for humid conditions: minimum estimates of 0 moles of H_2 per m^2 of steel per year or 0 moles per drum of waste per year and 0 μm of steel per year; best estimates of 0.02 moles of H_2 per m^2 per year or 0.1 moles of H_2 per drum per year and 0.2 μm per year; and maximum estimates of 0.2 moles of H_2 per m_2 per year or 1 moles of H_2 per drum per year and 2 μm per year (Table 1).

Finally, I propose that the estimated gas production potential from anoxic corrosion remain at 900 moles per drum of waste. This value, estimated by Brush and Anderson (1989), Lappin et al. (1989), and Brush (1990), is 60% of the total gas production potential.

MICROBIAL ACTIVITY

D. Grbic-Galic and her colleagues at Stanford University observed significant microbial gas production by halophilic microorganisms in brine collected from G Seep in the WIPP underground workings with glucose, a relatively biodegradable substrate, but did not report significant gas production with cellulose, a much less biodegradable substrate. Furthermore, brine from G Seep inhibited significant gas production by nonhalophilic microorganisms, although a few experiments did show some evidence for possible microbial activity. These results seem to suggest that microbial gas production may be significant under overtest conditions (relatively biodegradable substrates, amendment of brine with nutrients, etc.), but not under realistic conditions. However, I believe that, for the reasons described below, the results obtained by Grbic-Galic and her colleagues do not rule out significant microbial gas production.

First, N. Black of Stanford University, R. H. Vreeland of West Chester University, and I compared the recent study at Stanford University and studies carried out during the 1970s (Barnhart et al., 1980; Caldwell, 1981; Caldwell et al., 1988; Molecke, 1979; Sandia National Laboratories, 1979). We concluded, as others have before us (Molecke, 1979; Brush and Anderson, 1989; Lappin et al., 1989), that the earlier results implied significant microbial gas production under both realistic and overtest conditions.

Second, Vreeland observed significant degradation of filter paper by his enrichments of halophilic and halotolerant microorganisms from the salt lakes in Nash Draw. Although he could not quantify gas production rates from these experiments, the results suggest that microorganisms could consume paper under realistic conditions in WIPP disposal rooms. Paper constitutes 70% of the 10 kg of cellulosics per equivalent drum of contact handled TRU waste to be emplaced in the repository (Brush, 1990).

Third, Black, Vreeland, and I reviewed the methods used in the earlier and recent studies in detail. We concluded that the study at Stanford University was not sensitive enough to detect gas production rates equivalent to a few tenths of a mole of gas per drum of waste per year. Davies (1990) has demonstrated that gas production rates greater than about 0.1 mole per equivalent drum of waste per year are significant from the standpoint of the long-term performance of the repository.

Because the results obtained at Stanford University do not rule out significant microbial gas production under realistic conditions, I propose using the same best estimate for the microbial gas production rate under inundated conditions proposed by Brush and Anderson (1989), Lappin et al. (1989), and Brush (1990), 1 mole of various gases per drum per year. However, I propose new minimum and maximum rates for inundated conditions, 0 and 5 moles per drum per year, respectively. The minimum estimate is analogous to the minimum estimate for anoxic corrosion under inundated conditions. The maximum estimate is Molecke's (1979) maximum estimate for microbial activity under inundated conditions. I also propose new minimum and best estimates for microbial gas production rates under humid conditions, 0 and 0.1 moles per drum per year. These estimates, both arbitrary, are analogous to the arbitrary minimum and best estimates for anoxic corrosion under humid conditions. The maximum estimate for microbial activity under humid conditions remains unchanged from the value estimated by Brush and Lappin (1990), 1 mole per drum per year (Table 1).

To convert these estimates of microbial gas production rates to units of moles per kg of cellulosics per year, I divided each rate by 10 kg of cellulosics per drum, the estimate used by Brush (1990), to obtain the estimates given in Table 1. Strictly speaking, this is inconsistent with the fact that the rate of 1 mole per drum per year is based on experiments carried out with simulated waste that included materials other than cellulosics (Molecke, 1979). It is also inconsistent with the assumption of Molecke (1979), Brush and Anderson (1979), and Lappin et al. (1989) that microorganisms will degrade 100% of the cellulosics, 50% of the Hypalon, and 50% of the Neoprene in the waste. However, about 90% of the microbial gas production potential (below) and hence 90% of the microbial gas production rate estimated by Brush and Anderson (1989) and Lappin et al. (1989) would result from biodegradation of cellulosics and only 5% each from Hypalon and Neoprene. Furthermore, Francis will use cellulosics as the sole substrate in his study of microbial gas production, at least initially. Finally, it will be much easier to use rates normalized only to the mass of cellulosics present than rates normalized to cellulosics, Hypalon, and Neoprene in performance-assessment calculations.

I also propose that the estimated gas production potential from microbial activity stay at 600 moles per drum of waste, the value estimated by Brush and Anderson (1989), Lappin et al. (1989), and Brush (1990). This is 40% of the total gas production potential.

RADIOLYSIS

D. T. Reed of Argonne National Laboratory is carrying out a low-pressure study of gas production by α radiolysis of Brine A as a function of dissolved Pu concentration. He has observed small, linear pressure increases from the solution with the highest dissolved Pu concentration, $1 \cdot 10^{-4}$ M, but does not have enough data to convert these rates to moles of gas per drum of waste per year yet. As expected, he has not observed pressure increases yet from the solutions with lower dissolved Pu concentrations, $1 \cdot 10^{-6}$ and $1 \cdot 10^{-8}$ M. After completion of these 3-month experiments, Reed will carry out 2-month runs with a dissolved Pu concentration of $1 \cdot 10^{-4}$ M in other WIPP brines to determine the effect of compositional variations on the radiolytic gas production rate.

As soon as he obtains longer-term data from Brine A with a dissolved Pu concentration of $1 \cdot 10^{-4}$ M, data with lower dissolved Pu concentrations in Brine A, and results from other WIPP brines with a dissolved Pu concentration of $1 \cdot 10^{-4}$ M, Reed will calculate experimentally based radiolytic gas-production rates for the radionuclide concentrations estimated by the Radionuclide Source Term Expert Panel. In addition to rates in units of moles of gas per drum of waste per year, he will provide rates in moles per cubic meter of brine for various concentrations. Until then, I propose using the radiolytic gas production rates proposed by Brush and Lappin (1990), who estimated a minimum rate of $1 \cdot 10^{-7}$ mole of various gases per drum of waste per year, a best rate of $1 \cdot 10^{-4}$ mole per drum per year, and a maximum rate of $1 \cdot 10^{-1}$ mole per drum per year (Table 1).

EXPECTED CHEMICAL CONDITIONS RELEVANT TO RADIONUCLIDE CHEMISTRY

Development of the source term for radionuclide-transport calculations will require: (1) estimates of the quantity of each nonradioactive constituent of design-basis TRU waste to be emplaced in the repository; (2) predictions of the microenvironments (Eh, pH, and the concentrations of organic and inorganic ligands) for each nonradioactive waste constituent; (3) quantification of the chemical behavior of the important radionuclides in the waste for each of these microenvironments; (4) construction of a frequency distribution of radionuclide concentrations based on the relative quantity of each nonradioactive waste constituent and the concentration associated with that constituent.

Currently, inventories of radioactive and nonradioactive waste constituents and estimates of radionuclide concentrations in brines as a function of Eh and pH are available. However, the high priority placed on the gas issue in laboratory studies of repository chemistry has precluded efforts to predict microenvironment for waste constituents. Therefore, I propose that oxidizing, acidic conditions, oxidizing, basic conditions, reducing, acidic conditions, and reducing, basic conditions be considered equally probable for interpreting Eh-pH-dependent estimates of radionuclide concentrations in WIPP brines.

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TABLE 1. CURRENT ESTIMATES OF GAS PRODUCTION RATES

Process	Gas Production Rate (various units)		
	Minimum	Best	Maximum
Anoxic corrosion, inundated:[1]			
moles/m^2 · year	0	0.2	0.4
moles/drum · year	0	1	2
μm/year	0	2	3
Anoxic corrosion, humid:[1]			
moles/m^2 · year	0	0.02	0.2
moles/drum · year	0	0.1	1
μm/year	0	0.2	2
Microbial activity, inundated:			
moles/drum · year	0	1	5
moles/kg cellulosics · year	0	0.1	0.5
Microbial activity, humid:			
moles/drum · year	0	0.1	1
moles/kg cellulosics · year	0	0.01	0.1
Radiolysis of brine:			
moles/drum · year	0.0000001	0.0001	0.1

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1. See text for estimates of H_2O consumption by anoxic corrosion of steels.

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APPENDIX E: BRUSH (1993)

Sandia National Laboratories

Albuquerque, New Mexico 87185

date: June 18, 1993

to: M. S. Tierney, 6342

from: L. H. Brush, 6348

subject: Likely Gas-Generation Reactions and Current Estimates of Gas-Generation Rates for the Long-Term WIPP Performance Assessment

INTRODUCTION

This memorandum identifies likely gas-generation reactions (Table 1), provides current estimates of humid and inundated gas-generation rates (Tables 2 and 3), and calculates the gas-generation potential for radiolysis of H_2O in brine by ^{239}Pu for the 1993 long-term WIPP performance-assessment (PA) calculations. A. R. Lappin, 6305, has provided estimates of gas-generation potentials for other processes.

I understand that because of severe time constraints and the higher priorities assigned to other changes in the models to be used for the 1993 PA calculations, you will not have time to incorporate the current version of the gas-generation model J. W. Garner and I provided to P. Vaughn in February 1993. Therefore, I understand you will use the same gas-generation model used in the 1991 and 1992 calculations. This approach consists of listing likely gas-generation reactions, calculating the average stoichiometric gas-production ratio of these reactions, estimating average gas-production rates, and allowing gas production to proceed until the total quantity of gas expected (the gas-generation potential) is attained for a given set of assumptions. I refer to this model as the "average-stoichiometry model." The assumptions include (but are not necessarily limited to): (1) the inventory of reactants (steels and other Fe-base alloys, Al and Al-base alloys, and, perhaps, other metals; cellulosics, plastics, and rubbers); (2) the extent to which these materials are convertible to gas (this is especially important in the case of plastics and rubbers); (3) whether sufficient H_2O will be available (this is especially significant in the case of reactions that occur only in the presence of brine, such as anoxic corrosion of steels). Of course, assumptions such as these are also necessary for the gas-generation model Garner and I are developing.

Given the severe time constraints and the higher priorities assigned to other improvements in the PA models, I concur with your decision to retain the average-stoichiometry model used in the 1991 and 1992 PA calculations. However, I recommend using additional gas-generation reactions, if possible, and current estimates of gas-generation rates. I describe these reactions and rates below. Of course, I realize that there may not be time to make <u>any</u> changes in the average-stoichiometry model at this point.

Garner and I will continue to develop a thermodynamic and kinetic reaction-path gas-generation model. The current version of this model includes the following processes: (1) corrosion of steels and other Fe-base materials by O_2, H_2O, H_2O and

CO_2, or H_2S; (2) passivation of steels by CO_2; (3) depassivation of steels by destabilization of $FeCO_3$; (4) microbial degradation of cellulosics with O_2, NO_3^-, Fe(III) hydroxide, or SO_4^{2-} as the electron acceptor; (5) consumption of CO_2 by $Ca(OH)_2$ (in cementitious materials) and CaO (a potential backfill additive). The main differences between the reaction-path model and the average-stoichiometry model used in the 1991 and 1992 PA calculations are that: (1) the reaction-path model includes more gas-producing reactions than the average-stoichiometry model; (2) the reaction-path model includes gas-consuming reactions; (3) the reaction-path model includes interactions among gas-producing and gas-consuming processes, such as passivation of steels by microbially-produced CO_2 and depassivation of steels due to consumption of CO_2 by $Ca(OH)_2$ and CaO. We will provide you with the latest version of this model as soon as you are ready to incorporate it in the PA models.

CORROSION

Oxic corrosion of steel waste containers (drums and boxes), Fe-base alloys in the waste, and, perhaps, other metals would consume O_2 in mine air trapped in WIPP disposal rooms at the time of filling and sealing. Oxic corrosion would also consume O_2 produced by radiolysis of H_2O in brine. After depletion of the O_2 initially present, anoxic corrosion of Fe-base and other metals could produce significant quantities of H_2, at least in microenvironments without radiolytically produced O_2. Other metals that could consume O_2 and produce H_2 include (but are not necessarily limited to) Al, Al-base alloys, Pb, and Pu. Oxic and anoxic corrosion could also consume significant quantities of brine and H_2O vapor.

