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RADIOLYTIC GAS GENERATION IN CRYSTALLINE SILICOTITANATE SLURRIES

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RADIOLYTIC GAS GENERATION IN CRYSTALLINE SILICOTITANATE SLURRIES

By D. D. WALKER

SUMMARY

This study measured the impact of crystalline silicotitanate (CST) solids on the rate of formation and composition of radiolytically generated gases in simulated Savannah River Site liquid waste. The tests used IONSIV™ IE-911 (UOP LLC, Molecular Sieves Division, Des Plaines, IL), the engineered form of CST. The test results show the following.

- Radiolytically generated gas bubbles form rapidly at expected process dose rates.
 - Bubbles formed within 8 hours at a dose rate of 1 Mrad/h.
 - Bubbles can move by displacing IONSIV™ IE-911 particles if close to the surface.
 - In a 6 cm column, the bed expanded ~20% due to trapped bubbles, before steady state release of bubbles occurred.
- Alkaline waste solutions extracted a component of the IONSIV™ IE-911 and subsequently deposited the component as a finely divided solid.
- Irradiation of IONSIV™ IE-911 slurries produces hydrogen, oxygen, and nitrous oxide (N₂O).
 - Oxygen is the major product from irradiation of high nitrate waste; hydrogen is the major product from irradiation of high hydroxide waste.
 - IONSIV™ IE-911 does not effect hydrogen production from high nitrate waste, but doubled hydrogen production from high hydroxide waste.
 - N₂O is a minor product (<4 vol % of gases produced).
- Researchers measured total radiolytic gas generation rates lower than those used in a preliminary gas generation calculation for a full-scale process column.¹
 - High nitrate waste solutions yield the largest gas generation rates.
 - The previous calculation¹ for total gas generation remains bounding because test results showed less oxygen formation (G values up to 0.15 molecules/100 eV) than assumed in the calculation (0.3 molecules/100 eV).

INTRODUCTION

A non-elutable ion exchange process is one of the alternatives for removing cesium from Savannah River Site (SRS) soluble radioactive waste.² Crystalline silicotitanate particles in the engineered form (IONSIV™ IE-911) are the reference ion exchange medium for the process. An IONSIV™ IE-911 ion exchange column sorbs Cs-137 and, when fully

loaded, contains ~500 Ci/L.¹ The Cs-137 produces a dose rate approaching 1 Mrad/h which generates hydrogen, oxygen, and possibly other gases from the waste stream. The effect of the gas on column performance is a significant concern for the ion exchange process alternative. This study examined the rate and composition of the gases produced when simulated waste was irradiated in the presence of IONSIV™ IE-911. A previous study examined hydrogen gas generation in the presence of IONSIV™ IE-911.³ The earlier test results indicated IONSIV™ IE-911 did not enhance production of hydrogen gas compared to expected gas generation from the liquid phase. Energy deposited in the IONSIV™ IE-911 did not transfer to the liquid phase in a manner producing hydrogen gas when tested in water, sodium hydroxide, or simulated SRS average waste. The author initiated additional tests to quantify generation rates of gases other than hydrogen and from waste simulants other than the average composition.

This work partially fulfills a request from J. R. Fowler, Technical Task Request, "Ion Exchange Column Tests to Reflect Effects of Radioactive Waste, 9.1 Gas Generation Tests," #HLW-SDT-TTR-99-09.1, January 21, 1999. The work complies with the following test plan: D. D. Walker, "Task Technical and Quality Assurance Plan for Non-Elutable Ion Exchange Process Gas Generation Tests," WSRC-RP-99-00189, Rev.0, February 26, 1999.

TEST DESCRIPTION AND RESULTS

Researchers conducted two types of experiments. In the first, researchers photographically recorded the growth of gas bubbles in irradiated IONSIV™ IE-911 slurries. In the second, researchers measured the formation rate and composition of the gas bubbles. Table I lists the composition of the salt solutions used in the experiments. Appendix A provides further details of the experimental methods.

