Conf-9104261-3

SAND91-0675C

SAND--91-0675C

DE91 019052

Received

SEP 3

LABORATORY AND BIN-SCALE TESTS OF GAS GENERATION FOR THE WASTE ISOLATION PILOT PLANT*

L. H. Brush,[1] M. A. Molecke,[1] A. R. Lappin,[2] R. E. Westerman,[3] X. Tong,[4]
J. N. P. Black,[4] D. Grbic-Galic,[4] R. E. Vreeland,[5] and D. T. Reed[6]

1. Disposal Room Systems Division 6345, Sandia National Laboratories,** Albuquerque,** NM 87185, USA
2. Bin Test Programs Division 6340A, Sandia National Laboratories, Albuquerque, NM 87185, USA
3. Materials Sciences Department, Pacific Northwest Laboratory, PO Box 999, Richland, WA 99352, USA
4. Department of Civil Engineering, Stanford University, Stanford, CA 94305, USA
5. Department of Biology, West Chester University, West Chester, PA 19383, USA
6. Chemical Technology Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, USA

ABSTRACT

The design-basis, defense-related, transuranic (TRU) waste to be emplaced in the Waste Isolation Pilot Plant (WIPP) could, if sufficient H_2O and nutrients were present, produce as much as 1,500 moles of gas per drum of waste. Anoxic corrosion of Fe and Fe-base alloys and microbial degradation of cellulosics are the processes of greatest concern, but radiolysis of brine could also be important.

After 6 months, laboratory studies of anoxic corrosion of low- and medium-C steels have yielded an H_2 production rate of 1.26 moles per equivalent drum of waste under brine-inundated conditions with initially pure N_2 present in the headspace at low pressures (about 150 psig). Inundated conditions with initially pure CO_2 present at low pressures apparently passivated these steels after about 3 or 4 months. The results of 6-month, high-pressure (1,000 psig) experiments with the same two heats of low-C steel

---

*This work was supported by the US Department of Energy (DOE) under Contract DE-AC04-76DP00789.

**A US DOE facility.

MASTER

DISCLAIMER

under inundated conditions imply that elevated H_2 pressure decreases the H_2 production rate, but that the same N_2 pressure increases it. Under humid (74% relative humidity), low-pressure conditions, no anoxic corrosion has occurred after 6 months. The results obtained under humid conditions suggest that, in the absence of a thin film of brine introduced by capillary rise or condensation followed by dissolution of salts from the backfill, 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.

Laboratory studies of microbial activity have not yet yielded measurable gas production under expected repository conditions. A laboratory study of gas production from α radiolysis of WIPP brines and a laboratory and modeling study of the proposed backfill additives $CaCO_3$, CaO, $CuSO_4$, KOH, and NaOH, which may remove or prevent the production of some of the expected gases, are also under way.

The in-situ, bin-scale tests will quantify gas production from about 970 drums of both design-basis and treated contact-handled (CH) TRU waste, the first waste to be emplaced in the WIPP, in about 146, 1-m^3, instrumented, steel test containers. We have designed the bins to allow for periodic sampling and analysis of gases produced or released by the wastes, to control internal gas pressures, and to safely isolate radionuclides during testing. We will maintain the waste in some of the bins in its dry, as-received state and add brine to other bins to determine the effect of inundated conditions on gas production. We will compare data from the bin tests, which reflect the simultaneous operation of gas-producing processes, with those from laboratory studies with simulated waste, which isolate these processes. We will also use the bin-scale tests to determine rates of release of volatile, hazardous compounds from CH TRU waste. The bin-scale test program, including instrumentation and control equipment, is currently in place in the WIPP. We are now awaiting the first shipment of actual TRU waste.

1. LABORATORY STUDIES OF GAS GENERATION

1.1 Anoxic Corrosion

Brush [1] estimated that, if sufficient brine were present and the concentration of O_2 were low, anoxic corrosion of all of the steel containers (drums and boxes) and Fe and Fe-base alloys in the design-basis TRU waste to be emplaced in WIPP disposal rooms would produce about 2 moles of H_2 per equivalent drum of waste per year for 400 to 500 years, or a total of 900 moles per drum. (There will be about 6,800 equivalent drums of waste per 3,640-m^3 room; each of the 56 rooms will contain 2,300 m^3 of void volume immediately after emplacement of the drums and crushed-salt or crushed-salt-and-bentonite backfill.) Anoxic corrosion of steel containers would produce 600 moles of H_2 per drum; anoxic corrosion of Fe and Fe-base alloys in the waste would produce 300 moles of H_2 per drum. These estimates did not include H_2 from anoxic corrosion of Al and Al-base alloys in the waste because there was no estimate of the quantity of these metals in the WIPP inventory at that time. Anoxic corrosion is the process of greatest concern from the standpoint of the gas budget of the repository.

