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RADIOLYSIS OF LIQUID WASTE DURING BEDROCK STORAGE

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RADIOLYSIS OF LIQUID WASTE DURING BEDROCK STORAGE

by

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ABSTRACT

A proposed method for long-term containment of radioactive wastes produced at the Savannah River Plant is storage in vaults excavated in crystalline rock 1500 ft beneath the surface of the plant. Radiolysis of the waste to form gases will occur during storage of the waste. This report summarizes tests with synthetic wastes to develop design data on the radiolytic gas evolution rates. These tests showed that a vapor volume of ∿15% of the total sealed volume would be sufficient to keep the pressure in the storage vault below the surrounding 1500-ft hydrostatic pressure. These tests also provide part of the basic data necessary to predict the behavior of the gases and the liquid waste over the ∿1000 years of storage necessary for the decay of ^{90}Sr and ^{137}Cs to innocuous levels.

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INTRODUCTION

All high level radioactive wastes from separations processes at the Savannah River Plant are stored as liquids or slurries in double-walled concrete and steel tanks buried just beneath the surface of the ground. The rate of radioactive decay is such that this waste must be contained for at least several hundred years. Alternative concepts for long-term storage of this waste requiring a minimum of surveillance are being investigated.

One concept for long-term waste containment is storage in vaults excavated in crystalline bedrock ∿1500 feet beneath the surface of the plant. Under the proposed design, the waste would be transferred from the waste tanks to the bedrock caverns, and the caverns would be sealed off after a period of monitoring. As the principal radioactive constituents (^{90}Sr and ^{137}Cs) decay, the resulting radiation will decompose a portion of the waste to form gases. As the gas accumulates, the pressure in the gas space will increase. This gas pressure will oppose the surrounding hydrostatic pressure (∿1500 ft of water) on the vault with the result that the net pressure driving force acting to transport water into the cavern will be reduced.

This report summarizes radiolysis studies with synthetic waste solutions and a ^{60}Co radiation source. These data provide a basis for determining the void volume necessary to maintain the gas pressure less than the 1500-ft hydrostatic pressure. These tests also provide part of the basic data necessary to evaluate the behavior of the system over the hundreds of years of storage necessary for the ^{90}Sr and ^{137}Cs to decay to innocuous levels. The consequences of having a void volume less than that required to maintain the gas pressure below the surrounding hydrostatic pressure are being analyzed as part of the safety analysis of the bedrock storage proposal.

In addition to studies of the radiolysis of synthetic liquid waste, the relative effects of the various waste salts in forming gases were determined. The effects of various modifications of the waste were also studied.

SUMMARY

Radiolysis tests were completed with synthetic waste to develop data necessary for the design and analysis for the proposed waste storage vault, which would be excavated 500 ft deep in crystalline bedrock, 1500 ft below ground.[1] The tests showed that a vapor volume of ∿15% of the total sealed volume is sufficient to keep the pressure in the storage vault less than the surrounding (1500 ft) hydrostatic pressure. The gas produced by the radiolytic decomposition of liquid waste was approximately 80% oxygen, 18% hydrogen, and 2% oxides of nitrogen.

The main source of gas was radiolytic decomposition of the $NaNO_3$ in the waste. Approximately 90% of the oxygen is produced by direct action of the radiation and radiolytically produced electrons and H atoms on the NO_3^-. The remainder of the oxygen and the hydrogen are a result of radiolysis of the water. The nitrate and other ions in the waste are indirectly responsible for the gases produced by water radiolysis, by removing species that normally remove these gases as rapidly as they are formed in pure water.

Gas yields were also determined for synthetic waste solutions that were modified to simulate changes that might be made purposly before final disposal (adding organic solvents, mixing with bentonite) or that might be a result of the interaction of the waste with the bedrock environment (reaction with bedrock or cement grout, dilution by water). These modifications either had no effect or decreased the net rate of gas production.

DISCUSSION

BEDROCK STORAGE OF WASTE

In the bedrock storage concept currently being considered, a total storage volume of ∿100 million gallons is to be excavated 500 ft deep in crystalline bedrock, 1500 ft below the ground. The waste will be cooled for several years before final storage to allow the short-lived isotopes to decay; therefore, ^{137}Cs and ^{90}Sr will be the primary sources of radiation. The stored waste will consist of an alkaline liquid phase containing ^{137}Cs and a sludge layer containing ^{90}Sr. As a result of the reaction of the waste with the walls of the cavern, the ^{90}Sr may migrate to the liquid phase. The design basis for the wastes is shown in Table I.

The composition of synthetic liquid waste used in this study was 4M $NaNO_3$, 2M $NaNO_2$, 0.5M Na_2CO_3, 0.3M Na_2SO_4, 0.6M $NaAlO_2$, and 1M NaOH. ($NaNO_2$ is produced by radiolysis of $NaNO_3$ in the cooling period preceding bedrock storage.) The sludge was 50 wt % $Fe(OH)_3$ and 50 wt % MnO_2 in contact with supernatant liquid. These compositions represent the maximum salt concentrations expected for high level wastes from separations processes at Savannah River.

TABLE I

Wastes to be Stored in the Proposed Bedrock Storage Facility

Total Volume of Wastes	80,000,000 gallons
Volume of Settled Sludges	5,000,000 gallons
Specific Gravity of Supernate	1.2 - 1.4
Specific Gravity of Sludge	1.5 - 1.8
Upper boundary for Inventory	
Strontium-90 ($t_{1/2}$ = 28 years)	200,000,000 curies
Cesium-137 ($t_{1/2}$ = 30 years)	200,000,000 curies
Plutonium-239 ($t_{1/2}$ = 24,400 years)	17,000 curies

RADIOLYSIS OF SIMULATED WASTE SOLUTIONS

Experimental

Sealed capsules containing waste solutions were irradiated with a ^{60}Co source (Figure 1). The capsules were immersed in water at a constant temperature of ~50°C. Pressure was recorded throughout the exposure. At the end of a test, the apparatus was cooled to room temperature, and the gas was sampled. Total radiolysis gas was calculated from the volume in the apparatus and the final pressure. Absorbed dose rates were calculated from the intensity of radiation, which is a function of location in the ^{60}Co source. Dose rates up to 1.8×10^7 rads/hr were attained; absorbed doses equivalent to ~1000 years of storage could be obtained in ~50 hours.