Gas Bubble Formation

Researchers placed slurries of IONSIV™ IE-911 in 0.1 M NaOH solution or in high nitrate simulated waste (composition shown in Table I) into 1.5-cm diameter quartz cylinders and irradiated them at 1.01 Mrad/h for seven days. Figure 1 shows the growth of gas bubbles. The scale shown behind the cylinders is marked in centimeters and provides an estimate of the volume changes in the slurry.

Researchers observed gas bubbles when examining the cylinders eight hours after starting the irradiation. After 24 hours, discrete gas bubbles from 1 mm to 1 cm in diameter appeared in the upper half of the packed bed. In the lower half of the packed bed, the gas displaced the liquid phase without moving the IONSIV™ IE-911 particles. The different behavior between the upper and lower portions of the bed likely results from pressure differences from the mass of overlying particles. The packed bed of IONSIV™ IE-911 and the total liquid level increased by 15 to 20% during irradiation, indicating the amount

TABLE I. Composition of Simulated Waste Solutions

<u>Component</u>	<u>Concentration (molar)</u>	
	<u>High OH⁻</u>	<u>High NO₃⁻</u>
Na ⁺	5.6	5.6
K ⁺	0.030	0.0041
Cs ⁺	0.00037	0.00014
OH ⁻	3.05	1.17
NO ₃ ⁻	1.10	2.84
NO ₂ ⁻	0.74	0.37
AlO ₂ ⁻	0.27	0.32
CO ₃ ²⁻	0.17	0.16
SO ₄ ²⁻	0.030	0.22
Cl ⁻	0.010	0.040
F ⁻	0.010	0.050
PO ₄ ³⁻	0.008	0.010
C ₂ O ₄ ²⁻	0.008	0.008
SiO ₃ ²⁻	0.004	0.004
MoO ₄ ²⁻	0.0002	0.0002
Density (g/mL)	1.236±0.017	1.250±0.016

of gas trapped in the bed. Neither sample increased significantly in volume after the first day, although the 0.1 M NaOH slurry decreased in volume. The changing shape and distribution of the bubbles on subsequent days indicate that gas formation did not cease, but rather, bubbles of gas escaped the packed bed and rose to the surface. Researchers noted that tapping the sides of the apparatus dislodged additional bubbles.

During the irradiation test, the simulated waste solution above the packed bed became yellowish, cloudy, and deposited a white solid on the walls of the quartz apparatus. The following control tests in the quartz apparatus failed to produce the white solids on the upper walls:

- simulated waste solution held at 37 °C (no solids present),
- simulated waste solution irradiated at 37 °C (no solids present), and
- IONSIV™ IE-911 in simulated waste solution at 37 °C.

Using energy-dispersive x-ray spectroscopy (EDXS), researchers determined that the deposits contained primarily a proprietary component of the IONSIV™ IE-911. Similar solids formed during pretreatment of the IONSIV™ IE-911 in the radioactive waste column test.⁴ Researchers postulate that the solids form by extraction of the proprietary component under high pH conditions followed by precipitation as a different compound. Gas bubbles formed during radiolysis stirred the packed bed and dispersed the precipitated solids in the waste solution above the bed. The third control test failed to produce the solids on the upper surface because of the absence of a transport mechanism.