Anoxic corrosion could consume significant quantities of H_2O, as much as 200 m^3 of brine per room [1]. The quantity of intergranular brine in the disturbed rock zone (DRZ) available for transport to the waste by brine inflow or diffusion of H_2O vapor through the gaseous phase is, perhaps, 80 to 160 m^3 [2]. Therefore, in the absence of transport from the undisturbed salt surrounding the repository, from fractured anhydritic marker beds close to the repository horizon, or from underlying formations in the event of human intrusion, the quantity of brine available may be insufficient for the production of 900 moles of H_2 per drum. An integrated model of the effects of gas pressurization, room closure, brine inflow and outflow, and vapor-phase transport of H_2O is still at an early stage of development. However, preliminary calculations suggest that absorption of H_2O by crushed salt and any bentonite in the backfill and the possible consumption of H_2O by microbial degradation of cellulosics may limit the extent of anoxic corrosion of metals.

Based on thermodynamic calculations and a review of previous kinetic data, Brush [3] concluded that, in the absence of microbially produced CO_2 and H_2S, anoxic corrosion of Fe and Fe-base alloys by WIPP brines at 30°C, the expected temperature of the repository, would probably produce Fe_3O_4 (magnetite) or $(Fe,Mg,Mn)(OH)_2$ (amakinite). He calculated equilibrium H_2 fugacities of about 400 and 60 atm, respectively, for these corrosion products. Because the former value is well above lithostatic pressure at the repository horizon (about 150 atm) and the latter well below it, the identity of the corrosion product formed would appear to affect the long-term performance of the repository significantly. However, pure $Fe(OH)_2$ is unstable with respect to Fe_3O_4 below an H_2 fugacity of 100,000 atm. In the presence of microbially produced CO_2 or H_2S, anoxic corrosion of Fe or Fe-base alloys would produce phases such as $FeCO_3$ (siderite) or FeS_2 (pyrite).

The activity of H_2O vapor in equilibrium with intergranular brine from the Salado Fm. at or near the stratigraphic horizon of WIPP disposal rooms is equal to the activity of H_2O in the brine, about 0.7 [3]. Therefore, the thermodynamic calculations described above apply to H_2O vapor as well as to brine. Significant anoxic corrosion would thus be possible if there were sufficient H_2O vapor present. Brush [3] found no kinetic data relevant to the corrosion of Fe and Fe-base alloys by H_2O vapor under conditions similar to those expected for the repository.

We are studying anoxic corrosion of specimens from two heats each of ASTM A 366 and ASTM A 570 steels by WIPP brine (referred to as inundated conditions) and by H_2O vapor in equilibrium with brine (humid conditions) in 2.4-L, seal-welded, Hastelloy C-22 containers at 30°C and low pressures (about 150 psig) at Pacific Northwest Laboratory, or PNL [3]. The specimens of cold-rolled ASTM A 366, which contain about 0.08 wt % C, simulate the drums to be emplaced in WIPP disposal rooms; those of hot-rolled ASTM A 570, which contain about 0.13 wt % C, simulate boxes and tools in the waste. For both humid and inundated conditions, we are carrying out experiments with two atmospheres, pure N_2 and pure CO_2, in the headspace above synthetic WIPP Brine A [4] for periods of 3, 6, 12, and 24 months. Brine A is a synthetic brine with a composition similar to that of many intergranular brines from the Salado Fm. at or near the stratigraphic horizon of the WIPP underground workings. The 3- and 6-month tests are now complete.

We are also studying anoxic corrosion of the same two heats of ASTM A 366 steel by Brine A in Hastelloy C-276 autoclaves at 30°C and high initial N_2 and H_2 pressures (500 and 1,000 psig) for periods of 6 and 12 months at PNL [3]. The objective of this study is to determine if elevated H_2 pressures decrease the H_2 production rates observed under inundated, low-pressure conditions.