As γ radiation from the ^{60}Co source is absorbed in the waste, it produces electrons (β rays) with an energy of about one Mev by Compton scattering.[2,3] This radiation is equivalent to the principal radiation present in the waste (Appendix A). Although the dose rate used in these studies is ~10^4 greater than in the waste, it is still well below the level (10^{11} rads/hr) at which the number of "spurs" is so great that they begin to interact to cause dose rate effects in aqueous solutions.[2]

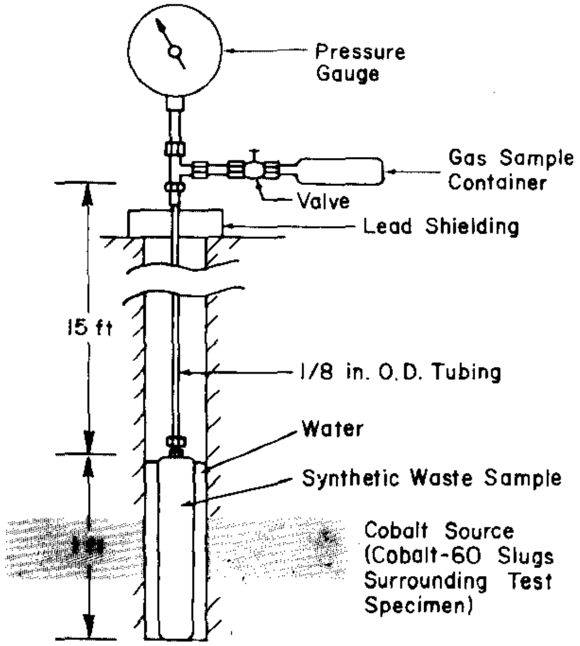

FIG. 1 RADIOLYSIS APPARATUS

Radiolysis Results

The volume of radiolytic gas was the same for sludge and liquid, although the gas composition was different; therefore, the phase that contains the radionuclides is not important in determining total volumes of gas produced. Gas from the sludge was 90% O_2, 8% H_2, and 2% N_2 and its oxides; gas from the liquid was 80% O_2, 18% H_2, and 2% N_2 and its oxides. If all of the ^{90}Sr were to remain in the sludge, the gas would have an overall composition of 85% O_2, 13% H_2, and 2% N_2 and its oxides. In either case the H_2 concentration in the off-gas will be above the lower flammability limit (4%). The sludge was not included in the liquid in subsequent tests.

The gas yields were independent of dose rate and temperature (Table II). When waste solutions were neutralized with nitric acid before exposure, the gas yield was the same as for the alkaline solutions.

TABLE II

Initial Rate of Radiolysis of Synthetic Liquid Waste

Dose Rate, 10^6 rads/hr		Initial Gas Yield, molecule/100 eV
1.75		0.34
7.20		0.46
13.8		0.31
18.0		0.35
	Avg	0.37 ±0.12[a]
Temp, °C		
40		0.36
110		0.30
120		0.33

---

[a] 2σ limits

The pressure developed in the enclosed system is:

$$P = \frac{D}{V_w} \frac{V_w}{V_g} NRT$$

where

P = pressure, atm
D = total dose, eV
V_w = volume of waste, cm^3
V_g = volume of gas, cm^3
N = radiolytic gas yield, moles/eV
R = ideal gas constant
T = temperature, °K

From the total dose per unit volume (D/V_w) and the waste composition, the final pressure·for the actual waste can be determined for various waste/gas volume ratios V_w/V_g, assuming that the average radiolytic gas yield, N, is independent of dose rate. The total specific dose expected in the storage vault is ∿6.1 x 10^{22} eV/cm^3, based on 200 million curies each of ^{137}Cs and ^{90}Sr in 80 million gallons.

Radiolysis of synthetic liquid waste to an absorbed dose as great as that expected in the storage vault shows that a vapor volume equal to ∿15% of the total storage volume is sufficient to keep the pressure in the storage vault below the surrounding 1500 ft (∿650 psi) hydrostatic pressure (Figure 2). This analysis assumes a idealized leak-tight vault. The decrease in the rate