FIGURE 1. Gas Bubble Formation During Irradiation

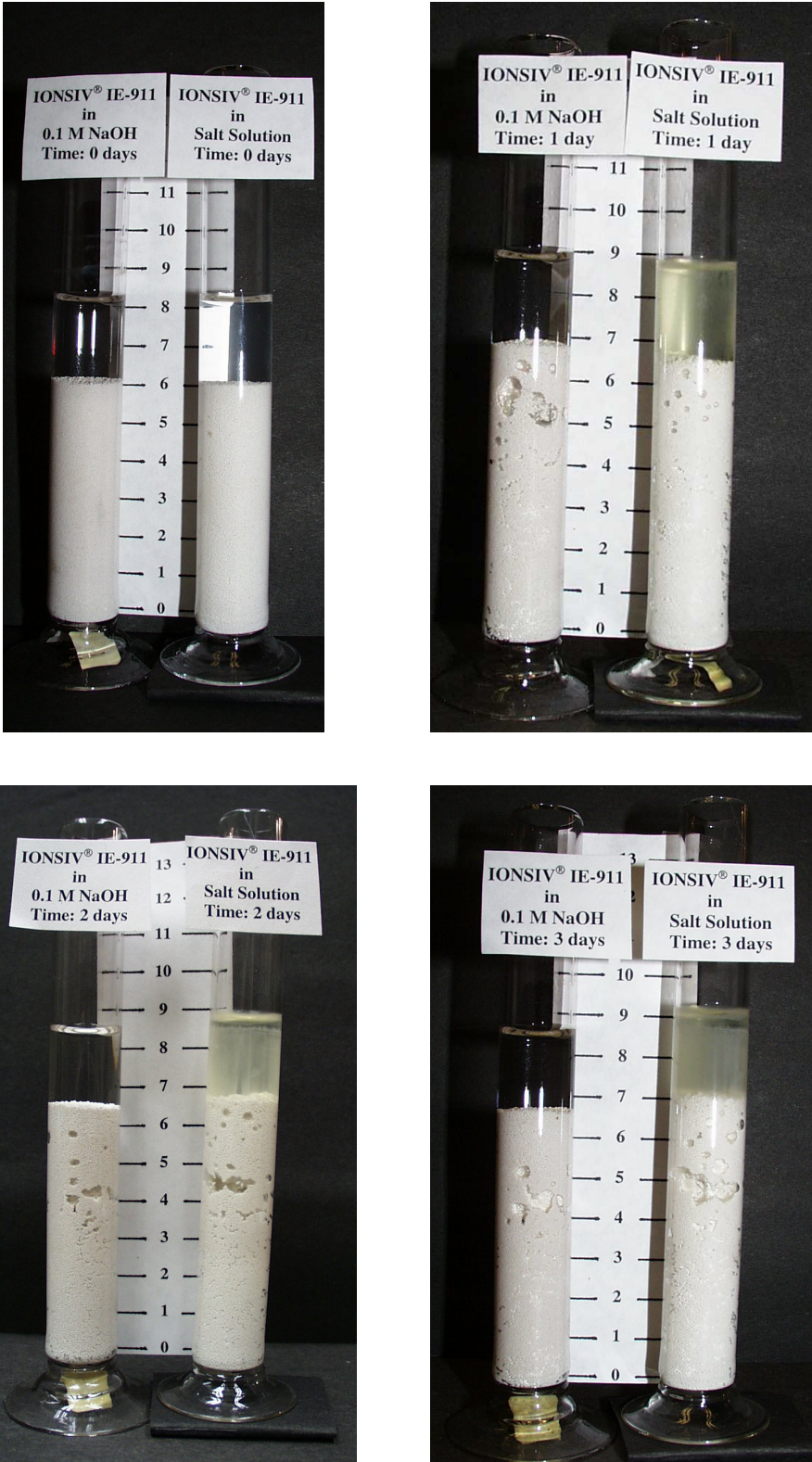
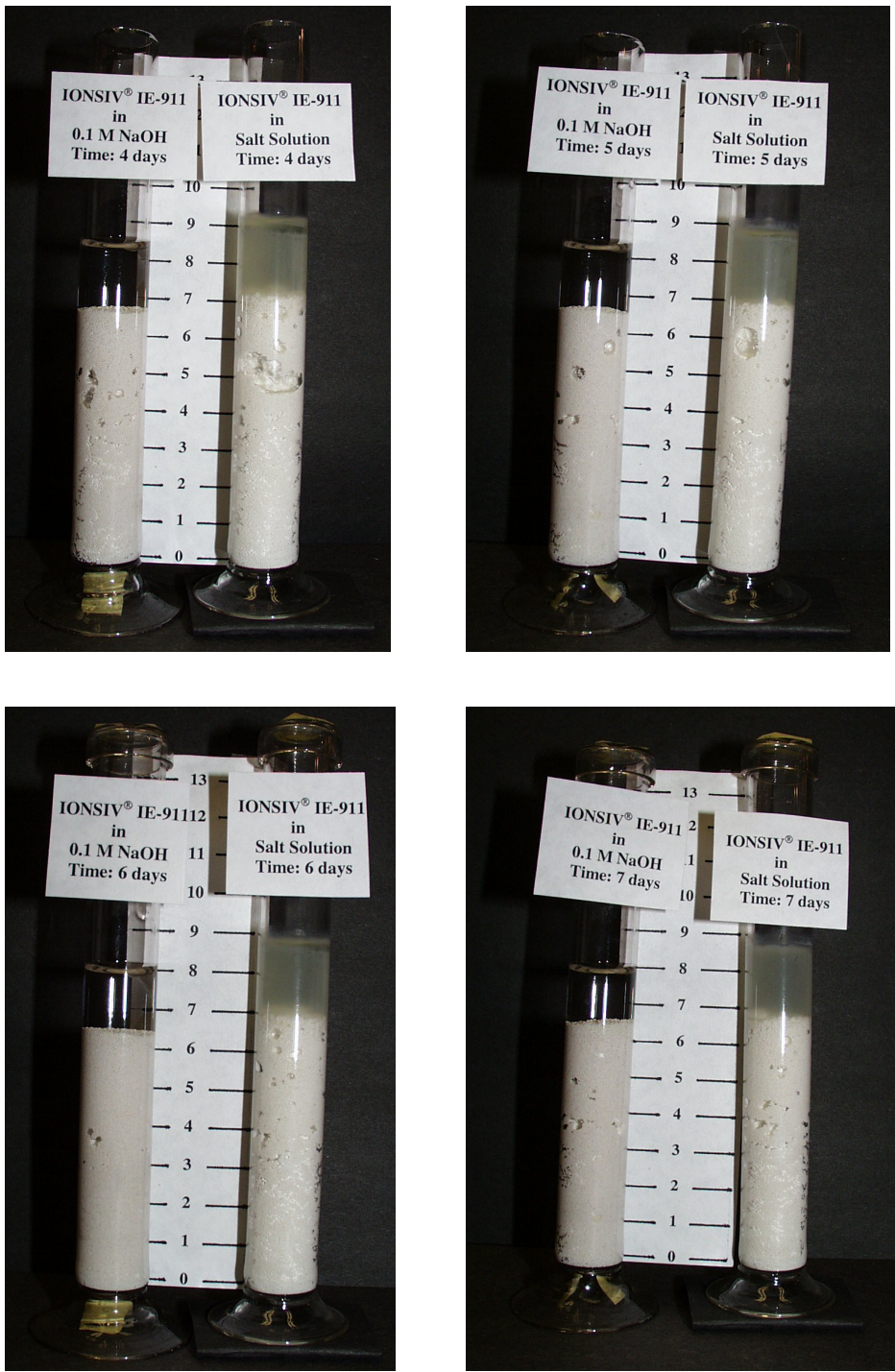