Finally, we have just begun 3-month experiments to quantify anoxic corrosion of one the heats of ASTM A 366 steel by simulated crushed-salt backfill at 30°C and low N_2 pressures (about 150 psig). We placed salt collected from the WIPP underground workings around steel specimens in a stainless-steel, mesh basket suspended in each of two autoclaves used for high-pressure experiments. We used a coarse fraction (1/16- to 1/4-in diameter) of the salt to allow rapid diffusion of H_2O and H_2 to and from the specimens. In one experiment, we suspended the basket above Brine A to determine the effects of vapor-phase transport of H_2O on anoxic corrosion. In another, we allowed the bottom of the salt to contact the brine to examine the effects of capillary rise. We will use the results of these preliminary experiments to plan longer runs with this backfill and a backfill consisting of 70% crushed salt and 30% bentonite.

The results of the 3- and 6-month, low-pressure experiments imply that anoxic corrosion of steels produces significant quantities of H_2 under inundated conditions with initially pure N_2 present. The linear pressure increases observed during these runs (Figure 1) and posttest H_2 analyses yielded nearly constant H_2 production rates, with an average value for all four heats of 0.21 moles per m^2 of steel or 1.26 moles per equivalent drum of waste per year for the 6-month runs. Posttest gravimetric (weight-loss) analysis yielded an average corrosion rate of 1.72 μm of steel per year for the 6-month runs. However, both the 3- and 6-month results also imply that anoxic corrosion of steels does not occur under humid conditions. Posttest examination of the specimens from the humid experiments revealed no anoxic corrosion, except for about 10% of the surface area of the specimens splashed by brine during pretest handling associated with welding, leak-checking, and placement of the containers in the incubator. About 90% of the surface area of the specimens was shiny, untarnished, and indistinguishable from the abraded appearance of the specimens prior to the experiments. Corrosion of about 10% of the surface area of the specimens is consistent with the small pressure increases observed during the runs and the small quantities of H_2 detected by posttest analysis.

Although the H_2 production rate has been constant for 6 months at low N_2 pressures, the results of high-pressure experiments at PNL imply that the build-up of H_2 pressure would eventually reduce this rate significantly. After 6 months, the corrosion rate of two heats of ASTM A 366 steel under inundated conditions with pure H_2 at an initial 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 after 6 months. 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. We did not measure H_2 production rates during the high-pressure experiments. Furthermore, we have still not