Oxic Corrosion

Brush (1990) concluded that oxic corrosion of steels, other Fe-base alloys, and, perhaps, other metals would not have a significant, direct effect on the gas and H_2O budget of WIPP disposal rooms. However, this process could be important from the standpoint of the O_2 budget of the repository. The O_2 budget will in turn affect how soon the repository becomes anoxic after filling and sealing, the extent to which microenvironments dominated by brine radiolysis remain oxic, whether gas is consumed or produced, and which gases are consumed and produced. The O_2 budget will also affect the oxidation state of radionuclides and hence their chemical behavior. Therefore, Garner and I have added the following reaction to the reaction-path gas-generation model to simulate oxic corrosion:

$$2Fe + H_2O + 1.5O_2 = 2\gamma FeO(OH) \qquad (1)$$

We are using this reaction because N. R. Sorensen, 1832, observed that γFeO(OH) (lepidocrocite) was the most abundant corrosion product in oxic, inundated experiments carried out for the Strategic Petroleum Reserve Project. Sorensen also observed Fe_3O_4 as a major corrosion product and βFeO(OH) as a minor corrosion product. Therefore, Garner and I may also add an equation simulating the formation of Fe_3O_4. (Addition of an equation for βFeO(OH) would not change the stoichiometry of Reaction 1).

For my best estimate of the O_2-consumption rate for oxic corrosion, I recommend 5 moles per m^2 of steel per year, the value (rounded off to one significant figure) reported by Molecke (1979). Lappin et al. (1989) estimated that there are 6 m^2 of steels and other Fe-base alloys per drum of CH TRU waste, 4 m^2 for CH TRU waste containers and an estimated 2 m^2 for the Fe-base alloys in CH TRU waste. (These values do not include steel or other Fe-base alloys in canisters or plugs to be used for RH TRU waste, any steels or other Fe-base alloys contained in RH TRU waste, or steels or other Fe-base alloys used for ground support in the WIPP underground workings.) Therefore, this rate is equivalent to 30 moles of O_2 per drum of CH TRU waste per year. I computed the oxic-corrosion rate as follows.

The rate at which Fe is consumed by Reaction 1 is:

$$((2 \text{ moles Fe}) / (1.5 \text{ moles } O_2)) \cdot 5 \text{ moles } O_2/(m^2 \cdot yr)$$
$$= 6.67 \text{ moles Fe}/(m^2 \cdot yr). \qquad (2)$$

(Only one of the figures in this and the following equations are significant, but I did not round off until the end of these calculations.) This rate is equivalent to:

$$6.67 \text{ moles}/(m^2 \cdot yr) \cdot 5.5847 \cdot 10^{-2} \text{ kg/mole}$$
$$= 3.7231 \cdot 10^{-1} \text{ kg}/(m^2 \cdot yr). \qquad (3)$$

In Equation 2, "$5.5847 \cdot 10^{-2}$ kg" is the mass of a mole of metallic Fe. The thickness of the layer of Fe removed from the surface per year is:

$$3.7231 \cdot 10^{-1} \text{ kg}/(m^2 \cdot yr) / 7.86 \cdot 10^3 \text{ kg}/m^3$$
$$= 5 \cdot 10^{-5} \text{ m/yr}. \qquad (4)$$

In Equation 4, "$7.86 \cdot 10^3$ kg/m^3" is the density of metallic Fe. This rate is equivalent to about 50 μm of steel per year (Table 2). I cannot compare these estimates of O_2-consumption or corrosion rates with previous estimates because I did not estimate these rates for oxic corrosion of steels for the 1991 and 1992 PA calculations (see Brush, 1991).

My minimum estimates of O_2-consumption and corrosion rates for oxic corrosion of steels and other Fe-base alloys under inundated conditions, 0 moles per per m^2 of steel per year or 0 moles of O_2 per drum of CH TRU waste per year and 0 μm of steel per year (Table 2), are based on the possibility of passivation by formation of an adherent corrosion product (see Anoxic Corrosion below), or by precipitation of salts on the surfaces of corroding metals due to the consumption of H_2O during oxic corrosion of steels, other Fe-base alloys, and, perhaps, other metals. Although laboratory studies have not demonstrated these mechanisms yet, they are possible, especially (in the case of the latter mechanism) if microbial degradation of cellulosics and brine radiolysis also consume significant quantities of H_2O.

My maximum estimates of O_2-consumption and corrosion rates for oxic corrosion of steels and other Fe-base alloys under inundated conditions (Table 2) are based on estimates of the effects of pH on these rates. I have not yet considered the effects of total pressure, the partial pressures of gases expected in WIPP disposal rooms, or temperature on oxic corrosion. However, I have considered the effects of these factors on anoxic corrosion (see below); the analysis for anoxic corrosion suggests that pH is the most important of these factors. In the case of oxic corrosion, O_2-consumption and corrosion rates are inversely proportional to pH. I used the inverse relationship between pH and oxic-corrosion rates observed experimentally for applications other than the WIPP Project and estimates of the range of pH expected in WIPP disposal rooms after filling and sealing to estimate the maximum values of these rates.

I assume that the O_2-consumption rate of 5 moles per m^2 of steel per year (Molecke, 1979), which I used for my best estimate of this and other rates under inundated conditions (Table 2), pertains to Reaction 1 at a neutral or nearly neutral pH. Furthermore, I expect that the pH in WIPP disposal rooms will vary between about 3 and 12. Although obtained with deionized H_2O, the results of Uhlig and Revie (1963) suggest that the O_2-consumption and corrosion rates for oxic corrosion of steels are constant or essentially constant between a pH of about 4 and 10, that these rates are higher by about a factor of 1.5 at a pH of 3, and that they are lower by a factor of 0.6 at a pH of 11 and by a factor of 0.4 at a pH of 12. Therefore, the possibility of pH values as low as 3 in WIPP disposal rooms necessitates multiplying my best estimates in Table 2 by a factor of 1.5:

$$1.5 \cdot 5 \text{ moles/m}^2 = 8 \text{ moles/(m}^2 \cdot \text{yr)}; \tag{5a}$$

$$1.5 \cdot 30 \text{ moles/(drum} \cdot \text{yr)} = 50 \text{ moles/(drum} \cdot \text{yr)}; \tag{5b}$$

$$1.5 \cdot 50\ \mu\text{m/yr} = 80\ \mu\text{m/yr}. \tag{5c}$$

These are my maximum estimates, rounded to one significant figure, of these rates under inundated conditions (Table 2). Because they are maximum estimates, I have rounded them up in all three cases. The effects of basic conditions on oxic corrosion need not be considered at this point because, although they decrease these rates, my minimum estimates are already 0 moles of O_2 per m^2 of steel per year, 0 moles of O_2 per drum of CH TRU waste per year, and 0 μm of steel per year because of possible passivation (see above).

My best estimates of O_2-consumption and corrosion rates for oxic corrosion of steels and other Fe-base alloys under humid conditions are 0.5 moles of O_2 per m^2 of steel per year, 3 moles of O_2 per drum of CH TRU waste per year, and 5 μm of steel per year (Table 3). I arbitrarily assume that these rates are one tenth of my current best estimates for oxic corrosion under inundated conditions (Table 2). I did not estimate these rates for oxic corrosion of steels for the 1991 and 1992 PA calculations (Brush, 1991).

My arbitrary minimum estimates of O_2-consumption and corrosion rates for oxic corrosion of steels and other Fe-base alloys under humid conditions are also 0 moles of O_2 per m^2 of steel per year, 0 moles of O_2 per drum of CH TRU waste per year, and 0 μm of steel per year (Table 3).

My maximum estimates of O_2-consumption and corrosion rates for oxic corrosion of steel and other Fe-base alloys under humid conditions are 5 moles of O_2 per m^2 of steel per year, 30 moles of O_2 per drum of CH TRU waste per year, and 50 μm of steel per year (Table 2). I arbitrarily assume that these rates are identical to my current best estimates for oxic corrosion under inundated conditions (Table 2).

If oxic-corrosion rates under humid conditions affect the overall performance of the repository significantly, laboratory studies will be necessary to replace these arbitrary estimates with experimentally-based results.

Anoxic Corrosion

Anoxic corrosion of steels, other Fe-base alloys, and, perhaps, other metals may, if brine is present, produce significant quantities of H_2 and consume significant quantities of H_2O (Lappin et al., 1989; Brush, 1990).

I used thermodynamic calculations and laboratory studies carried out for applications other than the WIPP Project to predict the behavior of steels and other Fe-base alloys under expected WIPP conditions (see Brush, 1990). I am extending these thermodynamic calculations to support of the development of the reaction-path gas-generation model (see INTRODUCTION above).

R. E. Westerman and M. R. Telander of Pacific Northwest Laboratory (PNL) are carrying out laboratory studies of anoxic corrosion for the WIPP Project. So far, they have studied two heats each of the low-C steels ASTM A 366 and ASTM A 570 under inundated conditions (specimens immersed in Brine A) and humid conditions (specimens suspended above Brine A) with initially pure atmospheres of N_2, CO_2, and H_2S at low pressures (about 1 to 15 atm) at 30 ± 5°C. ASTM A 366 simulates the waste drums to be emplaced in the repository; ASTM A 570 simulates the boxes. Brine A is a synthetic brine that, although developed to simulate fluids equilibrated with K^+- and Mg^{2+}-bearing minerals in overlying potash-rich zones prior to entering the repository (Molecke, 1983), is coincidentally similar in composition to intergranular brines from the Salado Fm. at or near the stratigraphic horizon of the WIPP underground workings. Westerman and Telander have also conducted experiments with these steels under inundated conditions with initially pure N_2, CO_2, and H_2 at high pressures (about 35 or 70 atm). Finally, they have performed preliminary experiments with these steels in simulated backfill materials (crushed salt and a mixture of 70 wt % crushed salt and 30 wt % bentonite) at low pressures. Westerman and Telander also plan to study anoxic corrosion of Al and Al-base materials.

Telander and Westerman (in prep.) have identified three likely anoxic-corrosion reactions. At low fugacities (similar to partial pressures) of CO_2 and H_2S, the reaction observed in 3-, 6-, 12-, and 24-month experiments appears to be:

$$Fe + 2H_2O = Fe(OH)_2 + H_2. \tag{6a}$$

However, Brush (1990) calculated that $Fe(OH)_2$ is unstable with respect to Fe_3O_4. Therefore, significant quantities of steels and other Fe-base alloys could eventually corrode via the reaction:

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2. \tag{6b}$$

At relatively high CO_2 fugacities, the experimentally observed reaction is:

$$Fe + H_2O + CO_2 = FeCO_3 + H_2. \tag{7}$$

Formation of the adherent corrosion product $FeCO_3$ (siderite) by this reaction will passivate steels and, presumably, other Fe-base alloys after the consumption of various quantities of CO_2. Currently, laboratory studies at PNL suggest a range of 0.33 to 2.2 moles of CO_2 per m^2 of steel for the amount of CO_2 required for passivation, depending on the CO_2 partial pressure and the pH of the brine. However, I do not recommend revision of the average-stoichiometry gas-generation model to include passivation. To avoid potential criticism, inclusion of this process would also necessitate the inclusion of depassivation, the simulation of which would require a reaction-path model such as the one Garner and I are developing.

Finally, at relatively high H_2S fugacities, the experimentally observed reaction appears to be:

$$Fe + 2H_2S = FeS_2 + 2H_2. \tag{8a}$$

Laboratory studies at PNL suggest that this reaction also passivates steels and other Fe-base alloys. However, I do not recommend revision of the average-stoichiometry model to include passivation by this reaction for the reasons given in connection with Equation 3 (above).

A literature review by Telander and Westerman (in prep.) and thermodynamic calculations for the reaction-path model have identified another possible reaction involving H_2S:

$$Fe + H_2S = FeS + H_2. \tag{8b}$$

The literature reviewed by Telander and Westerman (in prep.) suggests that this reaction does not passivate steels and other Fe-base alloys. Table 1 summarizes these anoxic-corrosion reactions.