FIGURE 1. Gas Bubble Formation During Irradiation (continued)



Gas Generation and Composition

Researchers irradiated a high nitrate simulated waste solution and slurries of IONSIV™ IE-911 in high nitrate or high hydroxide waste solutions (Table I). The irradiation apparatus trapped the radiolytically generated gas. Table II lists the total gas generation rates. Figure 2 shows results of a typical experiment. Corrections applied to the observed volume changes account for loss of liquid sample as gas accumulates. The results of the experiments are expressed as G_{tot} values (yield of gas per unit amount of adsorbed energy, or molecules/100 eV). G_{tot} values are the sum of G values for individual gases.

The G_{tot} value for the high nitrate salt solution exceeds that for the corresponding slurry because the solids in the slurry adsorb a portion of the radiation. The high nitrate slurry produces more gas than the high hydroxide slurry because nitrate ion decreases hydrogen production and increases oxygen production. The effects increase as the nitrate ion concentration increases. The following equations summarize these reactions.

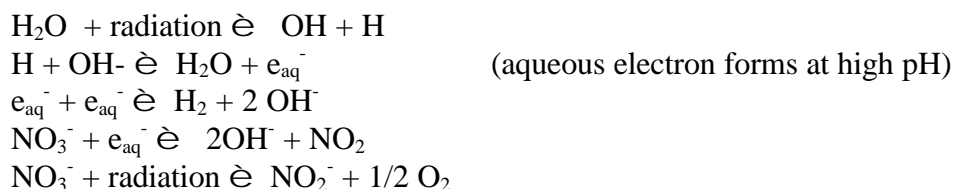


Table III lists the gas compositions. Hydrogen and oxygen were the major gases produced. Small amounts of N_2O were found. Since N_2O is slightly soluble in aqueous solutions, the actual yield is likely larger than indicated by the gas analysis. Carbon dioxide was not detected in any of the experiments (detection limit 0.01 vol %). This result was expected because the alkaline salt solution adsorbs CO_2 to form carbonate ion. Minor amounts of carbon monoxide, methane, and ethane were detected, but these likely originate from irradiation of the septum used to seal the apparatus. However, the amounts appear to vary consistently with the composition of the sample being irradiated, suggesting a connection.

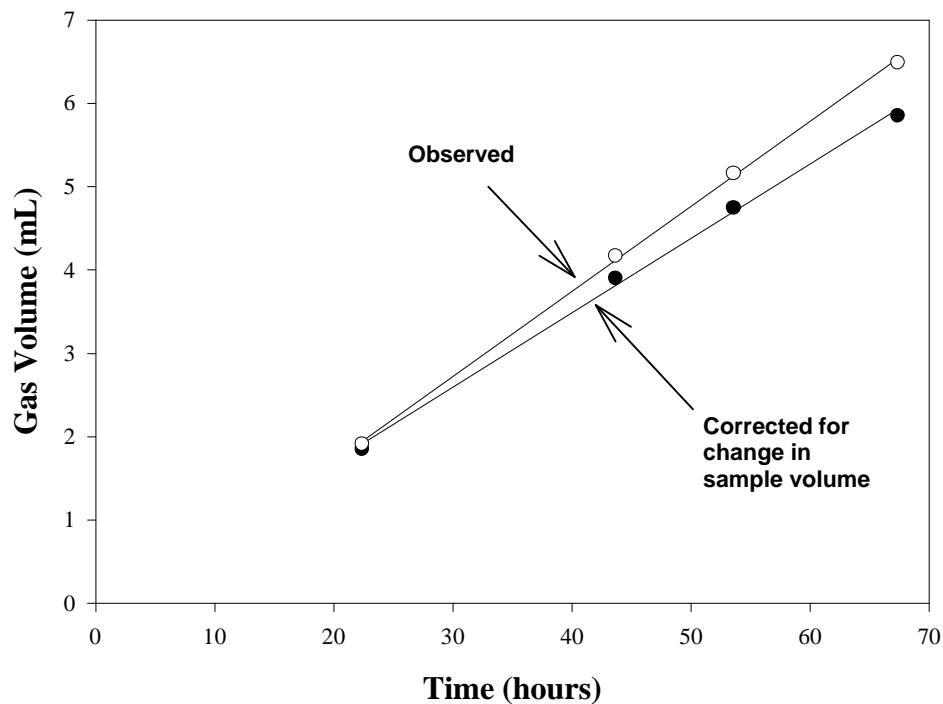
The high nitrate solution and slurry produce predominantly oxygen gas (Table III). The presence of IONSIV™ IE-911 appears to have minor effects: the hydrogen yield increases by 10%, the oxygen yield decreases by 5%, and the N_2O yield becomes 2.3%. These calculations assume a portion of the oxygen (proportional to the nitrogen), the methane, ethane, and carbon monoxide are sampling impurities. Although consistent, the differences in produced gases between solution and slurry are small and approach the analytical error. The high hydroxide slurry produces predominantly hydrogen gas. With the high nitrate solution or slurry, the sum of the gases measured was near 100%. In the high hydroxide slurry, the sum of the gases is ~90%, suggesting production of an unidentified gas or a bias in the measurement of large amounts of hydrogen.