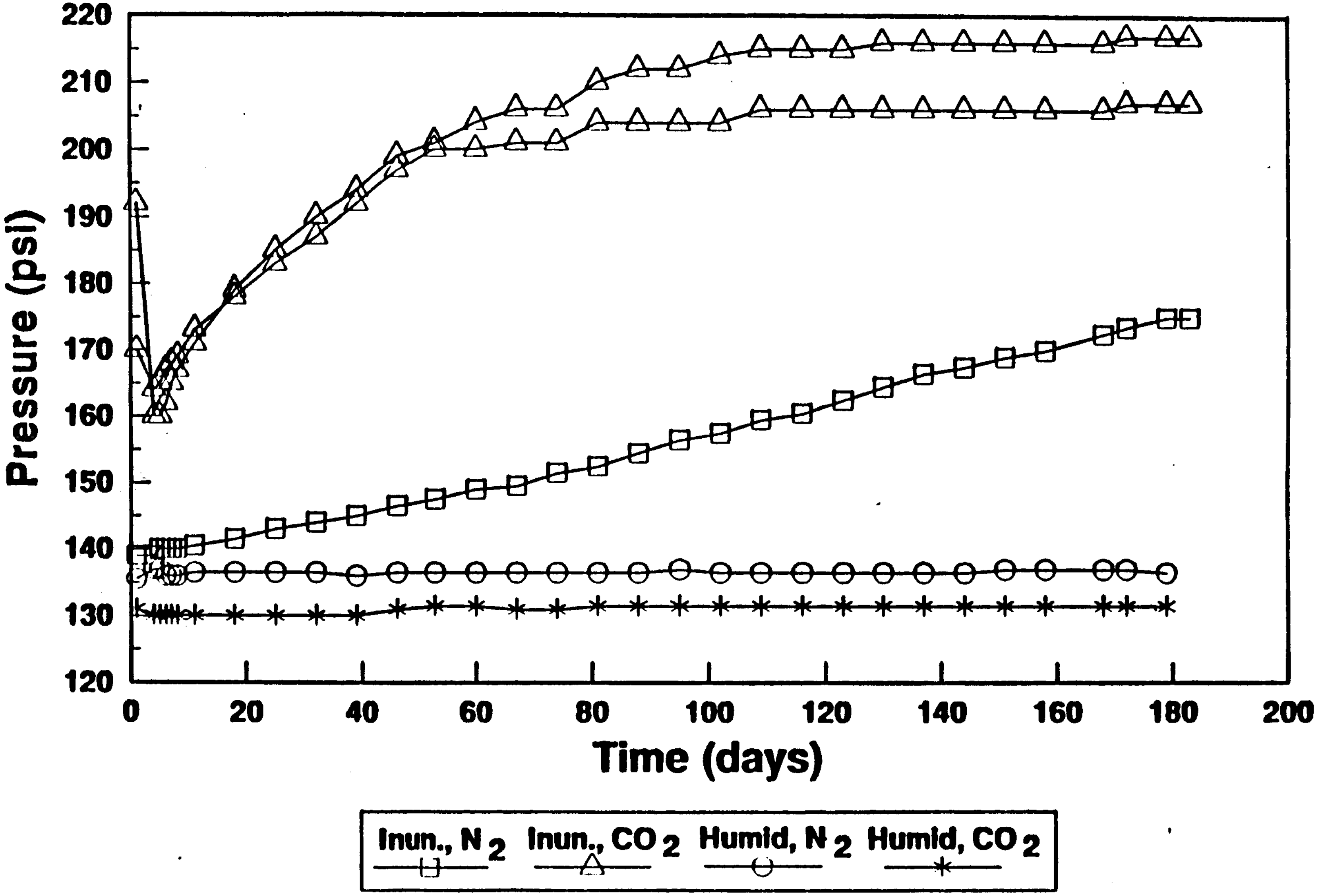

Figure 1. Pressure-Time Curves for 6-Month Experiments at PNL. Data for duplicate containers averaged to obtain each curve.

identified the corrosion product or products from these or the low-pressure experiments with N_2 present yet. Nevertheless, it is possible to estimate H_2 production rates of 0.046 moles per m^2 per year or 0.275 moles per drum per year for 1,000 psig H_2 and 0.38 moles per m^2 per year or 2.29 moles per drum per year for 1,000 psig N_2. At present, we have not measured corrosion rates for any pressures other than 150 and 1,000 psig. We will, however, obtain 12-month data for 500 and 1,000 psig H_2 in a few months.

Under low-pressure, inundated conditions with initially pure 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. 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.

In 3- and 6-month, low-pressure, humid experiments with either initially pure CO_2 or N_2, we 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 suggest 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, anoxic corrosion of other metals, especially Al and Al-base alloys, may continue under humid conditions. Furthermore, 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 could cause additional anoxic corrosion of steels and H_2 production after brine is driven away from corroding steels. The low-pressure experiments with simulated backfills will soon provide more realistic data than the experiments under humid conditions.

1.2 Microbial Activity

Brush [1] also estimated that, if sufficient brine and nutrients were present in WIPP disposal rooms, microbial degradation of cellulosics (mainly paper, treated and untreated lumber, and plywood) in TRU waste would produce about 1 mole of various gases per equivalent drum of waste per year for 600 years, or a total of 600 moles per drum. Brush [1] estimated that the 10 kg of cellulosics per equivalent drum of waste to be emplaced in the repository comprise 70% paper, 16% lumber, 10% plywood, and 4% cloth. The gases produced could include CH_4, CO_2, H_2S, N_2, and NH_3, but Brush [1] did not estimate the relative proportions at any given time or as a function of time. Microbial activity is the process of second greatest concern from the standpoint of the gas budget of the repository.

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

Conceptual models of the sequential use of electron acceptors by microorganisms in natural systems [5, 6] and estimates of the quantities of electron acceptors expected in WIPP disposal rooms [1] imply that the microbial processes denitrification, SO_4^{2-} reduction, fermentation, and methanogenesis could affect the gas and H_2O budgets of the repository significantly. Aerobic respiration, reduction of Mn(IV) oxides and hydroxides, and reduction of Fe(III) oxides and hydroxides, on the other hand, would probably be insignificant.

We attempted to use a batch bioassay procedure at Stanford University [1, 7, 8] to determine which of the potentially significant microbial processes denitrification, SO_4^{2-} reduction, fermentation, and methanogenesis occur under overtest conditions (relatively biodegradable substrates such as glucose, amendment of brine with nutrients, etc.) and to quantify the effects of those processes that occur on the gas and H_2O budgets of WIPP disposal rooms under realistic conditions (cellulose as the sole substrate, no amendment with nutrients, etc.). As inocula, we used various nonhalophilic microorganisms from sewage sludge and dust collected from a laboratory at Stanford to simulate those present in TRU waste. We also used various halophilic microorganisms sampled from the WIPP Site and vicinity and enriched at West Chester University. These enrichments simulate microorganisms that could enter the repository on dust particles transported from the salt lakes in Nash Draw (a few kilometers west of the WIPP Site) by wind and the mine ventilation system or in crushed-salt backfill from the WIPP tailings pile. Table I shows the types of halophilic microorganisms enriched from the WIPP Site and vicinity to date.