In addition to these corrosion reactions, there exist numerous likely reactions among Fe-bearing corrosion products such as $Fe(OH)_2$, Fe_3O_4, $FeCO_3$, FeS, and FeS_2. Garner and I are incorporating these reactions in the reaction-path model to predict, among other things, if and when depassivation of steels will occur. I do not recommend revising the average-stoichiometry model to include reactions among corrosion products.

My best estimates of H_2-production and corrosion rates for anoxic corrosion of steels and other Fe-base alloys under inundated conditions are based on data reported by Telander and Westerman (in prep.) They obtained average H_2-production rates of 0.19, 0.21, 0.16, and 0.10 moles per m^2 of steel per year in experiments carried out under inundated conditions with initially pure N_2 at low pressures (about 10 to 15 atm) for 3, 6, 12, and 24 months, respectively. Because there are 6 m^2 of steels and other Fe-base alloys per drum of CH TRU waste (Lappin et al., 1989), these rates are equivalent to 1.14, 1.26, 0.96, and 0.60 moles of H_2 per drum of CH TRU waste per year. The average corrosion rates in the 3-, 6-, 12-, and 24-month runs were 1.97, 1.72, 1.23, and 0.99 μm of steel per year. For my best estimates, I prefer values of 0.1

moles of H_2 per m^2 of steel per year or 0.6 moles of H_2 per drum of CH TRU waste per year and 1 μm of steel per year (see Table 2). These rates, from the 24-month experiments at PNL, are less by as much as about a factor of two than the rates observed in the 3-, 6-, and 12-month runs. Therefore, my best estimates are now half or about half those provided for the 1991 and 1992 PA calculations (Brush, 1991), 0.2 moles of H_2 per m^2 of steel per year, 1 mole of H_2 per drum of CH TRU waste per year, and 2 μm of steel per year, for which I used the 6-month results.

Strictly speaking, my best estimates of H_2-production and corrosion rates for anoxic corrosion of steels and other Fe-base alloys under inundated conditions (Table 2) pertain only to Reaction 6a, the reaction which apparently occurs with initially pure N_2 at low and high pressures. However, I arbitrarily assume that, at any given pH, Reactions 6b, 7, 8a, and 8b occur at the same rate as Reaction 6a. Therefore, my best estimates also apply to these reactions. Clearly, Reaction 7 proceeded much faster than Reaction 6a in low-pressure, inundated experiments at PNL, at least prior to passivation (below). However, this was probably because the pH of Brine A was much lower in runs with initially pure CO_2 at low pressures than in runs with initially pure N_2 at low pressures. I describe the effects of pH in the discussion of my maximum estimates for anoxic corrosion under inundated conditions (below).

My minimum estimates of H_2-production and corrosion rates for anoxic corrosion of steels and other Fe-base alloys under inundated conditions (Table 2) are based on passivation observed by Telander and Westerman (in prep.) in 6-, 12-, and 24-month, low-pressure (about 12 to 15 atm) experiments with initially pure CO_2. In these runs, the H_2-production and corrosion rates were high initially but decreased to 0 moles of H_2 per m^2 of steel per year or, 0 moles of H_2 per drum of CH TRU waste per year and 0 μm of steel per year after about 3 or 4 months due to passivation by Reaction 7 (above). Passivation at these pressures apparently required 0.33 moles of CO_2 per m^2 of steel, a very small quantity relative to the total microbial CO_2 production potential. My minimum estimates of these rates are identical to those provided for the 1991 and 1992 PA calculations (Brush, 1991). However, Telander and Westerman (in prep.) have now completed 12- and 24-month experiments, which confirm the results of the 6-month runs. Furthermore, since preparing their report, Westerman and Telander have also observed passivation in 6- and 12-month, high-pressure (about 36 to 40 atm) runs. These high-pressure tests partially address the concerns of those who claimed that high CO_2 partial pressures and concomitant acidification of brine would destabilize the passivating film of $FeCO_3$ and restart anoxic corrosion and H_2 production. Experiments carried out to date suggest that these high CO_2 partial pressures increase the quantity of CO_2 required to passivate steels somewhat, from 0.33 to 2.2 moles per m^2 of steel. However, this requirement is still very small relative to the total microbial CO_2 production potential. On the other hand, these high CO_2 partial pressures apparently decrease the time required for passivation somewhat, from about 3 or 4 months to 2 months.

At least two other passivation mechanisms are possible. First, after a few days of H_2 production, Telander and Westerman (in prep.) have observed passivation of steels under inundated conditions with initially pure H_2S at low pressures (about 5 to 6 atm) for up to about 200 days. This is probably due to formation of the adherent corrosion product FeS_2 (pyrite) by Reaction 8a (above). Based on preliminary results obtained with the reaction-path model, Garner and I think that FeS_2 formation may be unlikely in WIPP disposal rooms. This is because H_2S fugacities high enough and CO_2 and H_2 fugacities low enough to stabilize FeS_2 may be unlikely, given expected stoichiometries for microbial gas-production reactions. Therefore, passivation by $FeCO_3$ appears more likely than passivation by FeS_2. However, the latter is still possible.

A second passivation mechanism is precipitation of salts on the surfaces of corroding metals due to the consumption of H_2O during anoxic corrosion (see Oxic Corrosion above).

The results of laboratory studies of anoxic corrosion at PNL demonstrate that passivation of steels, at least by $FeCO_3$, is a real phenomenon under at least some combinations of conditions expected in WIPP disposal rooms. However, based on preliminary results of modeling studies, Garner and I believe that depassivation of steels is also possible, especially if consumption of CO_2 by $Ca(OH)_2$ (in hydrated cementitious materials) and CaO (a potential backfill additive) decrease the fugacity of CO_2 below values required to stabilize $FeCO_3$. Nevertheless, minimum estimates of 0 moles of H_2 per m^2 of steel per year or 0 moles of H_2 per drum of CH TRU waste per year and 0 μm of steel per year seem justified at this time.

For my maximum estimates of H_2-production and corrosion rates for anoxic corrosion of steels and other Fe-base alloys under inundated conditions (Table 2), I estimated the effects of pH, pressure, and temperature on these rates. These H_2-production and corrosion rates are: (1) inversely proportional to pH; (2) proportional to the partial pressures of CO_2 and, probably, H_2S (both of these gases decrease the pH of any brine they are in contact with as their partial pressures increase); (3) proportional to the partial pressure of N_2 and hence the total pressure; (4) inversely proportional to the partial pressure of H_2; (5) probably proportional to temperature. I used estimated or experimentally measured relationships between these parameters and the H_2-production and corrosion rates, and estimates of the extreme values of these parameters in the repository after filling and sealing to estimate the maximum values of these rates.

Telander and Westerman (in prep.) reported that the pH of Brine A, initially 6.7, increased to values of 8.3, 8.3, and 8.4 after the 6-, 12-, and 24-month, low-pressure experiments with initially pure N_2. (They did not report the pH of Brine A after the 3-month runs.) Therefore, the best estimates of these rates (Table 2) pertain to Reaction 6a at a neutral or nearly neutral pH. I expect that the pH in WIPP disposal rooms will vary between about 3 and 12. Although obtained for applications other than the WIPP Project, the results of Uhlig and Revie (1963) and Grauer et al. (1991) suggest that the H_2-production and corrosion rates for anoxic corrosion of steels are constant or essentially constant between a pH of about 4 and 10, that these rates are higher by about a factor of 50 at a pH of 3, and that they are lower by a factor of 0.05 at a pH of 11 and by a factor of 0.005 at a pH of 12. Therefore, the possibility of pH values as low as 3 in WIPP disposal rooms necessitates multiplying my best estimates in Table 2 by a factor of 50:

$$50 \cdot 0.10 \text{ moles/m}^2 = 5 \text{ moles/(m}^2 \cdot \text{yr)}; \tag{9a}$$

$$50 \cdot 0.60 \text{ moles/(drum} \cdot \text{yr)} = 30 \text{ moles/(drum} \cdot \text{yr)}; \tag{9b}$$

$$50 \cdot 1\ \mu\text{m/yr} = 50\ \mu\text{m/yr}. \tag{9c}$$

If acidification is caused by CO_2 or, perhaps, H_2S (see below), the increase in rates described above may only be temporary due to passivation of steels by $FeCO_3$ or, perhaps, FeS_2. However, organic acids produced by microbial degradation of cellulosics in the waste (below) could also acidify the brines in WIPP disposal rooms. These acids may not result in passivation of steels. The effects of basic conditions on anoxic corrosion need not be considered here because, although they decrease these rates, my minimum estimates are already 0 moles of H_2 per m^2 of steel per year or 0 moles of H_2 per drum of CH TRU waste per year and 0 μm of steel per year because of passivation (see above).

Based on the results of 6-month experiments, Telander and Westerman (in prep.) reported that an N_2 partial pressure of 73 atm increased the average corrosion rate of steels by about a factor of two from that observed at an N_2 partial pressure of 10 atm. Because 73 atm is about half of lithostatic pressure at the depth of the WIPP underground workings, I assume that total pressure (the effects of which should be equivalent to those of high N_2 partial pressure) could increase the H_2-production and corrosion rates for steels and other Fe-base alloys by as much as a factor of four. Therefore, the effect of lithostatic pressure on the rates estimated for the lowest pH expected in the repository necessitates multiplying the rates obtained from Equations 9a, 9b, and 9c by a factor of four:

$$4 \cdot 5 \text{ moles/m}^2 = 20 \text{ moles/(m}^2 \cdot \text{yr)}; \tag{10a}$$

$$4 \cdot 30 \text{ moles/(drum} \cdot \text{yr)} = 120 \text{ moles/(drum} \cdot \text{yr)}; \tag{10b}$$

$$4 \cdot 50\ \mu\text{m/yr} = 200\ \mu\text{m/yr}. \tag{10c}$$

High CO_2 and H_2S partial pressures should increase the H_2-production and corrosion rates for anoxic corrosion of steels and other Fe-base alloys under inundated conditions, at least prior to passivation, because the solubilities of these gases in aqueous solutions are proportional to their partial pressures and they form the weak, diprotic acids H_2CO_3 and H_2S after dissolution. Although weak, these acids do deprotonate to some extent, thus acidifying solutions in contact with these gases. However, I have already included the effects acidification on anoxic corrosion (see above).

The results of 6- and 12-month experiments carried out by Telander and Westerman (in prep.) suggest that H_2 partial pressures of 35, 69, and 70 atm decreased the average corrosion rate of steels by about a factor of five from that observed at the H_2 partial pressures in the low-pressure runs. High H_2 partial pressures have the opposite effect of high N_2 partial pressures (or total pressure) because H_2 is a product of Reactions 6a, 6b, 7, 8a, and 8b. The effects of high H_2 partial pressures on anoxic corrosion need not be addressed further because, although they decrease these rates, my minimum estimates are already 0 moles of H_2 per m^2 of steel per year or 0 moles of H_2 per drum of CH TRU waste per year and 0 μm of steel per year because of passivation.

Telander and Westerman (in prep.) have carried out all of their laboratory studies of anoxic corrosion at 30 ± 5°C. I assume that the temperature during their experiments was normally distributed about a value of 30°C. Therefore, their average rates pertain to this temperature. I also assume a temperature of 30 ± 3°C in WIPP disposal rooms after filling and sealing. This is slightly above the in situ temperature of 27°C at a subsurface depth of 2,150 feet because of the small amount of heat produced by RH TRU waste and, to a much lesser extent, by CH TRU waste. Finally, I assume that a 10°C increase in temperature would increase the rates of Reactions 6a, 6b, 7, 8a, and 8b by a factor of two. Therefore, the effect of a temperature of 33°C on the rates estimated for the lowest pH and highest total pressure expected in the repository, based on experiments carried out at 30 ± 5°C, requires multiplying the rates obtained from Equations 10a, 10b, and 10c by a factor of 1.23 (obtained from $2^{((33 - 30)/10)}$):

$$1.23 \cdot 20 \text{ moles/(m}^2 \cdot \text{yr)} = 20 \text{ moles/(m}^2 \cdot \text{yr)}; \tag{11a}$$

$$1.23 \cdot 120 \text{ moles/(drum} \cdot \text{yr)} = 100 \text{ moles/(drum} \cdot \text{yr)}; \tag{11b}$$

$$1.23 \cdot 200\ \mu\text{m/yr} = 200\ \mu\text{m/yr}. \tag{11c}$$

These are my maximum estimates, rounded to one significant figure, of these rates under inundated conditions (Table 2). They are significantly higher than those provided for the 1991 and 1992 PA calculations (Brush, 1991), 0.4 moles of H_2 per m^2 of steel per year or 2 moles of H_2 per drum of CH TRU waste per year and 3 μm of steel per year, because the combined effects of pH, high N_2 partial pressure or total pressure, and temperature have a much greater effect on these rates than high N_2 partial pressure, the only factor I included in my previous estimates of the maximum rates under inundated conditions.