TABLE II. Total Gas Generation Rates*

<u>Sample</u>	<u>G_{tot} Value</u> <u>(molecules/100eV)</u>
High nitrate solution	0.170, 0.163
High nitrate IONSIV™ IE-911 slurry	0.105, 0.110, 0.111
High OH-/IONSIV™ IE-911 slurry	0.076, 0.071

*Based on total dose (i.e., energy adsorbed by solid and liquid phases).

FIGURE 2. Accumulation of Gas in Irradiation Apparatus



High OH-/IONSIV™ IE-911 slurry
G_{tot} = 0.076 molecules/100 eV (Table II)

TABLE III. Gas Compositions*

Sample	Gas Composition (vol %)						Sum
	<u>H₂</u>	<u>O₂</u>	<u>N₂O</u>	<u>CO</u>	<u>N₂</u>	<u>Other**</u>	
High nitrate solution	20.8	72.7	<.13	0.01	7.2	0.1	100.8
	22.1	74.3		<.1	2.5	0.1	
High nitrate/ IONSIV™ IE-911 slurry	24.4	67.0	2.3	0.30	1.9	1.0	96.9
	23.2	69.7		0.35	2.5	1.1	
	25.4	68.0		0.32	2.4	1.5	
High OH/ IONSIV™ IE-911 slurry	61.9	15.4	3.8	0.35	5.5	2.5	89.5
	63.2	14.8		0.23	6.0	3.6	

*Dose rate for all data was 9.8×10^5 rad/h.

**Sum of methane and ethane.

TABLE IV. G Values for Individual Gases

<u>Sample</u>	G Value (molecule/100 eV)		
	<u>H₂</u>	<u>O₂</u>	<u>N₂O</u>
High nitrate solution	0.038±.001	0.128±.004	<.0002
High nitrate/IONSIV™ IE-911 slurry	0.028±.002	0.078±.003	0.0026
High OH/IONSIV™ IE-911 slurry	0.058±.002	0.0124±.0011	0.0036

*Based on total dose (i.e., energy adsorbed by solid and liquid phases) and corrected for sampling impurities.

Combining the gas compositions in Table III with the total gas generation rates in Table II allows the calculation of G values for the production of each gas. Table IV lists G values for hydrogen, oxygen, and nitrous oxide. These calculations assume the nitrogen, a portion of the oxygen (proportional to the nitrogen), the methane, ethane, and carbon monoxide are sampling impurities. This correction to the oxygen yield is minor for the high nitrate solution (<3%) and the high nitrate IONSIV™ IE-911 slurry (<1%), but is significant for the high hydroxide slurry (~10%).

Table V lists the G values based on the doses to the liquid phase of each sample. A previous investigation³ found no evidence for enhanced hydrogen production in the presence of IONSIV™ IE-911 when calculated on a dose-to-solution basis. In this study, the G value observed for hydrogen generation in the high nitrate slurry (0.052 molecules/100 eV) is close to the expected value (0.047 molecules/100eV) based on the nitrate and nitrite concentrations.⁵ However, the high hydroxide slurry generated hydrogen at almost twice the expected rate. The expected rate was 0.063 molecules/100 eV compared to the observed 0.107 molecules/100 eV.