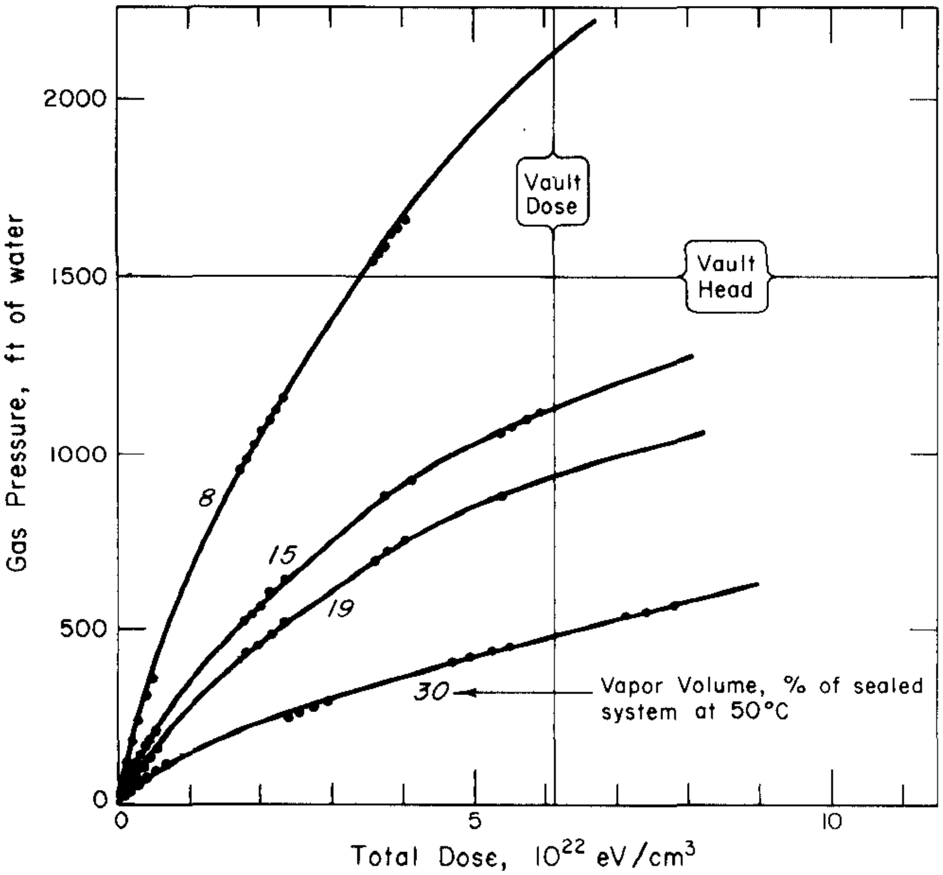

FIG. 2 PRESSURE OF RADIOLYSIS GAS IN BEDROCK STORAGE VAULT (T=50°C) AS A FUNCTION OF TOTAL DOSE

of gas production as the dose increases is due mainly to the conversion of nitrate to nitrite. After the ^{90}Sr and ^{137}Cs have decayed to innocuous levels (∿1000 years) approximately 0.6 mole/liter of nitrate will have been converted. Because the rate of gas formation will be a function of the radiation intensity and the nitrate concentration, over half of the radiolytic gas will be formed in the first 30 years of storage (approximately one half-life of the ^{90}Sr and ^{137}Cs), and most of the gas will be formed in ∿100 years (Figure 3). Total gas evolution is expected to be between 5 to 9 ft^3 (STP) per ft^3 of stored waste.

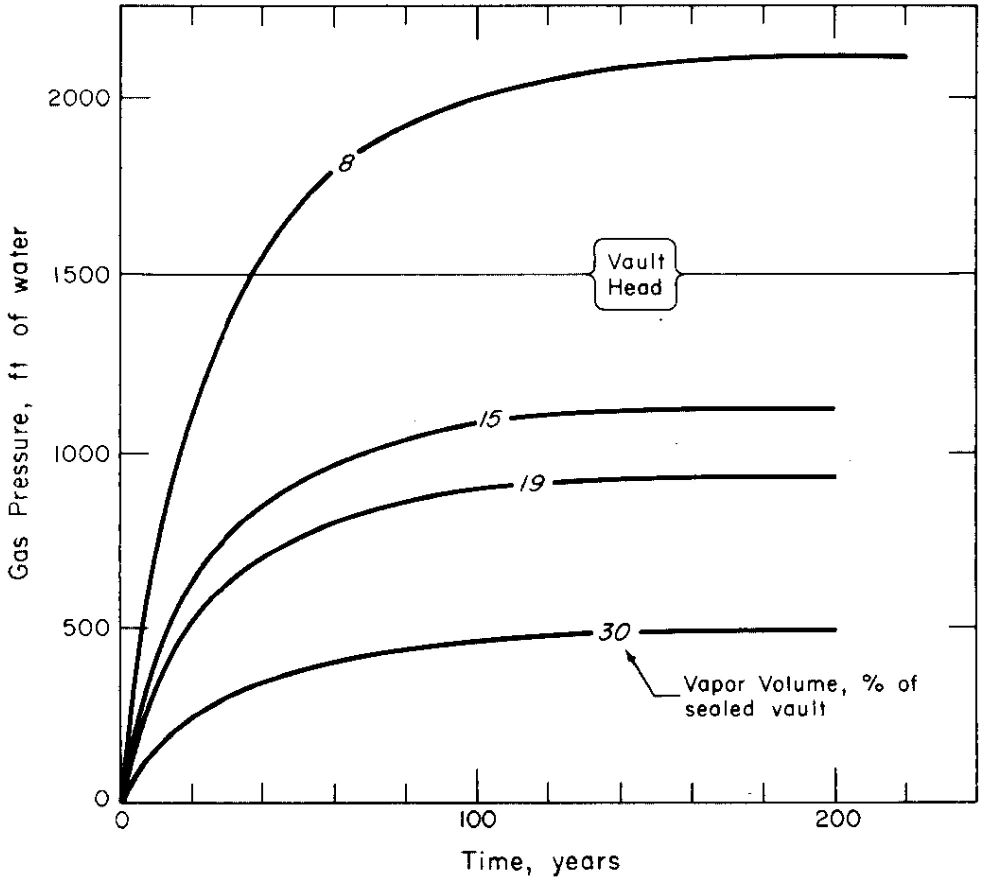

FIG. 3 PRESSURE OF RADIOLYSIS GAS IN BEDROCK STORAGE VAULT (T=50°C) AS A FUNCTION OF TIME

Recombination Reactions

Tests were made to determine whether recombination reactions might occur during the period of storage that would decrease the pressure below that measured in the radiolysis experiments. In the presence of radiation, H_2 and O_2 in the gas phase recombine slowly to form water. Since the radiation field in the gas phase was essentially the same as that expected for bedrock storage (Appendix B), the amount of recombination during the ^{60}Co tests was approximately the same as would be expected during bedrock storage.