My best estimates of H_2-production and corrosion rates for anoxic corrosion of steels and other Fe-base alloys under humid conditions are 0 moles of H_2 per m^2 of steel per year or 0 moles of H_2 per drum of CH TRU waste per year and 0 μm of steel per year (Table 3). These rates are less than those provided for the 1991 and 1992 PA calculations (Brush, 1991), 0.02 moles of H_2 per m^2 of steel per year or 0.1 moles of H_2 per drum of CH TRU waste per year and 0.2 μm of steel per year, which I arbitrarily assumed were one tenth of the best estimates provided at that time for inundated conditions. As of 1991, no H_2 production or corrosion had occurred in 3- and 6-month humid, low-pressure experiments with initially pure N_2 or CO_2, except for very limited H_2 production due to corrosion of some of the bottom 10% of the specimens splashed with brine during pretest preparation procedures. Since then, Telander and Westerman (in prep.) have obtained identical results from 6- and 12-month runs. These results confirm and extend the results of the 3- and 6-month runs. Therefore, I have reduced my best estimates as described above.

My minimum estimates of H_2-production and corrosion rates for anoxic corrosion of steels and other Fe-base alloys under humid conditions are also 0 moles of H_2 per m^2 of steel per year or 0 moles of H_2 per drum of CH TRU waste per year and 0 μm of steel per year (Table 3). These minimum estimates are identical to those provided for the 1991 and 1992 PA calculations (Brush, 1991).

My arbitrary maximum estimates of H_2-production and corrosion rates for anoxic corrosion of steels and other Fe-base alloys under humid conditions are 0.01 moles of H_2 per m^2 of steel per year or 0.06 moles of H_2 per drum of CH TRU waste per year and 0.1 μm of steel per year (Table 3). I arbitrarily assume that these rates are one tenth of my current best estimates for anoxic corrosion under inundated conditions. My maximum estimates for humid conditions are less than those provided for the 1991 and 1992 PA calculations (Brush, 1991), 0.2 moles of H_2 per m^2 of steel per year, 1 mole of H_2 per drum of CH TRU waste per year, and 2 μm of steel per year, which I arbitrarily assumed were identical to the best estimates provided at that time for inundated conditions.

If anoxic-corrosion rates under humid conditions significantly affect the behavior of the repository, additional laboratory studies will be necessary to replace these arbitrary estimates with actual experimental results.

MICROBIAL ACTIVITY

Microbial degradation of cellulosics and, perhaps, plastics and rubbers in the waste to be emplaced in WIPP disposal rooms may, if sufficient brine or H_2O vapor, nutrients, and viable microorganisms are present, produce or consume significant quantities of various gases and produce or consume significant quantities of H_2O (Lappin et al., 1989; Brush, 1990). The gases produced could include CO_2, CH_4, H_2S, N_2, and NH_3; the gases consumed could include CO_2, H_2 and O_2.

Brush (1990) applied the conceptual model of sequential usage of electron acceptors by microorganisms in natural environments (see, for example, Froelich et al., 1979; Berner, 1980) to WIPP disposal rooms. In natural environments, the observed sequence is aerobic respiration, NO_3^- reduction, reduction of Mn(IV) oxides and and hydroxides, reduction of Fe(III) oxides and and hydroxides, SO_4^{2-} reduction, and methanogenesis. Alternatively, reduction of Mn(IV) oxides and hydroxides may precede NO_3^- reduction. Based on which potential electron acceptors will be present in significant quantities in the repository after filling and sealing, I concluded that denitrification, SO_4^{2-} reduction, fermentation, and methanogenesis are potentially significant microbial processes (see Brush, 1990).

A. J. Francis and J. B. Gillow of Brookhaven National Laboratory (BNL) are carrying out laboratory studies of microbial gas production for the WIPP Project. Currently, they are conducting short- and long-term (up to 24-month) studies of microbial degradation of papers under inundated conditions with and without addition of electron acceptors and bentonite, amendment with nutrients, and inoculation with halophilic microorganisms from the WIPP Site and vicinity. They are also planning similar experiments under humid conditions and experiments with other potential substrates such as irradiated and unirradiated plastics and rubbers.

Aerobic Microbial Activity

I concluded that aerobic microbial activity will not affect the gas and H_2O budgets of WIPP disposal rooms directly (see Brush, 1990). However, this process could affect the O_2 budget of the repository significantly. The O_2 budget will in turn affect the chemical behavior of the repository (see Oxic Corrosion above). Furthermore, Francis and Gillow (in prep.) have observed significant aerobic microbial activity. Therefore, Garner and I have added it to the reaction-path gas-generation model.

During aerobic microbial activity (or any other microbial process) the degradation of organic matter is complex and involves several intermediate steps usually mediated by different microorganisms. Geochemists have described microbial processes by writing simplified overall equations. Berner (1980) used the following equation to represent aerobic microbial activity:

$$CH_2O + O_2 = H_2O + CO_2. \qquad (12)$$

This equation uses the formula CH_2O (a simplified formula for glucose) to represent the substrate (mainly papers and other cellulosics in the case of the WIPP) and does not include the synthesis of cellular material (biomass) by microorganisms. These approximations are certainly adequate for the average-stoichiometry gas-generation model, but may not be for the reaction-path model.

Anaerobic Microbial Activity

I also concluded that microbial denitrification could significantly affect the gas and H_2O budgets of WIPP disposal rooms (see Brush, 1990). Furthermore, Francis and Gillow (in prep.) have observed production of significant quantities of N_2O, a precursor of N_2 and an indicator of denitrification. According to Berner (1980), the overall equation for denitrification is:

$$CH_2O + 0.8H^+ + 0.8NO_3^- = 1.4H_2O + CO_2 + 0.4N_2. \qquad (13)$$

Microbial reduction of Fe(III) oxides and hydroxides will not affect on the gas and H_2O budgets of WIPP disposal rooms significantly (Brush, 1990). However, Fe(III) reduction could affect the O_2 budget, which will in turn affect the chemical behavior of the repository (see Oxic Corrosion). Therefore, Garner and I added five possible Fe(III)-reduction reactions to the reaction-path model:

$$CH_2O + 4FeO(OH) + H_2O = 4Fe(OH)_2 + CO_2 \qquad (14a)$$

$$CH_2O + 4FeO(OH) = 1.33Fe_3O_4 + 1.67H_2O + CO_2 + 1.33H_2 \qquad (14b)$$

$$CH_2O + 4FeO(OH) + H_2O + 3CO_2 = 4FeCO_3 + 4H_2O \qquad (14c)$$

$$CH_2O + 4FeO(OH) + 4H_2S = 4FeS + 7H_2O + CO_2 \qquad (14d)$$

$$CH_2O + 4FeO(OH) + 8H_2S = 4FeS_2 + 7H_2O + CO_2 + 4H_2 \qquad (14e)$$

Finally, microbial SO_4^{2-} reduction could affect the repository gas and H_2O budgets significantly (Brush, 1990). Francis and Gillow (in prep.) have not analyzed for H_2S, a product of SO_4^{2-} reduction. However, they have observed blackening, an indicator of SO_4^{2-} reduction, in some of their experiments. Berner (1980) gave the following overall equation for SO_4^{2-} reduction:

$$CH_2O + H^+ + 0.5SO_4^{2-} = H_2O + CO_2 + 0.5\,H_2S. \qquad (15)$$

Finally, Brush (1990) concluded that microbial fermentation and methanogenesis could significantly affect the gas and H_2O budgets of WIPP disposal rooms. Francis and Gillow (in prep.) have not analyzed for CH_4, a product of methanogenesis. However, it would be almost impossible to rule out methanogenesis in the repository if other microbial processes are expected. Berner's (1980) overall equation for methanogenesis is:

$$2CH_2O = CH_4 + CO_2. \qquad (16a)$$

However, the simultaneous presence of CO_2 and H_2 in the repository could facilitate the following reaction proposed by Francis and Gillow (in prep.):

$$CO_2 + 4H_2 = CH_4 + 2H_2O. \qquad (16b)$$

Garner and I will include both of these equations in the reaction-path model and will probably use Equation 16b whenever both CO_2 and H_2 are present.

Francis and Gillow (in prep.) observed aerobic respiration, denitrification, and SO_4^{2-} reduction in their long-term study of microbial degradation of papers under inundated conditions. So far, the gas-production rates observed in these experiments have all been within the range estimated by Brush (1991) for the 1991 and 1992 PA calculations. There is probably no justification, at least on the basis of the results obtained by Francis and Gillow to date, for reducing the previously-estimated range. On the other hand, there is certainly no justification for extending it. Therefore, I recommend using the previously-provided rates again. My best estimate of the total microbial gas production rates from all of the processes described in Reactions 12 through 16a (above) under inundated conditions is 0.1 moles of gas (CO_2, CH_4, H_2S and N_2) per kg of cellulosics per year. There are 10 kg of cellulosics per drum of CH TRU waste (Brush, 1990). (These values do not include any cellulosics in RH TRU waste.) Therefore, this rate is equivalent to 1 mole of gas per drum of CH TRU waste per year. My minimum estimate for inundated conditions is 0 moles of gas per kg of cellulosics per year or 0 moles of gas per drum of CH TRU waste per year. My maximum estimate is 0.5 moles of gas per kg of cellulosics per year or 5 moles of gas per drum of CH TRU waste per year.

Methanogenesis by Reaction 16b could consume significant quantities of CO_2 and especially H_2. Francis and Gillow (in prep.) have not observed this reaction yet. However, if it occurs under expected WIPP conditions, this reaction could consume a significant fraction of the CO_2 produced by microbial activity, the H_2 produced by anoxic corrosion, or even both, depending on the ratio of CO_2 to H_2O in the repository and the extent to which it proceeds. I have not estimated rates for this reaction yet. Predictions of the effects of this methanogenic reaction on the gas and H_2O budgets of the repository will require measurements of its rates of gas consumption under expected WIPP conditions and its incorporation in the reaction-path model Garner and I are developing. However, it may be possible to estimate the rate of Reaction 16b from studies carried out for application other than the WIPP Project.

Because Francis and Gillow (in prep.) have not reported any results for humid conditions yet, I recommend using the same microbial gas-production rates provided for the 1991 and 1992 PA calculations (Brush, 1991). My arbitrary best estimate of the total microbial gas production rates from all of the processes described in Reactions 12 through 16a (above) under humid conditions is 0.01 moles of gas per kg of cellulosics per year or 0.1 moles of gas per drum of CH TRU waste per year. My arbitrary minimum estimate for humid conditions is 0 moles of gas per kg of cellulosics per year or 0 moles of gas per drum of CH TRU waste per year. My arbitrary maximum estimate is 0.1 mole of gas per kg of cellulosics per year or 1 mole of gas per drum of CH TRU waste per year. I have not estimated any rates for methanogenesis by Reaction 16b yet.

Francis and Gillow are now carrying out laboratory studies of microbial gas production under conditions at BNL. Results from these studies will eventually replace these arbitrary estimates.

RADIOLYSIS

The rates of gas production from radiolysis of H_2O in brine and sludges in WIPP disposal rooms and radiolysis of cellulosics, plastics and rubbers in the waste will probably be significantly less than those expected from anoxic corrosion or microbial activity (Molecke, 1979; Brush, 1990). However, even if these radiolytic gas-production rates are low, Garner and I will include radiolysis in the reaction-path gas-generation model we are developing to: (1) determine if, in the event that the rates and quantities of gas produced by anoxic corrosion and microbial activity turn out to be smaller than expected, radiolysis is still a minor gas-production mechanism; (2) predict the O_2 budget of the repository (see Oxic Corrosion above).