The oxygen yields agree with the relatively few previous measurements on SRS waste solutions. For the high nitrate slurry, oxygen was generated at three times the hydrogen rate. This is somewhat less than the six-fold rate difference observed in a measurement on SRS radioactive waste,⁶ but the discrepancy likely results from differences in solution composition.

Nitrous oxide is a relatively minor constituent of the radiolytically generated gases. Researchers previously reported finding N₂O when nitrite or a combination of nitrate and organic compounds are irradiated.⁷⁻⁸

SUMMARY

Researchers investigated both the rate of production and composition of gases generated from Co-60 gamma irradiation of IONSIV™ IE-911 slurries in simulated SRS waste. The dose rate in these studies (~1 Mrad/h) was similar to the dose rate expected in a large ion exchange column loaded with Cs-137 (0.8 Mrad/h).

Irradiating a small column (1.5 cm diam x 10cm long) produced gas bubbles in less than eight hours. A previous calculation suggests that bubbles could form in a few minutes.¹ This prediction could be easily verified by the method used in this test by simply making observations at shorter time intervals. Observations at longer time periods indicate the

TABLE V. G Values for Gas Generation Based on Dose to Liquid Phase*

<u>Sample</u>	<u>G Value (molecule/100 eV)</u>		
	<u>H₂</u>	<u>O₂</u>	<u>N₂O</u>
High nitrate/IONSIV™ IE-911 slurry	0.052	0.144	0.0017
High OH ⁻ /IONSIV™ IE-911 slurry	0.107	0.023	0.0067

*Based on dose to liquid phase with the energy apportioned by weight. The high nitrate and high hydroxide slurries contained 54 wt % liquid phase in the test apparatus.

behavior of the gas bubbles depends on their depth in the column. Bubbles near the surface of a static column percolate to the surface by pushing the IONSIV™ IE-911 particles aside. Bubbles at greater depths produce gas channels between static IONSIV™ IE-911 particles. Some expansion of the bed occurs. Greater pressures in large columns may produce significantly different behavior.

Under high dose rates in the presence of IONSIV™ IE-911, the composition of gases measured in these tests agrees with previous results in the absence of IONSIV™ IE-911. Radiation produces mainly hydrogen and oxygen with small amounts (<4%) of nitrous oxide. The ratio of hydrogen to oxygen varies depending on the waste composition. At low nitrate concentrations, hydrogen production exceeds oxygen by up to 500%. Alternatively, at high nitrate concentrations, oxygen production exceeds hydrogen by up to 300%. The hydrogen production rate in high nitrate IONSIV™ IE-911 slurries agrees with previous work without IONSIV™ IE-911 present. Previous tests indicated similar agreement in average waste IONSIV™ IE-911 slurries.³ However, the current tests in high hydroxide IONSIV™ IE-911 slurries generated twice as much hydrogen as expected. This unexpected result deserves additional investigation. The test with high hydroxide slurry was unusual in three aspects that may contribute to the calculated high rate of hydrogen production: the correction to the oxygen concentration, the impurity organics from the septum, and amount of unidentified gas were all larger than in the high nitrate tests. With the exception of the high hydroxide waste, gas generation can be calculated based on dose to the liquid phase using G values obtained from solutions without IONSIV™ IE-911 present.

ACKNOWLEDGMENTS

The authors thanks W. C. Sexton of the SRTC Glass Shop for the design and fabrication of the apparatus used in the experiments. J. A. Young of the Analytical Development Section provided nitrous oxide analyses. B. H. Croy of Waste Processing Technology Section prepared solutions, monitored gas generation, and operated the WPTS gas chromatograph.

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APPENDIX A Experimental

Preparation of Salt Solutions

Researchers prepared simulated SRS waste solutions with the compositions shown in Table I using reagent grade chemicals and volumetric glassware. Personnel measured the densities of the salt solutions by weighing the solutions in the volumetric flasks used in the preparation.