We observed significant microbial gas production by halophilic microorganisms in brine collected from G Seep, a 1-m-deep floor hole in the WIPP underground workings, with glucose as the substrate, but not with cellulose. Furthermore, brine from G Seep inhibited significant gas production by nonhalophilic microorganisms, although a few experiments did show some evidence for microbial activity. These results suggest that microbial gas production may be significant under overtest conditions, but not under realistic conditions. However, we believe that, for the reasons described below, these results do not rule out significant microbial gas production.

First, we compared the recent study at Stanford University and studies carried out during the 1970s [9, 10, 11, 12, 13]. We concluded, as others have before us [1, 12], that the earlier results implied significant microbial gas production under both realistic and overtest conditions.

Second, we observed significant degradation of filter paper at West Chester University by enrichments of halophilic and halotolerant microorganisms from the salt lakes in Nash Draw. Although we could not quantify gas production rates from these experiments, the results suggest that microorganisms could consume paper, the main constituent of the cellulosics in the waste to be emplaced in WIPP disposal rooms.

Third, we 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

Table 1: Halophilic Microorganisms Sampled from the WIPP Site and Vicinity and Enriched, Isolated, and Characterized at West Chester University

Salt Lakes in Nash Draw	Soils Adjacent to the WIPP Site	WIPP Tailings Pile	WIPP Underground Workings
Aerobes Denitrifiers SO_4^{2-} reducers[1] Fermenters Methanogens	None	Aerobes Denitrifiers	Aerobes Denitrifiers Fermenters

[1] SO_4^{2-} reducers are clearly present in sediments from these lakes but are proving difficult to enrich, isolate, and characterize.

a mole of gas per drum of waste per year. Davies [14] 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 activity under realistic conditions, we are evaluating other approaches to measuring gas-production rates which, while low from the standpoint of typical studies of microbial activity, are nevertheless significant for the long-term performance of the repository.

1.3 Radiolysis

Most of the data reviewed by Molecke [12] imply that the radiolytic gas production rate for TRU waste in WIPP disposal rooms will be significantly lower than estimates [1] of the gas production rates from anoxic corrosion or microbial activity. However, inundation of the waste with brine may increase the radiolytic gas production rate. The highest radiolytic gas production rates reviewed by Molecke [12] occurred in process sludges and resulted from the high H_2O contents of these materials. Furthermore, estimates of the microbial gas production potential, and hence the total gas production potential, are very sensitive to whether microorganisms will degrade plastics in the waste. Although plastics are generally considered nonbiodegradable, α radiolysis could increase the bioavailability of these materials [3]. Finally, compaction of previously or newly generated waste prior to emplacement and of emplaced waste during closure of WIPP disposal rooms may increase the radiolytic gas production rate by increasing the density of the waste and the extent to which α particles interact with it.

We are carrying out a laboratory study to measure gas production rates from α radiolysis of WIPP brines at Argonne National Laboratory. Currently, we are conducting 3-month experiments to measure radiolytic gas production rates with dissolved Pu concentrations of $1 \cdot 10^{-4}$, $1 \cdot 10^{-6}$, and $1 \cdot 10^{-8}$ M in Brine A. Eventually, we will determine the effects of compositional variations on the radiolytic gas production rate in runs with a Pu concentration of $1 \cdot 10^{-4}$ M in ERDA-6, a synthetic brine with a composition typical of fluids recovered from the exploratory drill hole ERDA-6, which penetrated a brine reservoir in the underlying Castile Fm., and in brines collected from DH36, a 15-m-deep downhole in the WIPP underground workings, and G Seep.

1.4 Proposed Backfill Additives

Several proposed backfill additives could remove or prevent the production of some of the gases expected in WIPP disposal rooms [3]. $CuSO_4$ would, if brine were present, oxidize Fe and Fe-base alloys without producing H_2. $CaCO_3$, CaO, $Ca(OH)_2$, KOH, and NaOH would remove microbially or radiolytically produced CO_2 with and in some cases without brine present.