D. T. Reed and S. Okajima of Argonne National Laboratory (ANL) have quantified gas production from α radiolysis of WIPP brines as a function of dissolved ^{239}Pu concentration and brine composition. It is possible to use their results to calculate gas-production rates for other Pu isotopes, particulate Pu in contact with brine (colloids suspended in brine, undissolved particles in the waste, and precipitated particles), and other actinide elements dissolved, suspended, or otherwise in contact with brine. However, I did not have time to do so prior to submission of these estimates to PA. Instead, I considered only dissolved ^{239}Pu. I am currently gathering the information required to extend these calculations to include other Pu isotopes, particulate Pu, and important isotopes of other actinide elements. Eventually, Garner and I may include some or all of these other factors in the reaction-path model.

Reed and Okajima (in prep.) have observed H_2 production, but not O_2 production, from brine radiolysis in experiments carried out with ^{239}Pu. Recently, they have observed production of both H_2 and O_2 in runs conducted with ^{238}Pu. These studies and previous laboratory studies reviewed by Reed and Okajima (in prep.) suggest that, given sufficiently high absorbed doses, the O_2 production rate eventually approaches 50% that of H_2 in both pure H_2O and brines. Strictly speaking, O_2 is not a direct product of the radiolytic decomposition of H_2O. Instead, O_2 forms by the breakdown of O-containing intermediate species, such as H_2O_2 in pure H_2O and, possibly, ClO_3^- (chlorate) or ClO_4^- (perchlorate) in brines. On the other hand, it is possible that these intermediate species will react with electron donors (reductants), such as steels, other Fe-base alloys, other metals, or organic matter, before they produce significant O_2. However, to simplify brine radiolysis for the reaction-path model, Garner and I are using the equation:

$$H_2O = H_2 + 0.5O_2. \qquad (17)$$

Initially, we will assume that this process produces O_2 immediately. We may include a realistic induction period to account for the necessary build-up of O-containing intermediate species once the laboratory studies under way at ANL quantify the absorbed dose required to initiate O_2 production. We will then be able to calculate the time required to attain this dose as a function of the dissolved and suspended concentrations of radionuclides in WIPP brines. Until these results become available, the reaction-path model may overestimate the time required for the repository to become anoxic and overestimate the proportion of the waste that remains oxic in microenvironments in which brine radiolysis is the predominant redox-determining process.

Reed and Okajima (in prep.) reported $G(H_2)$ values of 1.1 to 1.4 molecules per 100 eV for Brine A and ERDA-6, two synthetic WIPP brines, and DH-36 and G-Seep, two brines collected from the WIPP underground workings. The observed $G(H_2)$ values are independent of the dissolved ^{239}Pu concentration in these experiments. Garner and I plan to use units of moles of H_2, O_2, or H_2 plus O_2 per m^3 of brine per year in the reaction-path model. Therefore, I converted the results of Reed and Okajima (in prep.) from units of molecules per 100 eV to units of moles per m^3 of brine as follows.

For a dissolved ^{239}Pu concentration of 1 M, there are $2.39 \cdot 10^2$ g of ^{239}Pu per L of brine. The current estimate of the quantity of Pu to be emplaced in WIPP disposal rooms and the quantities of brine expected in the repository imply that there will not be enough Pu present to support an average Pu concentration of 1 M (see below). However, a local Pu concentration of 1 M may be possible in microenvironments in which Pu is highly soluble. Because there are $1 \cdot 10^3$ L of brine per m^3 of brine, the mass of ^{239}Pu per m^3 of brine is:

$$2.39 \cdot 10^2 \text{ g/L} \cdot 1 \cdot 10^3 \text{ L/m}^3 = 2.39 \cdot 10^5 \text{ g/m}^3. \qquad (18)$$

(Only two of the figures in this and the following equations are significant, but I did not round off until the end of these calculations.) The activity of ^{239}Pu per m^3 of brine is:

$$2.39 \cdot 10^5 \text{ g/m}^3 \cdot 0.0613 \text{ Ci/g} = 1.46507 \cdot 10^4 \text{ Ci/m}^3). \qquad (19)$$

In Equation 19, "0.0613 Ci/g" is the specific activity of ^{239}Pu. The disintegration rate of ^{239}Pu per m^3 of brine is:

$$\begin{aligned} &1.46507 \cdot 10^4 \text{ Ci/m}^3 \cdot 3.7 \cdot 10^{10} \text{ (d/s)/Ci} \\ &= 5.42076 \cdot 10^{14} \text{ d/(m}^3 \cdot \text{s)}. \qquad (20) \end{aligned}$$

In Equation 20, "d" is the abbreviation for "disintegrations," not "days!" The energy-deposition rate per m^3 of brine is:

$$5.42076 \cdot 10^{14} \text{ d/(m}^3 \cdot \text{s)} \cdot 5.15 \text{ MeV/d}$$

$$= 2.79169 \cdot 10^{15}\ \text{MeV}/(\text{m}^3 \cdot \text{s}). \qquad (21)$$

In Equation 21, "5.15 MeV/d" is the average energy of an α particle emitted during the disintegration of ^{239}Pu. Changing units gives:

$$2.79169 \cdot 10^{15}\ \text{MeV}/(\text{m}^3 \cdot \text{s}) \cdot 1 \cdot 10^6\ \text{eV/MeV} \cdot 3.15576 \cdot 10^7\ \text{s/yr}$$

$$= 8.80991 \cdot 10^{28}\ \text{eV}/(\text{m}^3 \cdot \text{yr}). \qquad (22)$$

I used a value of 1.25 molecules per 100 eV for G(H_2) (the midpoint of the range of 1.1 to 1.4 molecules per 100 eV reported by Reed and Okajima (in prep.) for Brine A, ERDA-6, DH-36, and G-Seep) to calculate the number of molecules of H_2 produced per m^3 of brine per year:

$$8.80991 \cdot 10^{28}\ \text{eV}/(\text{m}^3 \cdot \text{yr}) \cdot 1.25 \cdot 10^{-2}\ \text{molecules/eV}$$

$$= 1.10124 \cdot 10^{27}\ \text{molecules}/(\text{m}^3 \cdot \text{yr}). \qquad (23)$$

The number of moles of H_2 produced per m^3 of brine per year is:

$$1.10124 \cdot 10^{27}\ \text{molecules}/(\text{m}^3 \cdot \text{yr})\ /\ 6.0225 \cdot 10^{23}\ \text{molecules/mole}$$

$$= 1.8 \cdot 10^3\ \text{moles}/(\text{m}^3 \cdot \text{yr}). \qquad (24)$$

In Equation 24, "6.0225 $\cdot$ 10^{23} molecules/mole is Avogadro's number. Of course, "1.8 $\cdot$ 10^3 moles/(m^3 $\cdot$ yr)" is actually the midpoint of a range of 1.6 to 2.0 $\cdot$ 10^3 moles/(m^3 $\cdot$ yr).

I repeated these calculations for dissolved ^{239}Pu concentrations of $1 \cdot 10^{-1}$, $1 \cdot 10^{-2}$, $1 \cdot 10^{-3}$, $1 \cdot 10^{-4}$, $1 \cdot 10^{-5}$, $1 \cdot 10^{-6}$, $1 \cdot 10^{-7}$, $1 \cdot 10^{-8}$, and $1 \cdot 10^{-9}$ M (see Table 4). Again, the quantity of Pu to be emplaced in WIPP disposal rooms and the quantities of brine expected in the repository imply that there will not be enough Pu present to support some of these <u>average</u> Pu concentrations (see below). I calculated O_2-production rates for the same dissolved ^{239}Pu concentrations in these brines by assuming a value of 0.625 molecules per 100 eV for G(O_2) (half the midpoint of the observed range for G(H_2)) and neglecting the induction period for O_2 production from the breakdown of O-containing intermediate species (Table 4). (Bear in mind that O-containing intermediate species may react with electron donors in WIPP disposal rooms before they produce significant O_2.) Finally, I calculated total radiolytic gas-production rates by adding the H_2- and O_2-production rates (Table 4).

I converted these rates from units of moles of H_2, O_2, and H_2 plus O_2 per m^3 of brine per year to units of H_2, O_2, and H_2 plus O_2 per equivalent drum of CH TRU waste per year to compare them with the rates of gas production from anoxic corrosion and microbial activity. I multiplied each of the rates in Table 4 by 135, 305, 525, or 815 m^3 of brine per WIPP disposal room to convert them to units of moles of H_2, O_2, and H_2 plus O_2 per room per year. B. M. Butcher used these estimates of the residual gas-accessible void volume in a WIPP disposal room and immediate vicinity for his recent calculations of gas-storage capacities. I then assumed that these volumes could become inundated. Of course, brine volumes less than 135 m^3 are entirely possible. Next, I divided Butcher's volumes by 6,800 drums of CH TRU waste per room to obtain units of moles of H_2, O_2, and H_2 plus O_2 per drum per year. Tables 5, 6, and 7 give these rates for H_2, O_2, and H_2 plus O_2, respectively.

To calculate the maximum <u>average</u> Pu concentrations as a function of brine volume and time (Table 8), I used the quantities of brine required to saturate the residual gas-accessible void volume in a WIPP disposal room (see above) and referred to the PA code DECAY to obtain the initial Pu inventory and decay predictions used for the most recent PA calculations (WIPP Performance Assessment Department, 1992). (PA personnel will also use this inventory for the round of calculations to be presented to the EPA in February 1994.) At each time (0, 100, 200, 500, 1,000, 2,000, 5,000, and 10,000 years), I added the quantities of ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu, and ^{244}Pu present in both CH and RH TRU waste in the column labeled "Scaled Inventory" in the output files from the PA code DECAY. "Scaled inventory" refers to the quantity of Pu (or other) isotopes present in one WIPP disposal panel. I then divided these sums by 12.65, the number of equivalent WIPP disposal rooms in one panel. Next, I calculated the percentage of each isotope of Pu present at each time and calculated the average molecular weight of Pu at that time. I assumed that the molecular weight of each isotope has an integral value equal to its mass number. I then divided the total mass of Pu by 135,000, 305,000, 525,000, or 815,000 L, the quantities of brine present in 135, 305, 525, or 815 m^3 of brine, respectively. Finally, I divided the results by the average molecular weight of Pu at that time to obtain the concentrations shown in Table 8.

Clearly, both the dissolved ^{239}Pu and the volume of brine to which this concentration pertain will strongly affect the H_2-, O_2-, and H_2- plus O_2-production rates from brine radiolysis. If the dissolved ^{239}Pu concentration is low enough, these gas-production rates are obviously insignificant (see Tables 5, 6, and 7). On the other hand, if the dissolved ^{239}Pu concentration and the ^{239}Pu inventory are high enough, these gas-production rates can equal or even exceed those of anoxic corrosion and microbial activity, at least locally. Given a range of 135 to 815 m^3 of brine per room, the range of Pu solubilities and the Pu inventory assumed for WIPP disposal rooms will determine the range of radiolytic gas-production rates.

For my best estimates of the rates of gas production from brine radiolysis, I chose $6.0 \cdot 10^{-10}$ M, the midpoint of the range of Pu(V) solubilities estimated by the Radionuclide-Source-Term Expert Panel (Trauth et al., 1992). (The Expert Panel also estimated the same midpoint for the range of Pu(IV) solubilities.) For ^{239}Pu, this dissolved concentration yields rates of $1.1 \cdot 10^{-6}$ moles of H_2 per m^3 per year, $5.4 \cdot 10^{-7}$ moles of O_2 per m^3 per year, and $1.6 \cdot 10^{-6}$ moles of H_2 plus O_2 per m^3 per year, equivalent to rates of $6.6 \cdot 10^{-8}$ moles of H_2 per drum per year, $3.3 \cdot 10^{-8}$ moles of O_2 per drum per year, and $9.9 \cdot 10^{-8}$ moles of H_2 plus O_2 per drum per year (Table 2). To convert from units of moles per m^3 per year to moles per drum per year, I used the average of the rates for 305 and 525 m^3 of brine per room in Tables 5, 6, and 7.

