RADIOLYTICALLY-INDUCED GAS PRODUCTION IN PLUTONIUM-SPIKED WIPP BRINE

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ABSTRACT

Gas generation due to alpha particle deposition was investigated in four WIPP relevant brines; WIPP brine A, ERDA-6, DH-36 and G8-B. This was done by spiking each brine with plutonium-239 and periodically sampling the gas phase to determine the nature of the gaseous products and the rates of gas generation. The predominant gas generated radiolytically was hydrogen, with yields ranging from 0.6 to 1.5 molec/100 eV for the four brines tested. Plutonium (VI) was stable in two synthetic brines, WIPP brine A and ERDA-6 but was rapidly reduced in the underground collected brines DH-36 and G8-B, although most of the plutonium remained in solution.

INTRODUCTION AND BACKGROUND

Gas production in Waste Isolation Pilot Plant (WIPP) waste was identified by the WIPP project as a potentially important issue for final disposal[1-3] of transuranic (TRU) waste. The three major potential sources of gas generation identified by the WIPP project are anoxic corrosion, microbial degradation, and radiolysis. Of these three, it has been hypothesized by the WIPP project that radiolysis will be the least significant. The work reported herein was performed, in part, to test and confirm this hypothesis.

The source of ionizing radiation in the WIPP is the radioactive decay of the actinides present in the TRU waste (<100 nCi/g transuranic). A potential scenario being addressed by the WIPP project in its performance assessment is that gas will be produced due to the dissolution or mobilization of these transuranics into WIPP brine should the brine come in contact with the waste. The resultant deposition of alpha particles in the brine will break down water to generate primarily molecular hydrogen that will add directly to the repository gas "budget".

The experiments presented in this paper were designed to investigate 1) the effect of total plutonium concentration and 2) brine variability on gas generation. Plutonium-239, which is the most important transuranic isotope in WIPP waste, was added to the brine as plutonium(VI) in such a way as to minimize perturbation of the particular brine. Gas generation and oxidation state stability were determined for each of the four brines investigated.

EXPERIMENTAL

Two sets of experiments were performed using Plutonium-239 as the source of ionizing radiation. The first set was a variable-concentration study performed in WIPP brine A. The matrix for this experiment set is given in Table I.

Table I. Summary of Irradiation Conditions for the Gas Generation Experiments in WIPP Brine A

Experiment Designation	Duration (days)	[Pu-239][1],M		Energy Deposition Rate (MeV/d)	Absorbed Dose (rad)	Hydrogen Yield (molec/ 100eV)
		Initial	Final			
GG-B1-41	155	$3.4\pm0.2\times10^{-4}$	$\geq10^{-6}$	4.2×10^{13}	1.7×10^{5}	>0.8
GG-B1-42	155	$2.8\pm0.1\times10^{-4}$	$2.7\pm0.1\times10^{-4}$	3.4×10^{13}	1.4×10^{5}	1.1±0.1
GG-B1-61	162	$6.3\pm1\times10^{-7}$	$7.9\pm1\times10^{-7}$	1.7×10^{11}	373	1.3±0.1
GG-B1-62	162	$5.4\pm1\times10^{-7}$	$7.1\pm1\times10^{-7}$	7.4×10^{10}	524	1.4±0.1
GG-B1-81	162	$6.7\pm0.7\times10^{-9}$	$6.7\pm0.7\times10^{-9}$	1.6×10^{9}	3.4	ND
GG-B1-82	162	$7.1\pm0.7\times10^{-9}$	$7.5\pm0.7\times10^{-9}$	8.6×10^{8}	3.9	ND

[1]Data based on alpha-scintillation counting.
ND-not determined because H_2 yield was lower than background generation of Hydrogen.

The second set was a brine-variable study that was performed in the other three brines: ERDA-6, G8-B and DH-36. The matrix for this experiment set is given in Table II.