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

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

A laboratory and modeling study is under way at Sandia National Laboratories to determine whether the backfill additives $CaCO_3$, CaO, $CuSO_4$, KOH, and NaOH remove CO_2 or prevent the production of H_2 effectively and to quantify their effects on repository chemistry [3].

1.5 Extension of Laboratory Studies to Reprocessed Waste

The WIPP Project is considering engineered alternatives, including reprocessing the waste, to reduce the rate of or potential for gas production [15, 16]. Reprocessing options such as shredding, compacting, or grouting the waste could reduce the gas-production rate, but not necessarily the long-term gas-production potential. Incineration and vitrification would reduce the gas-production potential. Furthermore, reprocessing would reduce the range of Eh and pH expected for the repository. However, reprocessing would also result in near-term health risks for workers involved in waste treatment.

2. BIN-SCALE TESTS OF GAS GENERATION

The WIPP is scheduled to become the first operating nuclear waste repository in the United States. The first CH TRU wastes will be shipped to and emplaced in the WIPP in 1991. These TRU wastes are being used in a series of bin-scale tests that focus on both the measurement and predictive modeling of waste-gas generation. The tests include actual CH TRU wastes, both radioactive and hazardous-mixed wastes. These wastes are representative of the current and planned near-future output of various US Department of Energy (DOE) waste-generating facilities.

The bin-scale tests are being conducted to provide the necessary waste degradation/gas generation data and experience for WIPP safety and performance assessment programs. The tests also initiate limited-scale waste operations at the facility. Results from these tests will be used to help assess and predict WIPP environmental safety for both the long-term (post-repository closure) and near-term (operational phase) time periods. Data will be obtained on relevant gas quantities, compositions, and kinetic rate data on generation and consumption resulting from TRU waste materials degradation mechanisms. The mechanisms are identical to those described in the laboratory results section of this paper. Test interpretations also address any volatile hazardous compounds sorbed on, and potentially released by the wastes.

The bin-scale test program has been installed underground and most test equipment and procedures checked out. Actual gas testing will be initiated when the first TRU wastes are delivered to the WIPP. As such, there are no in situ data to report at this time. Therefore, the remainder of this paper will describe: (1) technical details of the test program, instrumentation, and associated preparation; (2) the types of gases quantified (3) the types and characterizations of the various TRU wastes used; (4) a brief summary of the gas data interpretation and modeling methodology.

2.1 Bin-Scale Gas Test Description

The WIPP bin-scale test includes about 970 drum-volumes of existing and specially prepared CH TRU wastes, both dry and intentionally brine-wetted. Wastes are contained within about 146 transportable, sealed test "bins." Each bin is a specially designed metal test container, about 1 m^3 in volume, and can contain and safely isolate about six drum-volume-equivalents of CH TRU waste. Bins are being prepared and filled at several DOE waste generator sites and shipped to the WIPP.

Individual bins serve as independently isolated and controlled test chambers. Each bin is extensively instrumented to allow for the: (1) preparation of the internal bin atmosphere (gas purging ports and manifolds, tracer gas and brine injection ports); (2) periodic sampling of gases (gas sampling ports, internal circulation manifolds, specific oxygen sensors); (3) monitoring and control of internal gas pressures within a safe operating range (pressure sensors, solenoid-actuated and mechanical pressure-relief valves, gas flow meters, thermocouples, etc.); (4) a computer-controlled and monitored data acquisition system.

All bin-scale testing will be conducted under realistic WIPP (rock salt) repository relevant conditions. Waste degradation and consequent gas production will be affected by, and tested as a function of many variables: synergistic interactions due to multiple degradation modes, e.g., radiolysis, microbial degradation, and anoxic corrosion; multiple TRU waste form types and various levels of waste processing; expected short- and long-term repository ambient gas atmospheres, i.e., aerobic or anaerobic, respectively; different levels of waste-repository moistness, from "dry as-received" to saturated by potentially intruding repository brine; engineered barrier materials in contact with the wastes including metals, WIPP salt, clay backfill, alkaline gas-getter materials, and cementitious grout materials; and, possibly, waste treatment modifications (currently being evaluated and developed) that can reduce the rates or potentials (quantities) of gases to be generated or released.

All further hardware and test-system design details are documented elsewhere [17, 18, 19].