For my minimum estimates of the rates of gas production from brine radiolysis, I used the lower limit of the range of Pu solubilities estimated by the Expert Panel and 135 m^3, the lower limit of the range of residual gas-accessible void volume expected in a WIPP disposal room. (Of course, there could be less than 135 m^3 of brine in a room.) The Expert Panel estimated that, for expected repository conditions, the lower limit of the range of Pu solubilities is $2.5 \cdot 10^{-17}$ M, the value estimated for Pu(V). For ^{239}Pu, this dissolved concentration yields rates of $4.5 \cdot 10^{-14}$ moles of H_2 per m^3 per year, $2.2 \cdot 10^{-14}$ moles of O_2 per m^3 per year, and $6.7 \cdot 10^{-14}$ moles of H_2 plus O_2 per m^3 per year, equivalent to rates of $8.9 \cdot 10^{-16}$ moles of H_2 per drum per year, $4.5 \cdot 10^{-16}$ moles of O_2 per drum per year, and $1.3 \cdot 10^{-15}$ moles of H_2 plus O_2 per drum per year (Table 2).

It may be more difficult to defend estimates of the maximum rates of gas production from brine radiolysis. The Expert Panel estimated that the upper limit of the range of Pu solubilities is $5.5 \cdot 10^{-4}$ M, the value estimated for Pu(V). Assuming that all of the Pu present is ^{239}Pu(V), this estimate and 815 m^3 of brine per room (the upper limit of the range of residual gas-accessible void volume) yield upper limits of $9.9 \cdot 10^{-1}$ moles of H_2 per m^3 of brine per year, $5.0 \cdot 10^{-1}$ moles of O_2 per m^3 per year, and $1.5 \cdot 10^{0}$ moles of H_2 plus O_2 per m^3 per year (Table 2). Again, the current estimate of the quantity of Pu to be emplaced in the repository and 815 m^3 of brine per WIPP disposal room imply that there will not be enough Pu present to support an average Pu concentration of $5.5 \cdot 10^{-4}$ M (see above). These rates are equivalent to $1.2 \cdot 10^{-1}$ moles of H_2 per drum of CH TRU waste per year, $6.0 \cdot 10^{-2}$ moles of O_2 per drum per year, and $1.8 \cdot 10^{-1}$ moles of H_2 plus O_2 per drum per year (Table 2). These are my favorite estimates of the maximum gas-production rates from brine radiolysis. I like them because the Expert Panel is responsible for defending $5.5 \cdot 10^{-4}$ M as the upper limit of the range of Pu solubilities. A reasonable way to estimate the probability distribution for values within the range of gas-production rates from brine radiolysis is to assume the same probability distribution estimated by the Expert Panel for Pu(V) solubilities.

However, I believe that $5.5 \cdot 10^{-4}$ M may not be a defensible upper limit of the range of Pu solubilities. Pu(III) is probably more soluble than Pu(IV) and Pu(V), the only oxidation states for which the Expert Panel estimated solubilities. Furthermore, Pu(VI) could well turn out to be more soluble than Pu(III)! Presumably, the Expert Panel did not estimate solubilities of Pu(III) and Pu(VI) because it accepted the hypothesis that Pu(III) and Pu(VI) will be unstable with respect to Pu(IV) and Pu(V) in WIPP disposal rooms and that Pu(IV) and Pu(V) will thus control the solubility of Pu. This hypothesis may be impossible to defend given the results of laboratory studies by Reed and Okajima (in prep.) in which Pu(VI) remained stable in WIPP brines for lengthy periods. They observed that Pu(VI) is the predominant form of Pu in Brine A and G Seep during stability experiments carried out for periods of over 300 and 400 days. (Stability runs are necessary to demonstrate that Pu remains in solution during an experiment to quantify gas production by brine radiolysis.) Reed and Okajima (in prep.) observed dissolved Pu(VI) concentrations on the order of 10^{-3} and 10^{-4} M in Brine A and G Seep during 300- and 400-day stability runs. Furthermore, they observed a Pu(VI) concentration of $2 \cdot 10^{-2}$ M in G Seep during an 80- or 90-day stability run. Because these experiments did not contain high concentrations of the inorganic ligand CO_3^{2-}, which could significantly increase both the stability and the solubility of Pu(VI), or any organic ligands, which could also increase the stability and solubility of Pu(VI), the results are clearly not worst-case. Nevertheless, ^{239}Pu concentrations on the order of 10^{-2} M would, if the inventory of ^{239}Pu were high enough, imply upper limits of the ranges of gas-production rates from brine radiolysis on the order of 10^{1} moles of H_2, O_2, and H_2 plus O_2 per m^3 of brine per year (see Table 4) or 10^{0} moles of H_2, O_2, and H_2 plus O_2 per drum of CH TRU waste per year (Tables 5, 6, and 7). These rates are similar to those expected from anoxic corrosion and microbial activity under inundated conditions.

If a significant fraction of Pu in WIPP disposal rooms is actually present as Pu(VI), its chemical behavior would probably be similar to that of its oxidation-state analog U(VI). G. R. Choppin observed dissolved U(VI) concentrations of about $1 \cdot 10^{-4}$ M in approximately 600-day dissolution experiments in Brine A at a pH of about

8 and 2 · 10^{-3} M in 250-day precipitation runs under the same conditions at Florida State University. (Dissolution and precipitation experiments, also referred to as undersaturation and supersaturation runs, bracket the solubility by approaching equilibrium from opposite directions.) These results are similar to those of the ANL stability runs. Even worse, the Expert Panel's estimate of 1.0 · 10^{0} M for the upper limit of the range of the solubility of U(VI) could apply to Pu(VI) as well. This would, if the inventory of ^{239}Pu were high enough, imply upper limits of the ranges of gas-production rates from brine radiolysis on the order of 10^{3} moles of H_2, O_2, and H_2 plus O_2 per m^3 of brine per year (Table 4) or 10^{2} moles of H_2, O_2, and H_2 plus O_2 per drum of CH TRU waste per year (Tables 5, 6, and 7). These rates are much higher than those expected from anoxic corrosion and microbial activity under inundated conditions.

Similarly, if a significant fraction of Pu is present as Pu(III), the Expert Panel's estimate of 1.4 · 10^{0} M for the upper limit of the range of the solubilities of Am(III) and Cm(III) could apply to Pu(III). This would also imply very high upper limits of the ranges of gas-production rates from brine radiolysis.

It is important to point out that such high solubilities may not persist indefinitely. For example, H. Nitsche of Lawrence Berkeley Laboratory observed dissolved Pu concentrations between about 1 · 10^{-4} and 1 · 10^{-3} M for over 1 year in a precipitation experiment started with initially pure Pu(VI) in Brine A at a pH of about 7. However, after about 400 days, the concentration of Pu dropped to between 1 · 10^{-7} and 1 · 10^{-6} M. This suggests that Pu(VI) may be unstable with respect to other, less soluble oxidation states and that, given enough time, the solubility of Pu will decrease to the ranges estimated by the Expert Panel for Pu(IV) and Pu(V). Therefore, it would probably be difficult at this time to defend upper limits of the ranges of gas-production rates from brine radiolysis based on a dissolved Pu(VI) concentration of 2 · 10^{-2} M observed by Reed and Okajima (in prep.) during an 80- or 90-day stability experiment. It might even be difficult to defend upper limits based on Pu(VI) concentrations on the order of 10^{-4} or 10^{-3} M in several-hundred-day solubility or stability runs. These are the maximum <u>average</u> Pu concentrations that can be supported by the current inventory (see Table 8). Furthermore, even if Pu is highly soluble under some combinations of conditions in WIPP disposal rooms, brine radiolysis would, like anoxic corrosion, probably be self-limiting. This is because neither anoxic corrosion nor brine radiolysis seems to occur under humid conditions. Therefore, small quantities of brine in the repository may produce H_2 (in the case of anoxic corrosion) or H_2 and O_2 (in the case of brine radiolysis), increase the pressure, prevent additional brine inflow or even cause brine outflow, and thus prevent or greatly reduce additional gas production, at least by these mechanisms. However, I still feel that it may be difficult to rule out the possibility of very high (relative to anoxic corrosion and microbial activity) upper limits of the ranges of gas-production rates from brine radiolysis, at least in some microenvironments with high Pu solubilities. Furthermore, if the <u>average</u> Pu solubility turns out to be high, increasing the <u>quantity</u> of Pu to be emplaced in WIPP disposal rooms could significantly affect the gas budget of the repository, and perhaps its performance.

I calculated the gas-production potential for radiolysis of H_2O in brine by ^{239}Pu as follows. According to the initial Pu inventory and decay predictions used for the most recent PA calculations (WIPP Performance Assessment Department, 1992), there will be 568,600 g of ^{239}Pu in CH TRU waste and 14,280 g of ^{239}Pu in RH TRU waste per WIPP disposal panel at the time of emplacement. After 10,000 years, there will be 426,300 g of ^{239}Pu in CH TRU waste and 10,710 g of ^{239}Pu in RH TRU waste per panel. The mass of ^{239}Pu in one panel that will decay during the 10,000-year period of performance of the repository is:

$$(568{,}600 \text{ g} + 14{,}280 \text{ g}) - (426{,}300 \text{ g} + 10{,}710 \text{ g}) = 145{,}870 \text{ g}. \qquad (25)$$

(I do not know how many of the figures in this and the following equations are significant, but I suspect not more than one!) The mass of ^{239}Pu in an equivalent drum of CH TRU waste that will decay in 10,000 years is:

$$145{,}870 \text{ g/panel} / 86{,}000 \text{ drums/panel} = 1.69616 \text{ g/drum}. \qquad (26)$$

I have included the ^{239}Pu in RH TRU waste in an "equivalent drum of CH TRU waste" for the sake of completeness, but this only increases the mass of ^{239}Pu per drum by about 2.5%! The number of ^{239}Pu disintegrations per drum in 10,000 years will be:

$$1.69616 \text{ g/drum} / 239 \text{ g/mole} \cdot 6.0225 \cdot 10^{23} \text{ d/mole}$$

$$= 4.27411 \cdot 10^{21} \text{ d}. \qquad (27)$$

Assuming that all of the Pu in a drum dissolves in brine at the time of emplacement and remains dissolved throughout the 10,000-year period of performance of the repository is the worst-case assumption from the standpoint of radiolytic gas production. This assumption results in initial dissolved total Pu concentrations of $1.60 \cdot 10^{-3}$, $7.09 \cdot 10^{-4}$, $4.12 \cdot 10^{-4}$, or $2.65 \cdot 10^{-4}$, depending on the volume of brine per WIPP disposal room (see Table 8). Half of these values are higher than $5.5 \cdot 10^{-4}$ M, the upper limit of the range of Pu solubilities estimated by the Expert Panel. However, the laboratory studies of radionuclide chemistry described above have yielded dissolved Pu(VI) concentrations higher than $1.60 \cdot 10^{-3}$ M, at least so far. The total quantity of energy deposited in brine by decay of ^{239}Pu in 10,000 years is:

$$4.27411 \cdot 10^{21} \text{ d} \cdot 5.15 \text{ MeV/d} = 2.20117 \cdot 10^{28} \text{ eV}. \qquad (28)$$

The number of moles of H_2 formed is:

$$2.20117 \cdot 10^{28} \text{ eV} \cdot 1.25 \text{ molecules/100 eV} /$$

$$6.0225 \cdot 10^{23} \text{ molecules/mole} = 4.57 \cdot 10^{2} \text{ moles/drum}. \qquad (29)$$

In Equation 29, "1.25 molecules per 100 eV" is the midpoint of the range of $G(H_2)$ (1.1 to 1.4 molecules per 100 eV) reported by Reed and Okajima (in prep.) for three WIPP brines (see above) and "$6.0225 \cdot 10^{23}$ molecules/mole is Avogadro's number. Therefore, "4.57 · 10^2 moles/drum" is actually the midpoint of a range of 4.02 to 5.12 · 10^2 moles per drum.

In addition to about 500 moles of H_2 per drum, the O_2-production potential for brine radiolysis by ^{239}Pu could be as high as about 250 moles per drum, depending on the induction period for O_2 production from the breakdown of O-containing intermediate species (above). However, Garner and I believe that oxic corrosion and aerobic microbial activity (above) will rapidly consume any O_2 produced by brine radiolysis. Therefore, we omit O_2 from the discussion that follows.

Although these results includes decay of ^{239}Pu but none of the other radionuclides in TRU waste, they are of the same order of magnitude as the H_2-production potential of 900 moles per drum from anoxic corrosion of steel CH TRU waste containers (drums and boxes) and steels and other Fe-base alloys in CH TRU waste (Brush, 1990). They are also similar to my calculated gas-production potential of 600 moles per drum from microbial degradation 100% of the cellulosics and 50% of the rubbers in CH TRU waste.