In order to estimate the maximum rate of H_2 and O_2 recombination, ^{60}Co irradiations were carried out with stoichiometric mixtures of H_2 and O_2 at the same radiation intensity to which the liquid had been exposed. The absorbed dose rate for these studies was $\sim 10^5$ rads/hr (1% of that for the liquid). Irradiations were carried out at pressures between 100 and 200 psig. Reaction rate was followed by the rate of pressure decrease. For these tests the rate of pressure decrease was ~ 0.2 psig/hr. The yield of water produced by radiolytic recombination was ~ 3 molecules/100 eV. The yield was not significantly affected by addition of CO_2 or pressure change.

The yield of H_2 during bedrock storage is expected to be ~ 0.08 molecules/100 eV. If it is assumed that H_2 is recombined with O_2 with the same yield as measured in the stoichiometric mixture (3 molecules/100 eV) and the absorbed dose in the gas phase varies from 0.05 to 0.5% of that in the liquid (Appendix B) it is estimated that approximately 3% of the H_2 would be removed from the gas phase by recombination with oxygen. This represents less than 1% of the total amount of gas present including O_2 and N_2.

Tests were also made to determine whether thermal recombination of oxygen and nitrite might take place in the liquid phase. Irradiated waste solutions were removed from the cobalt source and heated to ∿280°C for eight days. No recombination was detected. Based on these studies it is concluded that no gas phase or liquid phase recombination reactions will remove significant amounts of the radiolytic gases.

RADIOLYSIS STUDIES WITH SALTS

Individual salts and combinations of salts were studied to determine the relative contribution of each salt in the radiolytic gas production process.

Radiolysis of Single Salts

Single salts were irradiated in solutions at concentrations up to the maximum expected in the waste. Gas evolution is represented by the following gas production and gas removal reactions.[4-6]

Gas Production

Radiolysis of H_2O:

$$H_2O \rightsquigarrow H,\ OH,\ e^-_{aq},\ H_2O_2,\ H_2 \tag{1}$$

$$H + H \rightarrow H_2 \tag{2}$$

$$e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2\ OH^- \tag{3}$$

$$OH + OH \rightarrow H_2O_2 \tag{4}$$

$$H + O_2 \rightarrow HO_2 \tag{5}$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{6}$$

$$H_2O_2 \rightarrow H_2O + 1/2\ O_2 \tag{7}$$

$$H^+ + e^-_{aq} \rightarrow H \tag{8}$$

Radiolysis of salt:

$$NO_3^- \rightsquigarrow NO_2^- + 1/2\ O_2 \tag{9}$$

Gas Removal

Ionic and free radical reactions that remove H_2 and O_2 or their precursors:

$$NO_2^- + 1/2\ O_2 \rightsquigarrow NO_3^- \tag{10}$$

$$OH + H_2 \rightarrow H_2O + H \tag{11}$$

$$H + O_2 \rightarrow HO_2 \tag{12}$$

$$H + H_2O_2 \rightarrow OH + H_2O \tag{13}$$

As shown in Figure 4, salts can increase greatly the final steady-state pressure by direct radiolysis (Reaction 9) or by removal of the H and OH radicals which remove gas (Reactions 11-13). For concentrated salt solutions, gas production predominates initially. However, as the H_2 and O_2 concentrations increase, the rates of the gas removal reactions increase until they equal the rate of gas production, and pressure is at steady state. The composition of the gases produced are given in Table III.