2.2 Bin-Scale Test Gases

Gas samples are obtained periodically from each bin and analyzed for individual gas concentrations, and changes in those concentrations as a function of time, over the planned 5-year duration of this test program. The gases are quantified for purposes of reaction mechanism interpretations and predictions, safety (flammability and other hazards), and regulatory compliance (related to potential repository releases). The gases monitored include: major gases produced or depleted by waste degradation mechanisms, H_2, CO_2, CO, CH_4, O_2, H_2O; minor inorganic gases produced, Ar, N_2, HCl, NO_x, NH_3, H_2S; bin gas tracers, Kr and Xe; and, a list of approximately 30 volatile organic compounds (VOCs), specified by the US Environmental Protection Agency (EPA). The EPA VOC target analytes are regulated hazardous constituents that are suspected of being present in the waste based on process knowledge. All test gases detected at a level of 1 ppmv will be reported, after correction for potential bin leaks or releases and reference-blank gases.

2.3 Bin-Scale TRU Waste Types and Preparation

There are three broad categories of CH TRU wastes used in this test: "high-organics," including combustible wastes (e.g., cellulosics, plastics, and rubbers), organic filter media, organic solids, leader rubber, and cemented organic process solids; "low-organics," including graphite, metal, and glass wastes, plus pyrochemical salt wastes; and, "process sludges," including cemented or solidified inorganic or inorganic solids. These wastes are divided further into a total of about 17 specific classifications. All types and quantities of TRU waste used have been statistically selected and justified, as described elsewhere [19]. All bin tests are conducted in triplicate for each waste classification.

Existing types of wastes, even from within the same classification, are quite nonhomogeneous in nature, usually containing mixtures of many materials. To facilitate mechanistic interpretation of the gases quantified from a bin, the wastes to be loaded into each bin must be precharacterized into component materials, or "controlling variables," described and justified elsewhere [19]. Data from the characterization program also will be used to evaluate the "representativeness" of such test wastes in relationship to other CH TRU wastes in the DOE inventory that may eventually be sent to the WIPP facility for terminal isolation. Previous [12] and ongoing [3] laboratory studies have provided semiquantitative information about which gases or groups of gases are produced from individual "controlling variable" materials. Characterization includes visual and gravimetric evaluations of the individual material contents of all wastes placed into each test bin, coupled with some physical separations and input of process knowledge.

Bin waste characterization and associated preparatory bin-loading work is currently being conducted at several DOE waste generator sites, prior to the shipment to the WIPP for testing. Several bins have been loaded recently and are awaiting authorizations to be transported.

2.4 Gas Data Analysis and Modeling

The gas data from the bin-scale test program must be preliminarily interpreted, evaluated for total test-system uncertainties, and then predictively modeled prior to transfer to the WIPP performance assessment program. Measured rates and concentrations, with the quantitative waste characterization data, will be interpreted in terms of a gas partitioning mechanistic model. This model [19] can evaluate gas production and depletion in terms of specific waste degradation-gas generation mechanisms. This modeling effort also will be used to predict total gas generation potentials, as well as rates, from individual waste forms (classifications) based on the proportion of each waste matrix component "controlling variable" present.

The total gas modeling effort (mechanistic, statistical, and empirical) is intended to provide interpretations and relationships so that such information is indeed representative of and applicable to other CH TRU waste populations not tested. The gas mechanistic interpretations and modeling will incorporate both the statistical relationship of (included) waste distributions (by waste classification), statistical treatment of uncertainties in the accuracy of measured and/or estimated variables, and mathematical interpolations to other (non-included) wastes as a function of the quantified waste matrix "controlling variables." This test data modeling should enable CH TRU waste representativeness for gas production to be extended to, and/or inclusive of other wastes independent of waste generator source, independent of waste classification, independent of waste segregation differences, and, extrapolatable to future, to-be-generated TRU wastes.

Bin-scale gas generation data will be used to predict the expected repository room-scale gas generation behavior for the system-wide inventory of CH TRU wastes within the DOE complex. Bin-scale gas data and interpretations also will be used to validate the assumptions used in modeling and will help eliminate most speculative questions and concerns [19].

2.5 Summary

The data and interpretations concerning the gas behavior of CH TRU wastes gained in both the laboratory and bin-scale tests will be used in evaluating the ability of the WIPP to satisfy both performance assessment technical concerns and DOE and EPA regulatory requirements. These concerns must be satisfied before the WIPP can assume its intended long-term role as a permanent disposal site for defense-generated TRU wastes [19].

3. REFERENCES

1. Lappin, A. R., R. L. Hunter, D. P. Garber, and P. B. Davies: Systems Analysis, Long-Term Radionuclide Transport, and Dose Assessments, Waste Isolation Pilot Plant (WIPP), Southeastern New Mexico; March, 1989, SAND89-0462, Sandia National Laboratories, Albuquerque, NM (1989).