However, values of 500 moles of H_2 per drum and 750 moles of H_2 plus O_2 per drum for the gas-production potential from brine radiolysis by ^{239}Pu are probably far larger than what will actually be produced in WIPP disposal rooms. The assumption that all of the energy from decay of ^{239}Pu will be deposited in brine is probably far too pessimistic. It is much more likely that a significant fraction of this decay energy will be deposited in undissolved, particulate, Pu-bearing solids or other solids with which Pu is associated (cellulosics such as paper towels, articles of clothing, rubber gloves, other solids in sludges, etc.)

Preliminary results obtained after adding brine radiolysis to the PA code PANEL also suggest that actual radiolytic gas production will be much smaller than the gas-production potentials calculated above. (The addition of brine radiolysis to PANEL is the first step in the addition of brine radiolysis to the reaction-path gas-generation model.) PANEL calculates the quantities of radionuclides dissolved in brine in WIPP disposal rooms as a function of time. Currently, it uses either an internal analytical model or the two-phase flow code BRAGFLO to predict the quantity of Salado- or Castile-Fm. brine present as a function of time. It then uses Latin hypercube sampling of solubilities estimated by the Expert Panel to predict the solubilities of Pu and other important actinide elements, and uses the initial inventory and decay rates of individual isotopes of these elements to calculate the relative abundance of each dissolved radionuclide as a function of time. Garner added the equations used to calculate the gas-production potential from decay of ^{239}Pu (above) to PANEL and extended them to include other important α-emitting radionuclides in the WIPP inventory. For his preliminary calculations, Garner used predictions of brine inflow and outflow from BRAGFLO runs made for the last round of PA calculations (WIPP Performance Assessment Department, 1992), which included the average-stoichiometry gas-generation model. The brine volume in a panel varied with time in each vector (simulation). However, the gas-generation rates from anoxic corrosion and microbial activity and the dissolved concentration of each radioactive element did not vary within a given vector, unless brine was completely consumed or the quantity of a radioactive element in the inventory limited its concentration to a value less than the sampled solubility.

The largest quantity of H_2 produced by brine radiolysis during the 10,000-year period of performance of the repository was 90 moles per drum, a value significantly smaller than the 500-mole-per-drum H_2-production potential from decay of ^{239}Pu calculated above. In this vector, the ^{241}Am was the largest contributor to radiolytic H_2 production. Furthermore, 50% of the 70 vectors produced less than 2 moles of H_2 per drum, a value less than 0.5% of the H_2-production potential.

Clearly, the difference between the H_2-production potential and the values calculated using PANEL suggest that gas production in WIPP disposal rooms may actually be far less than the gas-production potentials. The main reasons for this appear to be: (1) calculations of gas-production potentials often include worst-case assumptions; (2) these calculations also neglect interactions between or among processes; these interactions may significantly decrease the amount of gas produced.

CONSUMPTION OF GASES

The compounds $Ca(OH)_2$ (in hydrated cementitious materials and CaO (a potential backfill additive) could consume significant quantities of CO_2 and H_2S by the reactions:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O; \tag{30a}$$

$$Ca(OH)_2 + H_2S = CaS + 2H_2O; \tag{30b}$$

$$CaO + CO_2 = CaCO_3; \tag{31a}$$

$$CaO + H_2S = CaS + H_2O. \tag{31b}$$

In bench-scale laboratory experiments, $Ca(OH)_2$, dissolved in WIPP brines, reacts very rapidly with gaseous CO_2. Dissolved, hydrated CaO, solid $Ca(OH)_2$ and solid CaO would probably also react very rapidly with gaseous CO_2. However, the effects of transport phenomena must be incorporated in predictions of the rates of CO_2 and, perhaps, H_2S uptake by these compounds in WIPP disposal rooms. Furthermore, estimates of the quantities of hydrated cementitious materials and the concentrations of $Ca(OH)_2$ in these materials are necessary for room-scale predictions. Therefore, I have not estimated rates for these reactions yet.

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TABLE 1. GAS-GENERATION REACTIONS

Reaction	Abbreviation
Oxic corrosion of steels and other Fe-base materials:	
1. $2Fe + H_2O + 1.5O_2 = 2\gamma FeO(OH)$	Fe to $\gamma FeO(OH)^1$
Anoxic corrosion of steels and other Fe-base materials:	
6a. $Fe + 2H_2O = Fe(OH)_2 + H_2$	Fe to $Fe(OH)_2{}^2$
6b. $3Fe + 4H_2O = Fe_3O_4 + 4H_2$	Fe to $Fe_3O_4{}^2$
7. $Fe + H_2O + CO_2 = FeCO_3 + H_2$	Fe to $FeCO_3{}^2$
8a. $Fe + 2H_2S = FeS_2 + 2H_2$	Fe to $FeS_2{}^2$
8b. $Fe + H_2S = FeS + H_2$	Fe to FeS^2
Microbial degradation of cellulosics and, perhaps, plastics and rubbers:	
12. $CH_2O + O_2 = H_2O + CO_2$	Aerobic respiration[1]
13. $CH_2O + 0.8H^+ + 0.8NO_3^- = 1.4H_2O + CO_2 + 0.4N_2$	Denitrification[2]

TABLE 1. GAS-GENERATION REACTIONS (cont.)

Reaction	Abbreviation
Microbial degradation of cellulosics and, perhaps, plastics and rubbers (cont.):	
14a. $CH_2O + 4FeO(OH) + H_2O$	
$= 4Fe(OH)_2 + CO_2$	Fe(III) reduction[1]
14b. $CH_2O + 4FeO(OH)$	
$= 1.33Fe_3O_4 + 1.67H_2O + CO_2 + 1.33H_2$	Fe(III) reduction[1]
14c. $CH_2O + 4FeO(OH) + H_2O + 3CO_2$	
$= 4FeCO_3 + 4H_2O$	Fe(III) reduction[1]
14d. $CH_2O + 4FeO(OH) + 4H_2S$	
$= 4FeS + 7H_2O + CO_2$	Fe(III) reduction[1]
14e. $CH_2O + 4FeO(OH) + 8H_2S$	
$= 4FeS_2 + 7H_2O + CO_2 + 4H_2$	Fe(III) reduction[1]
15. $CH_2O + H^+ + 0.5SO_4^{2-}$	
$= H_2O + CO_2 + 0.5\ H_2S$	SO_4^{2-} reduction[2]
16a. $2CH_2O = CH_4 + CO_2$	Methanogenesis[2]
16b. $CO_2 + 4H_2 = CH_4 + 2H_2O$	Methanogenesis[2]

TABLE 1. GAS-GENERATION REACTIONS (cont.)

Reaction	Abbreviation
Radiolysis:	
17. $H_2O = H_2 + 0.5O_2$	Radiolysis of brine[1]
Consumption of gases by cementitious materials and backfill additives:	
25a. $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$	$Ca(OH)_2$ to $CaCO_3$[2]
25b. $Ca(OH)_2 + H_2S = CaS + 2H_2O$	$Ca(OH)_2$ to CaS[2]
26a. $CaO + CO_2 = CaCO_3$	CaO to $CaCO_3$[2]
26b. $CaO + H_2S = CaS + H_2O$	CaO to CaS[12]

---

1. Probably will not have a significant, direct effect on the gas and H_2O budget of WIPP disposal rooms, but could be important from the standpoint of the O_2 budget of the repository (see text).
2. Could have a significant, direct effect on the gas and H_2O budget of the repository (see text).

TABLE 2. INUNDATED GAS-PRODUCTION RATES

	Gas-Production Rate		
Process	Minimum	Best	Maximum
Oxic corrosion of steels and other Fe-base materials:			
moles O_2/(m^2 steel · yr)	0	- 5	- 8
moles O_2/(drum · yr)	0[1]	- 30[1]	- 50[1]
μm steel/yr	0	50	80
Anoxic corrosion of steels and other Fe-base materials:			
moles H_2/(m^2 steel · yr)	0	0.1	20
moles H_2/(drum · yr)	0[1]	0.6[1]	100[1]
μm steel/yr	0	1	200
Microbial degradation of cellulosics (Reactions 12 through 16b):			
moles gas/(kg cellulose · yr)	0[2]	0.1[2]	0.5[2]
moles gas/(drum · yr)	0[1, 2]	1[1, 2]	5[1, 2]
Microbial degradation of cellulosics (Reaction 16b):			
moles gas/(kg cellulose · yr)	Not est.[3]	Not est.[3]	Not est.[3]
moles gas/(drum · yr)	Not est.[3]	Not est.[3]	Not est.[3]

TABLE 2. INUNDATED GAS-PRODUCTION RATES (cont.)

Reaction	Gas-Production Rate[1]		
	Minimum	Best	Maximum
Radiolysis of brine:			
moles $H_2/(m^3 \cdot yr)$	$4.5 \cdot 10^{-14}$	$1.1 \cdot 10^{-6}$	$9.9 \cdot 10^{-1}$
moles $H_2/(drum \cdot yr)$	$8.9 \cdot 10^{-16}$	$6.6 \cdot 10^{-8}$	$1.2 \cdot 10^{-1}$
moles $O_2/(m^3 \cdot yr)$	$2.2 \cdot 10^{-14}$	$5.4 \cdot 10^{-7}$	$5.0 \cdot 10^{-1}$
moles $O_2/(drum \cdot yr)$	$4.5 \cdot 10^{-16}$	$3.3 \cdot 10^{-8}$	$6.0 \cdot 10^{-2}$
moles $(H_2 + O_2)/(m^3 \cdot yr)$	$6.7 \cdot 10^{-14}$	$1.6 \cdot 10^{-6}$	$1.5 \cdot 10^{0}$
moles $(H_2 + O_2)/(drum \cdot yr)$	$1.3 \cdot 10^{-15}$	$9.9 \cdot 10^{-8}$	$1.8 \cdot 10^{-1}$
Consumption of CO_2 by cementitious materials and backfill additives:			
moles gas/(drum · yr)	Not est.[4]	Not est.[4]	Not est.[4]

1. Estimates do not include steels or other Fe-base alloys associated with RH TRU waste or steels or other Fe-base alloys used for ground support.

2. Gases produced by Reactions 12 through 16a could include CO_2, CH_4, H_2S, N_2, and NH_3 (see text).

3. Not estimated yet, but gases consumed by Reaction 16b could include significant quantities of CO_2 and especially H_2 (see text).

4. Not estimated yet, but gases consumed by $Ca(OH)_2$ and CaO in cementitious materials and backfill additives could include significant quantities of CO_2 and, perhaps, H_2S (see text).

TABLE 3. HUMID GAS-PRODUCTION RATES

	Gas-Production Rate		
Process	Minimum	Best	Maximum
Oxic corrosion of steels and other Fe-base materials:			
moles O_2/(m^2 steel · yr)	0	- 0.5	- 5
moles O_2/(drum · yr)	0[1]	- 3[1]	- 30[1]
μm steel/yr	0	5	50
Anoxic corrosion of steels and other Fe-base materials:			
moles H_2/(m^2 steel · yr)	0	0	0.01
moles H_2/(drum · yr)	0[1]	0[1]	0.06[1]
μm steel/yr	0	0	0.1
Microbial degradation of cellulosics (Reactions 12 through 16b):			
moles gas/(kg cellulose · yr)	0[2]	0.01[2]	0.1[2]
moles gas/(drum · yr)	0[1, 2]	0.1[1, 2]	1[1, 2]
Microbial degradation of cellulosics (Reaction 16b):			
moles gas/(kg cellulose · yr)	Not set.[3]	Not est.[3]	Not est.[3]
moles gas/(drum · yr)	Not est.[3]	Not est.[3]	Not est.[3]

TABLE 3. HUMID GAS-PRODUCTION RATES (cont.)

Process	Gas-Production Rate Minimum	Best	Maximum
Radiolysis of brine:			
moles $H_2/(m^3 \cdot yr)$	0	0	0
moles $H_2/(drum \cdot yr)$	0	0	0
moles $O_2/(m^3 \cdot yr)$	0	0	0
moles $O_2/(drum \cdot yr)$	0	0	0
moles $(H_2 + O_2)/(m^3 \cdot yr)$	0	0	0
moles $(H_2 + O_2)/(drum \cdot yr)$	0	0	0
Consumption of gases by cementitious materials and backfill additives:			
moles gas/(drum · yr)	Not est.[4]	Not est.[4]	Not est.[4]

1. Estimates do not include steels or other Fe-base alloys associated with RH TRU waste or steels or other Fe-base alloys used for ground support.