Table II. Matrix, Plutonium Concentrations and Gas Generation Yields for the Brine-Variable Studies

Experiment	WIPP Brine	Pu Concentration (M)[1]		Hydrogen Yield (molec/100eV)	
		Before	After	Initial	Range[2]
GG-B2-41	G8-B	9.9×10^{-5}	6.4×10^{-5}	1.3	
GG-B2-42[2]	G8-B	1.4×10^{-4}	7.0×10^{-5}	1.5	0.7-1.5
GG-B3-41	DH-36	1.1×10^{-4}	4.4×10^{-5}	1.3	
GG-B3-42[2]	DH-36	1.4×10^{-4}	5.7×10^{-5}	1.5	0.8-1.5
GG-B4-41	ERDA-6	1.1×10^{-4}	8.6×10^{-5}	0.9	
GG-B4-42[2]	ERDA-6	1.9×10^{-4}	1.1×10^{-4}	0.6	0.2-0.7

[1]Based on alpha scintillation counting (±20%).
[2]Experiments with a pressure gauge assembly.

Plutonium-239, typically in 50 mg quantities, was oxidized to the VI state by taking to near-dryness in perchloric acid. Plutonium (VI) was dissolved in triply distilled water and analyzed for oxidation-state purity using absorption spectrometry. The pH of this solution was subsequently adjusted to a near-neutral pH, to approximate the pH of the brine, by adding sodium hydroxide solution.

The plutonium-spiked brine was prepared by series dilution of the plutonium stock solution with the brine of interest to the number of moles needed to achieve the desired concentration of plutonium. The vessels utilized were 0.5 L and 1.0 L pyrex flasks that were fitted with a Kovar glass-to-metal joint and were embedded in epoxy for additional strength. The total volume of the Pu-spiked brine after the final dilution was either 0.5 or 1.0 L. Once prepared, all solutions were allowed to sit for a period of three days to equilibrate, then were sampled for alpha scintillation counting. For the higher concentration solutions (10^{-4} M), 3 mL of sample was placed in a 1x1 cm gas-tight cuvette for spectrometric analysis. These samples were kept at room temperature and periodically analyzed during the course of the experiment to track changes in the speciation of the plutonium in solution.

After the solutions were sampled, the vessels were sealed and placed in an incubator kept at 31 + 2°C. Both of the 10^{-4} M WIPP brine A solutions, and one each of the other three brines were fitted with a Validyne type AP-10 pressure transducer to continuously monitor the total pressure of the system. The lower concentration WIPP brine A experiments (i.e. nominal plutonium concentration of 10^{-6} M and 10^{-8} M) and one each of the experiments in the brine variable studies, were not fitted with pressure gauges. In the low concentration studies, this was done because the predicted pressure buildup was low relative to the vapor pressure of the brines. Here, the solutions were only slightly de-aerated (total pressure to $\leq$100 torr) to preserve the carbonate/bicarbonate content of the brine.

The gas phase in all experiments, was periodically sampled to determine the concentration of hydrogen, oxygen, carbon dioxide and nitrogen. The gas samples were analyzed using Varian type 3300 and type 3400 gas chromatographs. After completion of the experiment, an aliquot was taken from each vessel to determine the total solution concentration of plutonium by alpha scintillation counting. In the high-concentration samples, 3 mL of each solution was re-analyzed spectrometrically to establish or confirm the trends observed in the parallel stability studies. All spectrometric determinations were performed using a Hitachi model 340 spectrometer and were digitally recorded and analyzed.

GAS GENERATION DUE TO INTERACTION OF ALPHA PARTICLES WITH WIPP BRINE

Concentration-Variable Studies

The concentration-variable studies were performed using WIPP brine A at nominal plutonium concentrations of 10^{-4}, 10^{-6} and 10^{-8} M. These were performed to evaluate the effect of absorbed dose and dose rate on gas generation. The yield of radiolytically generated gases for these experiments are summarized in Table I.