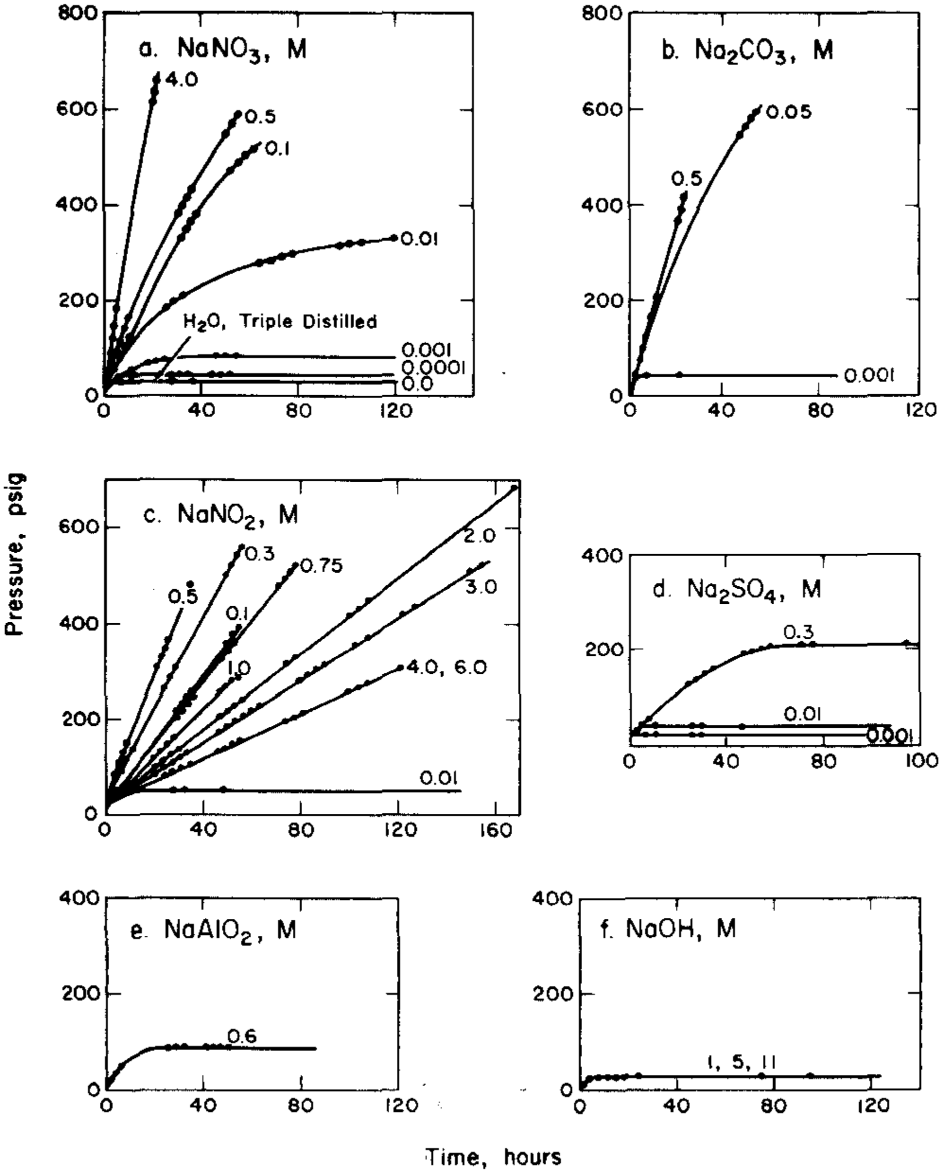

FIG. 4 EFFECT OF SALTS ON RADIOLYSIS GAS PRESSURE
Vapor Volume, 8%;
Dose Rate, $\sim$1.1 x 10^7 rads/hr; T, 50°C

TABLE III

Composition of Radiolysis Gas

Salt	Concentration, moles/liter	Gas Composition, %		
		O_2	H_2	N_2 and Its Oxides
$NaNO_3$	10^{-4}	29	71	-
	10^{-3}	33	67	-
	10^{-2}	31	69	-
	0.1	29	70	1
	0.5	43	56	1
	4	80	18	2
Na_2CO_3	0.05	32	68	-
	0.5	20	80	-
$NaNO_2$	0.01	3	97	-
	0.1	13	87	-
	0.5	91	9	-
	1	21	78	1
	2	18	80	2
	3	12	85	3
Na_2SO_4	10^{-3}	78	22	-
	10^{-2}	51	49	-
	0.5	35	65	-
$NaAlO_2$	0.6	36	64	-
NaOH	1	-	100	-

Both mechanisms for gas production by $NaNO_3$ (the principal source of gas in plant waste) are shown in Figure 4a. At about 0.1M $NaNO_3$, salt interferes with the normal gas removal reactions and greatly increases steady-state pressures. From solutions up to 0.1M $NaNO_3$, gases were ∿29% O_2, 70% H_2, and 1% N_2 and its oxides (Table III). A concentration of 0.1M was too low to yield any significant quantity of gas by Reaction 9. However, at ∿0.5M $NaNO_3$, the production of O_2 by Reaction 9 becomes quite significant, and the absolute rate of gas production increases. Gas from this solution was higher in O_2. These results are in agreement with previous studies.[5,6]

Na_2CO_3 solutions (Figure 4b) up to 0.5M interfere strongly with the gas-removal reactions. $NaNO_2$ solutions (Figure 4c) up to 0.5M interfere with the gas-removal reactions, the oxygen yield increasing rapidly (Table III). At higher concentrations, however, the pressures decrease as the nitrite removes O_2 by Reaction 10. The rate of gas production in >0.01M $NaNO_2$ solutions did not decrease at higher pressures, indicating that for presures up to $\sim$600 psi recombination reaction rates were not a function of the concentration of H_2 and O_2 in the liquid phase.

Na_2SO_4 and $NaAlO_2$ do not interfere significantly with gas-removal reactions at the concentrations in the waste (Figures 4d and 4e). NaOH solutions up to 1M yielded steady-state pressures that were not significantly greater than that for triple distilled water (Figure 4f).

Other Waste Salt Combinations

Radiolytic gas production was also studied with various synthetic combinations of waste salts. Figure 5 shows that the conversion of nitrate to nitrite in the waste decreases the radiolysis rate. If all of the nitrate were converted to nitrite, the total quantity of radiolysis gas would be decreased by a factor of $\sim$3. The gas would be mostly H_2. An increase in $NaNO_2$ concentration from 2 to 4M at $NaNO_3$ concentration of 4M inhibits radiolysis by a smaller amount.

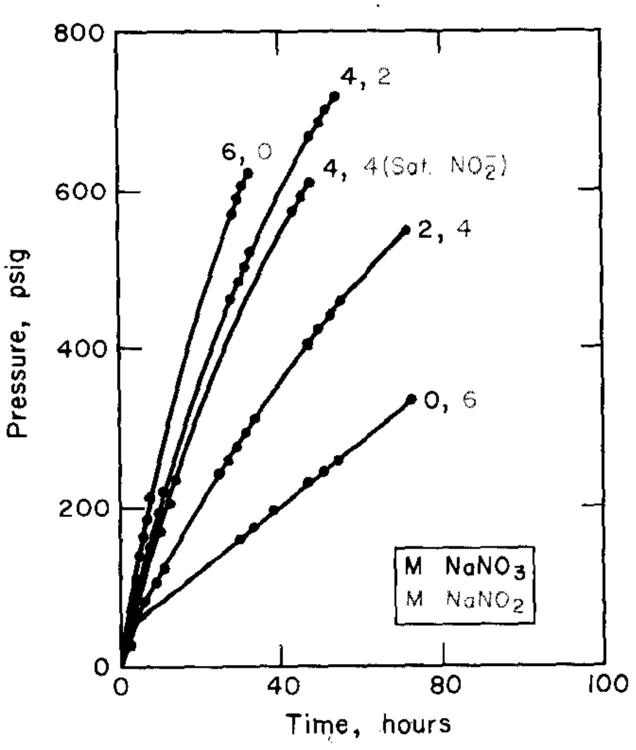

FIG. 5 NITRITE-NITRATE EFFECTS ON WASTE RADIOLYSIS
Vapor Volume, 8%;
Dose Rate, $\sim$1.1 x 10^7 rads/hr; T, 50°C

Initial yields are reported in Table IV for various combinations of salts at the same concentration as in synthetic waste. These data indicate that the presence of 2M $NaNO_2$ in the waste retards the radiolytic gas production.