2. Gases produced by Reactions 12 through 16a could include CO_2, CH_4, H_2S, N_2, and NH_3 (see text).

3. Not estimated yet, but gases consumed by Reaction 16b could include significant quantities of CO_2 and especially H_2 (see text).

4. Not estimated yet, but gases consumed by $Ca(OH)_2$ and CaO in cementitious materials and backfill additives could include significant quantities of CO_2 and, perhaps, H_2S (see text).

TABLE 4. RADIOLYTIC GAS-PRODUCTION RATES (mol/m^3 of brine·yr)[1, 2]

Dissolved ^{239}Pu Conc. (M)	Gas-Production Rate		
	H_2	O_2	$H_2 + O_2$
$1 \cdot 10^{0}$	**$1.8 \cdot 10^{3}$**	**$0.9 \cdot 10^{3}$**	**$2.7 \cdot 10^{3}$**
$1 \cdot 10^{-1}$	**$1.8 \cdot 10^{2}$**	**$0.9 \cdot 10^{2}$**	**$2.7 \cdot 10^{2}$**
$1 \cdot 10^{-2}$	**$1.8 \cdot 10^{1}$**	**$0.9 \cdot 10^{1}$**	**$2.7 \cdot 10^{1}$**
$1 \cdot 10^{-3}$	**$1.8 \cdot 10^{0}$**	**$0.9 \cdot 10^{0}$**	**$2.7 \cdot 10^{0}$**
$1 \cdot 10^{-4}$	$1.8 \cdot 10^{-1}$	$0.9 \cdot 10^{-1}$	$2.7 \cdot 10^{-1}$
$1 \cdot 10^{-5}$	$1.8 \cdot 10^{-2}$	$0.9 \cdot 10^{-2}$	$2.7 \cdot 10-2$
$1 \cdot 10^{-6}$	$1.8 \cdot 10^{-3}$	$0.9 \cdot 10^{-3}$	$2.7 \cdot 10^{-3}$
$1 \cdot 10^{-7}$	$1.8 \cdot 10^{-4}$	$0.9 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$
$1 \cdot 10^{-8}$	$1.8 \cdot 10^{-5}$	$0.9 \cdot 10^{-5}$	$2.7 \cdot 10^{-5}$
$1 \cdot 10^{-9}$	$1.8 \cdot 10^{-6}$	$0.9 \cdot 10^{-6}$	$2.7 \cdot 10^{-6}$

1. Rates in moles per m^3 of brine per year calculated from experimentally measured values of $G(H_2)$ (see text).
2. Values in bold type may exceed the maximum <u>average</u> Pu concentration or <u>average</u> gas-production rate depending on the quantity of brine present and time (see text).

TABLE 5. RADIOLYTIC H_2-PRODUCTION RATES (mol/drum·yr)[1, 2]

Dissolved	Brine Volume (m^3/room)			
^{239}Pu Conc. (M)	135	305	525	815
$1 \cdot 10^{0}$	**$3.6 \cdot 10^{1}$**	**$8.1 \cdot 10^{1}$**	**$1.4 \cdot 10^{2}$**	**$2.2 \cdot 10^{2}$**
$1 \cdot 10^{-1}$	**$3.6 \cdot 10^{0}$**	**$8.1 \cdot 10^{0}$**	**$1.4 \cdot 10^{1}$**	**$2.2 \cdot 10^{1}$**
$1 \cdot 10^{-2}$	**$3.6 \cdot 10^{-1}$**	**$8.1 \cdot 10^{-1}$**	**$1.4 \cdot 10^{0}$**	**$2.2 \cdot 10^{0}$**
$1 \cdot 10^{-3}$	$3.6 \cdot 10^{-2}$	**$8.1 \cdot 10^{-2}$**	**$1.4 \cdot 10^{-1}$**	**$2.2 \cdot 10^{-1}$**
$1 \cdot 10^{-4}$	$3.6 \cdot 10^{-3}$	$8.1 \cdot 10^{1-3}$	$1.4 \cdot 10^{-2}$	$2.2 \cdot 10^{-2}$
$1 \cdot 10^{-5}$	$3.6 \cdot 10^{-4}$	$8.1 \cdot 10^{-4}$	$1.4 \cdot 10^{-3}$	$2.2 \cdot 10^{-3}$
$1 \cdot 10^{-6}$	$3.6 \cdot 10^{-5}$	$8.1 \cdot 10^{-5}$	$1.4 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$
$1 \cdot 10^{-7}$	$3.6 \cdot 10^{-6}$	$8.1 \cdot 10^{-6}$	$1.4 \cdot 10^{-5}$	$2.2 \cdot 10^{-5}$
$1 \cdot 10^{-8}$	$3.6 \cdot 10^{-7}$	$8.1 \cdot 10^{-7}$	$1.4 \cdot 10^{-6}$	$2.2 \cdot 10^{-6}$
$1 \cdot 10^{-9}$	$3.6 \cdot 10^{-8}$	$8.1 \cdot 10^{-8}$	$1.4 \cdot 10^{-7}$	$2.2 \cdot 10^{-7}$

1. Rates in moles per drum per year calculated from values in moles per m^3 of brine per year (see text).

2. Values in bold type may exceed the maximum average H_2-production rate depending on the quantity of brine present and time (see text).

TABLE 6. RADIOLYTIC O_2-PRODUCTION RATES (mol/drum·yr)[1, 2]

Dissolved	Brine Volume (m^3/room)			
^{239}Pu Conc. (M)	135	305	525	815
$1 \cdot 10^{0}$	**$1.8 \cdot 10^{1}$**	**$4.0 \cdot 10^{1}$**	**$6.9 \cdot 10^{1}$**	**$1.1 \cdot 10^{2}$**
$1 \cdot 10^{-1}$	**$1.8 \cdot 10^{0}$**	**$4.0 \cdot 10^{0}$**	**$6.9 \cdot 10^{0}$**	**$1.1 \cdot 10^{1}$**
$1 \cdot 10^{-2}$	**$1.8 \cdot 10^{-1}$**	**$4.0 \cdot 10^{-1}$**	**$6.9 \cdot 10^{-1}$**	**$1.1 \cdot 10^{0}$**
$1 \cdot 10^{-3}$	$1.8 \cdot 10^{-2}$	**$4.0 \cdot 10^{-2}$**	**$6.9 \cdot 10^{-2}$**	**$1.1 \cdot 10^{-1}$**
$1 \cdot 10^{-4}$	$1.8 \cdot 10^{-3}$	$4.0 \cdot 10^{-3}$	$6.9 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$
$1 \cdot 10^{-5}$	$1.8 \cdot 10^{-4}$	$4.0 \cdot 10^{-4}$	$6.9 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$
$1 \cdot 10^{-6}$	$1.8 \cdot 10^{-5}$	$4.0 \cdot 10^{-5}$	$6.9 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$
$1 \cdot 10^{-7}$	$1.8 \cdot 10^{-6}$	$4.0 \cdot 10^{-6}$	$6.9 \cdot 10^{-6}$	$1.1 \cdot 10^{-5}$
$1 \cdot 10^{-8}$	$1.8 \cdot 10^{-7}$	$4.0 \cdot 10^{-7}$	$6.9 \cdot 10^{-7}$	$1.1 \cdot 10^{-6}$
$1 \cdot 10^{-9}$	$1.8 \cdot 10^{-8}$	$4.0 \cdot 10^{-8}$	$6.9 \cdot 10^{-8}$	$1.1 \cdot 10^{-7}$

1. Rates in moles per drum per year calculated from experimentally measured values of $G(H_2)$ (see text).

2. Values in bold type may exceed the maximum <u>average</u> O_2-production rate depending on the quantity of brine present and time (see text).

TABLE 7. RADIOLYTIC GAS- (H_2 + O_2)-PRODUCTION RATES (mol/drum·yr)[1, 2]

Dissolved	Brine Volume (m^3/room)			
^{239}Pu Conc. (M)	135	305	525	815
$1 \cdot 10^{0}$	**$5.4 \cdot 10^{1}$**	**$1.2 \cdot 10^{2}$**	**$2.1 \cdot 10^{2}$**	**$3.2 \cdot 10^{2}$**
$1 \cdot 10^{-1}$	**$5.4 \cdot 10^{0}$**	**$1.2 \cdot 10^{1}$**	**$2.1 \cdot 10^{1}$**	**$3.2 \cdot 10^{1}$**
$1 \cdot 10^{-2}$	**$5.4 \cdot 10^{-1}$**	**$1.2 \cdot 10^{0}$**	**$2.1 \cdot 10^{0}$**	**$3.2 \cdot 10^{0}$**
$1 \cdot 10^{-3}$	$5.4 \cdot 10^{-2}$	**$1.2 \cdot 10^{-1}$**	**$2.1 \cdot 10^{-1}$**	**$3.2 \cdot 10^{-1}$**
$1 \cdot 10^{-4}$	$5.4 \cdot 10^{-3}$	$1.2 \cdot 10^{-2}$	$2.1 \cdot 10^{-2}$	$3.2 \cdot 10^{-2}$
$1 \cdot 10^{-5}$	$5.4 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$	$3.2 \cdot 10^{-3}$
$1 \cdot 10^{-6}$	$5.4 \cdot 10^{-5}$	$1.2 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$	$3.2 \cdot 10^{-4}$
$1 \cdot 10^{-7}$	$5.4 \cdot 10^{-6}$	$1.2 \cdot 10^{-5}$	$2.1 \cdot 10^{-5}$	$3.2 \cdot 10^{-5}$
$1 \cdot 10^{-8}$	$5.4 \cdot 10^{-7}$	$1.2 \cdot 10^{-6}$	$2.1 \cdot 10^{-6}$	$3.2 \cdot 10^{-6}$
$1 \cdot 10^{-9}$	$5.4 \cdot 10^{-8}$	$1.2 \cdot 10^{-7}$	$2.1 \cdot 10^{-7}$	$3.2 \cdot 10^{-7}$

1. Rates in moles per drum per year calculated from experimentally measured values of G(H_2) (see text).
2. Values in bold type may exceed the maximum <u>average</u> gas-production rate depending on the quantity of brine present and time (see text).

TABLE 8. MAXIMUM AVERAGE Pu CONCENTRATIONS IN BRINES IN WIPP DISPOSAL ROOMS (M)[1]

	Brine Volume (m^3/room)			
Time (yr)	135	305	525	815
0	$1.60 \cdot 10^{-3}$	$7.09 \cdot 10^{-4}$	$4.12 \cdot 10^{-4}$	$2.65 \cdot 10^{-4}$
100	$1.56 \cdot 10^{-3}$	$6.91 \cdot 10^{-4}$	$4.02 \cdot 10^{-4}$	$2.59 \cdot 10^{-4}$
200	$1.54 \cdot 10^{-3}$	$6.84 \cdot 10^{-4}$	$3.97 \cdot 10^{-4}$	$2.56 \cdot 10^{-4}$
500	$1.52 \cdot 10^{-3}$	$6.73 \cdot 10^{-4}$	$3.91 \cdot 10^{-4}$	$2.52 \cdot 10^{-4}$
1,000	$1.49 \cdot 10^{-3}$	$6.61 \cdot 10^{-4}$	$3.84 \cdot 10^{-4}$	$2.47 \cdot 10^{-4}$
2,000	$1.44 \cdot 10^{-3}$	$6.39 \cdot 10^{-4}$	$3.71 \cdot 10^{-4}$	$2.39 \cdot 10^{-4}$
5,000	$1.31 \cdot 10^{-3}$	$5.78 \cdot 10^{-4}$	$3.36 \cdot 10^{-4}$	$2.16 \cdot 10^{-4}$
10,000	$1.11 \cdot 10^{-3}$	$4.92 \cdot 10^{-4}$	$2.86 \cdot 10^{-4}$	$1.84 \cdot 10^{-4}$

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1. Calculations include all isotopes of Pu expected in the repository, not just ^{239}Pu (see text).

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