The gas phase in the experiments containing 10^{-4} M plutonium (GG-B1-41,42) consisted of an increasing percentage of hydrogen with a significant but small amount of residual oxygen and nitrogen. No carbon dioxide was observed in the gas phase. This was due to the extensive de-aeration that was done prior to experiment start-up coupled with a loss in sensitivity for carbon dioxide because of the small free volume (6 and 8 cc) present above the plutonium solutions in these samples. Oxygen depletion, rather than formation, was observed in these experiments.

In the lower-concentration experiments, the gas phase consisted of air with a small amount of hydrogen and carbon dioxide. The carbon dioxide partial pressure was constant for all four samples at 12 $\pm$ 1 torr and was generated due to equilibration between the carbonate in solution and the gas phase present. At these dose rates, the nitrogen-oxygen mixture did not change significantly due to radiolytic processes. Hydrogen was the only gas generated that was clearly radiolytic in origin.

The rate of gas generation in the vessel, once outgassing stopped, was linear with time for both experiments GG-B1-41 and GG-B1-42. Pressure buildup, as a function of time, is shown in Figure 1 for experiment GG-B1-41. The net gas buildup in these experiments, the sum of hydrogen formation and oxygen depletion and amount of free volume available, was 1.6 and 1.3 torr/day, respectively. This corresponded to a gas generation yield of, G (net), 0.73 and 0.97 molec/100 eV, respectively.

The yield of hydrogen was also determined by calculating the moles of hydrogen generated as a function of irradiation time for all the experiments performed. Analysis

of the data, from this perspective, gave a gas generation yield of 0.8 and 1.1 for experiments GG-B1-41 and GG-B1-42, respectively.

For the 10^{-6}M experiments, the formation of hydrogen was the only criterion on which to evaluate radiolytic gas generation. The yields calculated were 1.4 and 1.3 molec/100 eV, respectively, for experiments GG-B1-61 and GG-B1-62. Correcting these data for hydrogen generated by other processes (subtracting hydrogen noted in the 10^{-8}M experiments) does not have a significant effect on the hydrogen yield obtained.

The hydrogen yield in the GG-B1-81 and GG-B1-82 experiments, could not be determined under the conditions of the experiments. The amount of hydrogen observed was only a factor of two above the detection limit of our gas phase analyses. This could not be clearly attributed to radiolytic processes since small amounts of hydrogen were generated due to corrosion of the Kovar joint.

Brine-Variable Studies

The experimental matrix, plutonium concentrations, and measured yields for gas generation in the brine-variable experiments are given in Table II. The objective of these experiments was to determine the effect, if any, of brine composition on the hydrogen gas-generation rate. The three brines used in this part of the study were ERDA-6 (without carbonate), DH-36 and G8-B (see ref. 1 for compositions). All these experiments were performed at a nominal plutonium concentration of 10^{-4} M and were compared directly to the high concentration set of experiments performed in WIPP brine A.

The six brine-variable experiments were extensively de-aerated prior to initiation. As a result of radiolysis, the only significant component of the gas phase was hydrogen although small amounts of air were always present. No carbon dioxide was observed. The absence of carbon dioxide was expected since the two brines, DH-36 and G8-B used did not have significant levels of carbonate present in solution (i.e. the carbon dioxide content had not been carefully preserved in solutions received from the WIPP) and a carbonate-free formulation was used for ERDA-6. Residual carbonate, i.e. that absorbed during sample preparation, was likely removed during the de-aeration process. There was no oxygen formation evident in these experiments.

The rate of pressure buildup in these experiments, for the given activity and solution/gas volume ratio, ranged between 1 and 2 torr/d. The initial hydrogen yields measured were 0.6, 1.5, and 1.5 molec/100 eV, respectively, for ERDA-6, DH-36, and G8-B. The observed initial yields were taken to be the most meaningful and were given in Table II. It cannot be concluded from these few experiments that the changes observed were due to the radiation chemistry of the brine system. Calibrations of the transducer performed before and after termination of the experiments were in agreement.