2. D. J. Borns, Sandia National Laboratories, personal communication.

3. Brush, L. H. : Test Plan for Laboratory and Modeling Studies of Repository and Radionuclide Chemistry for the Waste Isolation Pilot Plant, SAND90-0266, Sandia National Laboratories, Albuquerque, NM (1990).

4. Molecke, M. A. : A Comparison of Brines Relevant to Nuclear Waste Experimentation, SAND83-0516, Sandia National Laboratories, Albuquerque, NM (1983).

5. Froelich, P. N., G. P. Klinkhammer, M. L. Bender, N. A. Luedtke, G. R. Heath, D. Cullen, P. Dauphin, D. Hammond, B. Hartman, and V. Maynard: "Early Oxidation of Organic Matter in Pelagic Sediments of the Eastern Equatorial Atlantic: Suboxic Diagenesis," Geochimica et Cosmochimica Acta, 43 (1979), 1075-1090.

6. Berner, R. A. : Early Diagenesis: A Theoretical Approach, Princeton University Press, Princeton, NJ (1980).

7. Owen, W. F., D. C. Stuckey, J. B. Healy, Jr., L. Y. Young, and P. L. McCarty: "Bioassay for Monitoring Biochemical Methane Potential and Anaerobic Toxicity," Water Research, 13 (1979), 485-492.

8. Tong, X., L. H. Smith, and P. L. McCarty: "Methane Fermentation of Lignocellulosic Materials," Biomass, 21 (1989), 239-255.

9. Barnhart, B. J., E. W. Campbell, E. Martinez, D. E. Caldwell, and R. Hallett: Potential Microbial Impact on Transuranic Wastes Under Conditions Expected in the Waste Isolation Pilot Plant (WIPP), Annual Report, October 1, 1978-September 30, 1979, LA-8297-PR, Los Alamos Scientific Laboratory, Los Alamos, NM (1980).

10. Caldwell, D. E. : "Microbial Biogeochemistry of Organic Matrix Transuranic Waste," unpublished report submitted to M. A. Molecke, University of New Mexico, Albuquerque, NM (1981).

11. Caldwell, D. E., R. C. Hallett, M. A. Molecke, E. Martinez, and B. J. Barnhart: Rates of CO2 Production From the Microbial Degradation of Transuranic Wastes under Simulated Geologic Isolation Conditions, SAND87-7170, Sandia National Laboratories, Albuquerque, NM (1988).

12. Molecke, M. A. : Gas Generation from Transuranic Waste Degradation: Data Summary and Interpretation, SAND79-1245, Sandia National Laboratories, Albuquerque, NM (1979).

13. Sandia National Laboratories: Summary of Research and Development Activities in Support of Waste Acceptance Criteria for the WIPP, SAND79-1305, Sandia National Laboratories, Albuquerque, NM (1979).

14. Davies, P. B. : "Results from Recent Variable-Rate Gas Simulations that Examine the Impact of Vapor-Limited ("Humid") Gas-Generation Rates," unpublished memorandum to L. H. Brush and A. R. Lappin, Sandia National Laboratories, Albuquerque, NM (1990).

15. Engineered Alternatives Task Force: Recommended Initial Waste Forms for the WIPP Experimental Test Program, DOE/WIPP 90-009, US Department of Energy, Waste Isolation Pilot Plant, Carlsbad, NM (1990).

16. Engineered Alternatives Task Force: Evaluation of the Effectiveness and Feasibility of the Waste Isolation Pilot Plant Engineered Alternatives: Final Report of the Engineered Alternatives Task Force, Vol. I and II, DOE/WIPP 91-007, US Department of Energy Waste Isolation Pilot Plant, Carlsbad, NM (1991).

17. Molecke, M. A. : Test Plan: WIPP Bin-Scale CH TRU Waste Tests, SAND90-1974, Sandia National Laboratories, Albuquerque, NM (1990).

18. Molecke, M. A., and A. R. Lappin: Test Plan Addendum #1: Waste Isolation Pilot Plant Bin-Scale CH TRU Waste Tests, SAND90-2082, Sandia National Laboratories, Albuquerque, NM (1990).

19. Lappin, A. R., C. A. Gotway, M. A. Molecke, and R. L. Hunter: Rationale for Revised Bin-Scale Gas-Generation Tests with CH TRU Wastes, SAND90-2481, Sandia National Laboratories, Albuquerque, NM (1991).