TABLE IV

Initial Yield of Radiolytic Gas for Combinations of Salts

Solution Irradiated	Yield, molecule/100 eV
Waste	0.37
0.5M Na_2CO_3	0.50
4M $NaNO_3$	0.65
4M $NaNO_3$. 1M NaOH, 0.5M Na_2CO_3	0.82
4M $NaNO_3$, 1M NaOH	0.85
4M $NaNO_3$, 1M NaOH, 2M $NaNO_2$	0.44

RADIOLYSIS OF MODIFIED WASTE

Differences in the radiolytic gas yield were determined for waste which was modified to simulate changes which might be made purposely before bedrock storage or which might be a result of the interaction of the waste with the bedrock environment. The following modifications were studied:

- Addition of organic matter
- Addition of TBP and dodecane from solvent extraction processing
- Mixing with bentonite
- Reaction with bedrock
- Reaction with cement
- Dilution with water

Organic Additives

Several organic additives were tested for possible reduction of pressure by formation of soluble peroxy free radicals:[7]

$$R + O_2 \rightarrow RO_2 \tag{14}$$

n-propanol and n-butanol decreased the radiolytic gas pressure but only with acid-neutralized waste (Table V). The gas from these tests contained low oxygen and significant CO_2, which is produced by radiolysis of the organic additive. In certain cases (ethanol and benzene), the increased gas yield due to radiolysis of the organic was greater than the reduction in O_2 yield, resulting in higher overall gas yields.

TABLE V

Gas Yields for Waste Irradiated with Organic Additives

	Additive Concentration, vol %	Initial Yield. molecule/100 eV
Waste (basic or acid-neutralized)		0.37
Acid-neutralized waste, plus		
n-propanol	0.17	0.34
	1.33	0.14
	4.0	0.22
n-butanol	1.33	0.14
Ethanol	1.33	0.40
	8	0.68
Benzene	9	0.76
Sodium benzoate	4	0.42

The presence of tributylphosphate in neutralized waste was found to be more effective in reducing the gas yield as described in the following section.

Organic Additions from Solvent Extraction Processing

The main organic component expected in the waste is a 50-50 mixture of tributylphosphate (TBP) and dodecane which is added from solvent extraction processing. These organic compounds may be approximately 1% by volume in the waste initially. Intense radiolysis by short-lived isotopes in the cooling period before bedrock storage is expected to convert the TBP to dibutylphosphate (DBP) and other products which are comparatively radiation-resistant. In order to determine the potential effect of these organic components, wastes to which TBP and dodecane had been added were irradiated. At the 1% level and above, the organic compounds tend to reduce the total rate of gas radiolysis (Figure 6). It is estimated that the TBP was converted to DBP within approximately the first two hours of irradiation; however, the organic components continue to depress the gas evolution rate throughout the irradiation period (∿60 hr). It appears that the TBP and resulting DBP or other organic products (e.g. butanol) are mainly responsible for the decrease, by the removal of oxygen to form peroxides as in Equation 14. This mechanism is consistent with the lower oxygen content of the radiolysis gases produced (Figure 6). These data indicate that the organic compounds expected in the waste will not increase the gas pressure; however, no credit can be taken for gas reduction due to the presence of the organic phosphates since it is not known whether the organic phosphates or the resulting organic peroxides and other products would be thermally stable over the ∿1000 years of storage.