In the parallel experiments performed without a pressure transducer, hydrogen was also the predominant component of the gas phase. The yields determined for G8-B and DH-36 were comparable to that determined from the slopes of the pressure buildup and that measured for WIPP brine A. The hydrogen yield for plutonium-spiked ERDA-6 groundwater, however, was almost a factor of two lower.

DISCUSSION

The WIPP brines investigated in this study are all high ionic strength solutions (I > 10 M). The high concentration of ions in these systems are expected to perturb the

radiation chemistry and hence the yield of molecular hydrogen. This perturbation is complex and not easily delineated based on existing data.

The ~ 5.1 MeV Plutonium-239 alpha particle, used as the source of ionizing radiation in brine irradiation studies, is categorized as high LET (linear energy transfer) radiation. The track average LET of a 5 MeV alpha particle is approximately 40 keV/μm compared to 0.2 keV/μm typical of gamma and beta particles of comparable energy. Ionizing radiation at this energy and LET is deposited almost exclusively in short tracks that have a high concentration of the transient ion-pairs[4,5] that react to generate molecular products such as hydrogen. For this reason, significantly high concentrations of ionic scavengers are needed to perturb the yield of molecular products in these high LET systems.

In the four WIPP brines investigated, the most important anion is chloride which is approximately 5 M in each of the four brines. The relative concentration of the three major cations in these brines (sodium, magnesium and potassium with a lesser amount of calcium), however, varies from brine to brine. The relative concentrations are:

Na^+ - ERDA-6 $\geq$ G8-B $\geq$ DH-36 >> Brine A
K^+ - Brine A > DH-36 = G8-B > ERDA-6
Mg^{2+} - Brine A > DH-36 = G8-B >> ERDA-6

It can be seen that the brines irradiated range from a high-magnesium brine, Brine A, which is low in sodium, to a low magnesium high sodium brine, ERDA-6. Both underground-collected brines lie between the two synthetic brines although they more closely resemble Brine A.

The key reaction leading to the formation of molecular hydrogen, in dilute systems, is the recombination of the solvated electron:

$$e_{aq} + e_{aq} \xrightarrow{H_2O} H_2 + 2\ OH^- \qquad k = 5.5 \times 109\ M^{-1}\ s^{-1} \qquad (1)$$

This identifies the cationic species in WIPP brine as the most important relative to potential changes in molecular hydrogen formation. The mechanism for this is the modification of reaction (1) by either direct competition, i.e. reaction, with the solvated electron or changes in the solvation sphere of the ions. In this context, significant change in the hydrogen yield is an indication that some of the solvated electrons and perhaps the precursor of the solvated electron are being re-directed along other reaction pathways.

Although our data pertains to complex brine systems, which are in general difficult to interpret, there are some general observations that were apparent. First, the yields of hydrogen in WIPP brines are lower, or comparable to, those obtained in pure water systems, $G(H_2)$ = 1.6 molec/100 eV. The results in WIPP brine A, G8-B and DH-36 are within experimental uncertainty of the yield obtained in pure water systems. This indicates that high concentrations of primarily sodium has little effect on net hydrogen production.

The hydrogen yield determined for plutonium-spiked ERDA-6 was a factor of almost two lower than that observed in the other brines. A conclusive reason for this cannot be provided based on the few experiments that were performed. However, it may be important to note that ERDA-6 brine has the lowest concentration of potassium and, by far, the lowest concentration of magnesium. Magnesium is likely the most important of these two cations. That the absence of magnesium is in fact

causing the observed reduction in hydrogen formation, however, needs further experimental corroboration.

We did not expect a dose-rate effect in the range of concentrations that were utilized in the first experimental matrix. True dose-rate effects, i.e., those caused by overlapping alpha particle tracks, do not appear until dose rates are orders of magnitude greater than those used. The data generated in the concentration-dependent studies are consistent with this interpretation although the 10^{-8} M data need to be redone to more convincingly confirm this result. The best explanation for the nonlinearities noted in the pressure-buildup data is that the effective dose rate to solution was being reduced due to precipitation of the plutonium in solution. Plutonium (VI), based on the spectroscopy performed, was not stable in either Dh-36 or G8-B brines and as much as 50% of the plutonium in solution was removed during the course of the experiments. This could account for the lowering of the yield values.