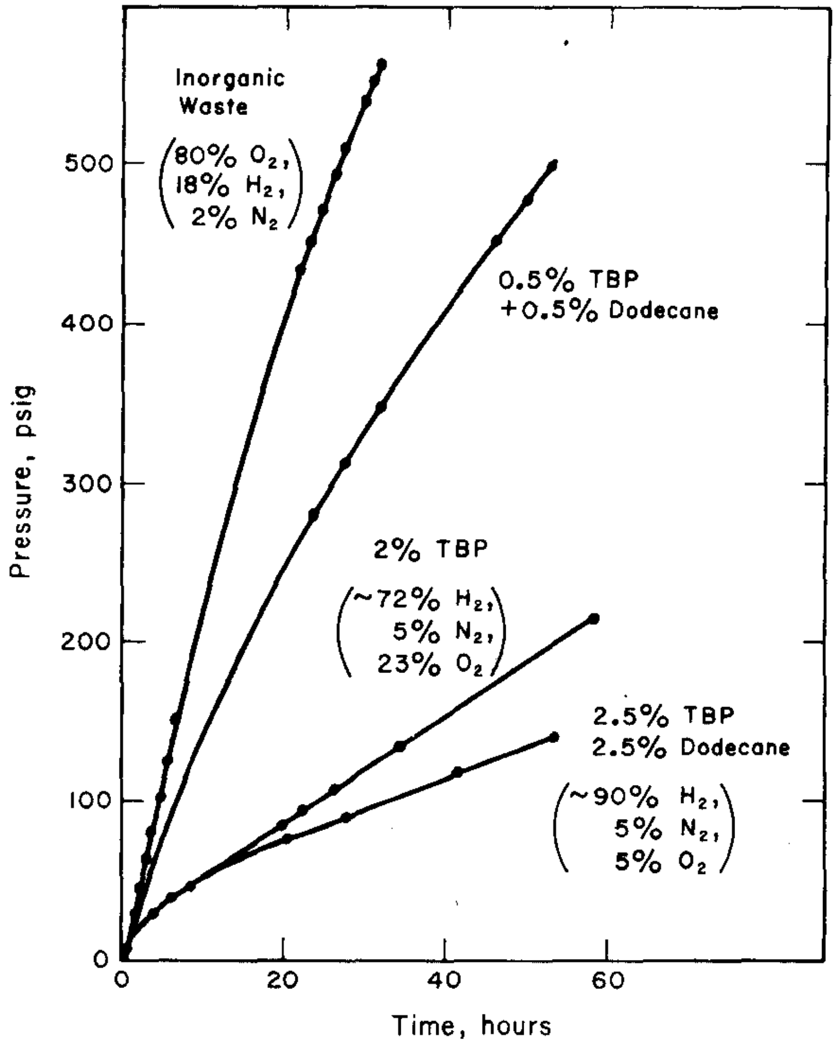

FIG. 6 RADIOLYSIS OF WASTE CONTAINING TBP AND DODECANE
Vapor Volume, 8%;
Dose Rate, 1.2 x 10^7 rads/hr; T, 50°C

Mixing with Bentonite

A quantity of bentonite* clay equal in weight to the liquid waste was found to be sufficient to give a damp immobile mix with no separate liquid phase. Radiolytic gas production from the mix was approximately 85% of that from liquid waste alone, due to a reduction in the amount of H_2 produced. The gas produced was 95% O_2, 3% H_2, and 2% N_2. Immobilization of the waste reduces the generation of H_2 from water radiolysis by retarding the free radical recombination reactions which produce the H_2.

---

* A sodium bentonite clay which swells as it absorbs liquid.

Reaction with Bedrock

The waste will react chemically with the rock resulting in a slow neutralization of the excess alkalinity in the waste. A piece of rock exposed to waste at 100°C for 35 days was attacked to an extent of ∿3 mm. A radiolysis test was made to determine what effect this reaction might have on the radiolytic gas yields. A 195-g sample of finely ground bedrock was added to 500 cm^3 of waste, and the mixture was heated at 100°C for 30 days. The mixture was then exposed to ^{60}Co irradiation. The radiolytic gas yield was approximately the same as for unreacted waste. At the end of the test the waste solution was titrated with HNO_3 (using phenolphthalein indicator) as a convenient measure of chemical change, and 1.83 moles of acid per liter were required. Blank waste solution required 2.36 moles acid per liter for neutralization.

Reaction with Cement

Cement grout will probably be used to seal the storage tunnels to control water in-leakage. In a preliminary test cylindrical samples of Portland cement grout were exposed to waste at 100°C for 42 days. The samples were attacked to an extent of ∿2 mm. For the radiolysis test, 103 g of finely ground cement grout and seven cylinders weighing a total of 103 g were added to 500 cm^3 of waste. The mixture was first heated at 100°C for 37 days and then irradiated. The radiolytic gas yield was approximately 80% of that from unreacted waste. The gas evolved was 76% O_2, 23% H_2, and 1% nitrogen and its oxides. After the test, the solution required 2.07 moles acid per liter for neutralization (vs 2.36 for a blank).

Dilution by Water In-leakage

After the waste has been added to the bedrock storage vault, there is a potential for dilution by water leaking into the vault. As waste is reduced in concentration by dilution with water, the yield of radiolysis gases is reduced (Figure 7). However, even at a level of 1% waste in triple distilled water, the concentration level of the salts is still high enough to cause significant interference with the gas removal reactions, resulting in high pressures. It is expected that the volume increase of the waste due to water in-leakage will be less than 10%. Under these conditions there would not be a significant reduction in the gas yield.

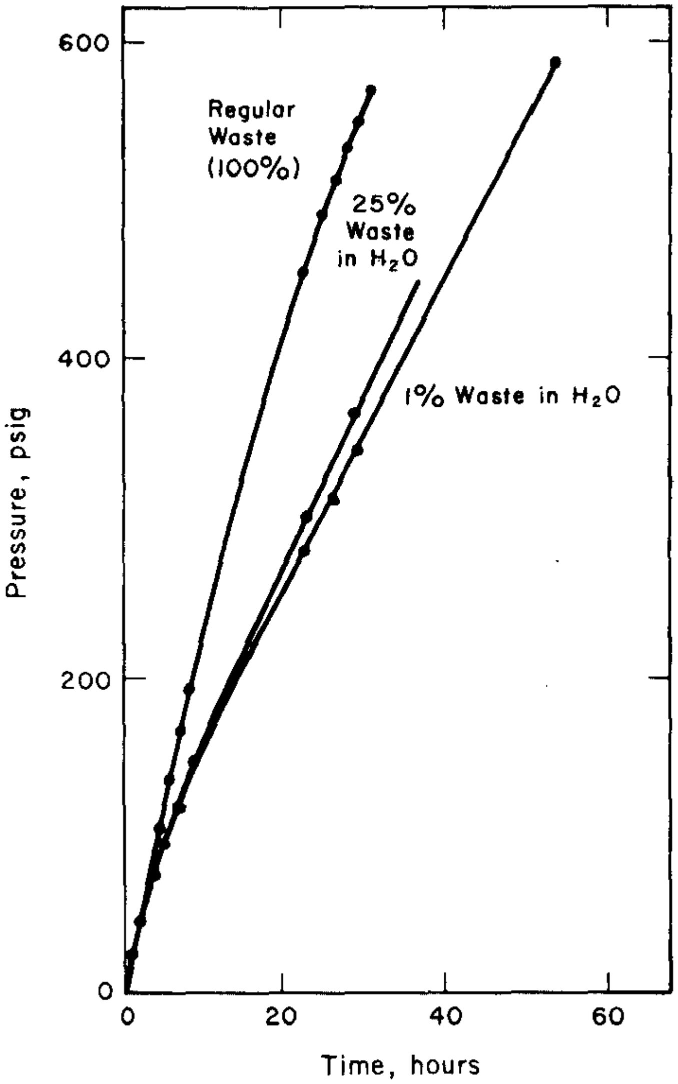

FIG. 7 RADIOLYSIS OF DILUTED WASTE
Vapor Volume, 8%;
Dose Rate, 1.2×10^7 rads/hr; T, 50°C

APPENDIX A

LIQUID PHASE RADIATION FIELD

Table A-I lists the source and energy of the radiation present in the waste. Data on the relative ranges of this radiation are also given.