An important difference in the results we reported and that reported for higher LET systems[6,7] is that we did not observe oxygen formation. In fact, some oxygen depletion was noted in the high-concentration brine A experiments. This absence of oxygen production is not surprising in our experiments since they were done at low concentrations and corresponded to lower absorbed doses. Although it is somewhat controversial, there has been no clear evidence that oxygen is formed as a primary product in high LET aqueous systems (i.e. $g(O_2) = 0$). Molecular oxygen, when observed, is formed in secondary processes due to the direct decomposition of an oxygen-containing aqueous intermediate. This leads to an induction period for the appearance of oxygen that depends on the dose rate and chemistry of the solvent of interest. In water, the oxygen-containing intermediate is hydrogen peroxide. In WIPP brines, this is expected to be oxygen chlorides,[8,9] although we did not specifically address this issue in our work.

CONCLUSIONS AND IMPLICATION OF RESULTS FOR THE WIPP

The contribution of radiolytic gas generation to the overall gas generation budget in the WIPP has already been estimated in previous reports.[2,3,10] The rate of gas generation and the relative concentration of hydrogen and oxygen generated are needed to provide site-relevant estimates of the radiolytic contribution to gas generation. Yield values, i.e., gas generation rates in terms of alpha energy deposition, are also needed to model the effect of waste form variability on the rate of gas generation observed.

"Best value" yields for the various brine systems investigated are tabulated in Table III:

Table III. "Best Value" Yields in WIPP Brines

WIPP BRINE	HYDROGEN YIELD ($G(H_2)$) MOLEC/100 eV
Brine A	1.4 ± 0.1
ERDA-6	0.9 ± 0.2
DH-36	1.3 ± 0.1
G8-B (GSEEP)	1.3 ± 0.1

The most important result obtained is that the yields measured in WIPP brine establish that the high ionic strength medium of WIPP brine does not cause a large change in the yield of hydrogen due to alpha radiolysis. Although yields actually measured vary by as much as a factor of 2, this is small relative to the uncertainty in defining the solubility of the various actinides in the brine of interest. As gas generation is expected to be proportional to solution activity, the range of values in solubility considered by the WIPP gas generation rates observed are most important in determining the amount of radiolytically-induced gas generation.

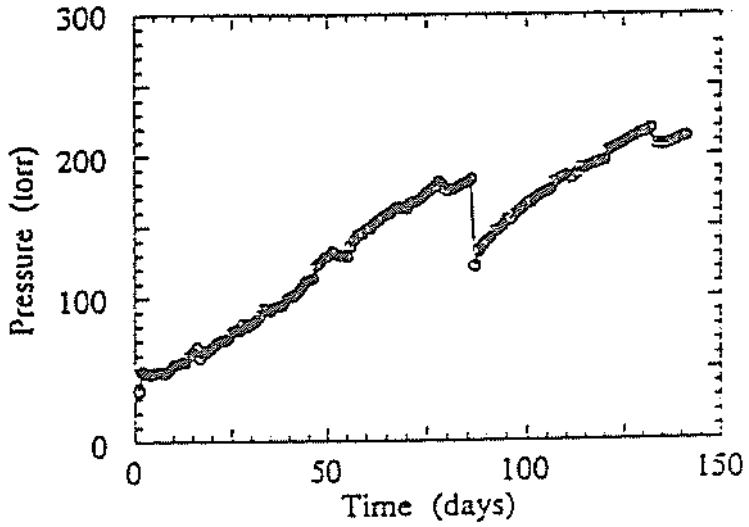

Figure 1. Pressure buildup as a function of time for Plutonium-spiked WIPP BRINE

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