TABLE A-I

Nuclear Decay Energies

Isotope	Type of Radiation	E_{max}, Mev	E_{avg},[8] Mev	Energy per Disintegration, Mev	Maximum Range[2] Water, cm	Air, m
^{90}Sr	β	0.536	0.197	0.182	0.18	1.85
^{90}Y	β	2.26	0.936	0.930	1.1	10.2
^{137}Cs	β	0.510	0.172	0.149	0.17[a]	1.7
^{137}Cs	β	1.17	0.41	0.027	0.5[a]	5.0[a]
^{137}Cs	γ	0.66	0.66	0.618	8.1[b]	80[b]

---

a. Estimate.
b. Half thickness values.

Since the depth of liquid in the caverns is expected to be 20 to 30 feet, ~98% of this radiation would be absorbed in the waste. The γ radiation from the ^{137}Cs interacts with the waste by Compton scattering to produce β radiation of approximately the same energy as that produced by the β emitters. The fast electrons (β rays) are capable of altering thousands of molecules; therefore, the chemical change in the first molecule struck by a photon is negligible in comparison with the effects produced by the fast electrons. Low energy electrons are produced along the paths of the fast electrons. The low energy electrons expend their energy over only a few molecular diameters, producing the chemically reactive ionic and free radical species. These species are therefore distributed as "spurs" or "clusters" along the paths of the fast electrons.

Irradiation of synthetic waste by γ radiation from the ^{60}Co source produces electrons of approximately the same energy as that in the waste (one Mev) by Compton scattering. The radiation field in the synthetic waste is therefore equivalent to that in the actual waste.

APPENDIX B

GAS PHASE RADIATION FIELD

Based on the data in Table A-I and the expected dimensions of the bedrock storage caverns, it is estimated that ∿0.05% of the β radiation and ∿1% of the γ radiation would escape from the liquid into the gas phase. Most of the β radiation which escaped into the gas would be absorbed, but only ∿1/4 of the γ radiation would be absorbed even after the gas phase reaches several hundred psig. The radiation intensity in the gas phase would be due mainly to the more penetrating ^{137}Cs γ rays and would be <10% of the intensity in the liquid.

The absorbed dose rate of the gas phase is estimated to be ∿0.05% of that of the liquid phase initially, and would increase to a maximum of ∿0.5% at the maximum gas pressure of 650 psig.

The nature of the radiation field in the gas would be similar to that in the liquid with the exception that the distance between "spurs" would be greater due to the lower density of the gas phase. It is estimated that during the ^{60}Co irradiation of synthetic waste ∿2% of the β radiation (produced by Compton scattering) and ∿20% of the γ radiation were scattered into the gas phase. During these tests there was an additional source of radiation due to direct radiation from the ^{60}Co source. Direct radiation intensity from the ^{60}Co source in the gas phase was ∿20% of that in the liquid. Table B-I compares the ^{60}Co and the ^{137}Cs γ radiation. The linear energy transfer (LET) for the ^{137}Cs γ is in the same range as that for the ^{60}Co γ rays. Both photons produce β rays of approximately the same energy by Compton scattering in the gas phase.

TABLE B-I

Comparison of ^{60}Co and ^{137}Cs γ Rays[2]

Isotope	Photon Energy, Mev	Half Thickness in Air, m	LET in Air, keV/mm
^{137}Cs	0.66	80	0.4
^{60}Co	1.25	110	0.3

Based on the radiation flux in the gas phase and the dimensions of the container, the absorbed dose rate of the gas phase relative to the liquid phase is estimated to increase from ∿0.05% initially to ∿1% at 650 psig for the ^{60}Co irradiations. This is approximately the same relative fraction as is expected for the bedrock system.

REFERENCES

1. K. J. Schneider. "Solidification and Disposal of High-Level Radioactive Wastes in the United States." *Reactor Technology 13*(4), 398 (1970).

2. J. W. T. Spinks and R. J. Woods. *An Introduction to Radiation Chemistry.* p 63,247, John Wiley & Sons, New York (1964).

3. F. M. Empson, Editor. *Status Report on Waste Disposal in Natural Salt Formations: III.* USAEC Report ORNL-3053, Oak Ridge National Laboratory, Oak Ridge, Tenn. (1961).

4. M. Anbar in *Fundamental Processes in Radiation Chemistry.* p 651, John Wiley & Sons, New York (1958).

5. M. L. Hyder. "The Radiolysis of Aqueous Nitrate Solutions." *J. Phys. Chem. 69*, 1858 (1965).

6. H. A. Mahlman. "The 'Direct Effect' on the Radiolysis of Aqueous Sodium Nitrate Solutions." *J. Phys. Chem. 67*, 1466 (1963).

7. V. I. Duzhenkov and P. I. Dolin in *Radiation Chemistry of Aqueous Solutions.* p 87, Consultants Bureau, Inc., New York (1959).

8. M. S. S. Murthy. "Shape and Average Energy of Beta Particle Spectra." *Int. J. Appl. Rad. & Isotopes 22*, 111 (1971).