Crystalline Silicotitanate

The experiments used crystalline silicotitanate in the engineered form, IONSIV™ IE-911, Lot #999098810005, manufactured by UOP LLC., Molecular Sieves Division, Des Plaines, IL. The as-received particles contained 5.9 ± 0.7 wt % water determined by drying 0.2 gram samples to constant weight at 105 °C. All experiments used pretreated portions of IONSIV™ IE-911. Pretreatment consisted of equilibration with moist air for 3 days, removal of fines with flowing water, and pH adjustment with sodium hydroxide solution. The sodium hydroxide solution was displaced with simulated waste solution by repeated batch dilutions.

Radiation Sources

Researchers used a Shepherd Model 109 Co-60 Gamma Source (Building 773-A, Room C-067) for high dose rate experiments and a Co-60 gamma ray source shielded by water (Building 774-A) for low dose rate experiments. The Building 774-A source is located under 28 feet of shielding water. Waterproof secondary containers hold the samples in an

TABLE A-1. Co-60 Gamma Ray Sources

Source name:	Shepherd Model 109	Source #2
Location:	773-A, C-067	774-A
Features:	Air cooled	Secondary container for samples cooled by shielding water
Temperature (°C)	35 ± 3	28 ± 3
Dose rate (rad/h) (7/1/99)*	9.8×10^5	1.04×10^5

* Experiments were conducted over a 4 month period between April and July 1999.

air atmosphere during irradiation. Although not cooled by air circulation as in the Shepherd source, sample temperatures are moderated due to the large volume of shielding water. Table A-1 lists significant conditions for each source. Researchers measured the dose rates for the experimental geometry using Fricke dosimeter solutions.⁵ Tests conducted over four months required small dose rate adjustments for decay of the Co-60.

Gas Bubble Formation Test

The SRTC Glass Shop fabricated fused-quartz cylinders (1.5 cm ID x 13 cm long) for this experiment (Figure 1). Quartz does not darken upon exposure to radiation as does borosilicate glass. Slurries of IONSIV™ IE-911 in high nitrate salt solution or 0.1 M NaOH solution filled the quartz cylinders to a depth of 6.0 cm (10.6 mL). The 6-cm deep packed bed was covered with 2.0 cm of clear liquid. The Shepherd gamma ray source irradiated the slurries for seven days at a dose rate of 1.01×10^6 rad/h. Researchers visually examined the quartz cylinders for gas bubbles after 8 hours of irradiation and daily thereafter. Room temperature air injected into the irradiation chamber maintained the sample temperature at 36 ± 1 °C.

Gas Generation and Composition Tests

The SRTC Glass Shop fabricated the borosilicate glass vessel illustrated in Figure A-1. The vessel consists of two chambers separated by a coarse porosity glass frit. One chamber holds the sample. A silicone septum covered with copper foil seals the sample chamber and provides access for syringe removal of gas samples for analysis. The other chamber is a graduated cylinder open to the atmosphere. Gases generated by irradiation of the sample are collected in the sealed chamber. Liquid displaced by the gas passes through the glass frit. The volume displaced from the sealed chamber is measured in the graduated cylinder.

Researchers placed a cork in the graduated cylinder and then filled the sample chamber with either salt solution or slurries of IONSIV™ IE-911. Weighing the apparatus empty and filled determined the amount of sample present. The cork was removed and about 1.5 mL of salt solution was placed in the graduated cylinder to seal the glass frit. The apparatus was placed in a Co-60 gamma source and irradiated for 3 days to 3 weeks. The volume of liquid in the graduated cylinder was periodically recorded. At the end of the irradiation, the vessel was allowed to return to room temperature. A portion of the trapped gas was removed and analyzed. Due to hardening of the septum during irradiation, a second septum was placed over the irradiated septum to maintain integrity when the gas sample was taken by syringe. During syringe sampling, researchers took care to avoid air contamination. However, 2-7 vol. % nitrogen was found. The variability of the nitrogen yield suggests its origin is air contamination rather than radiolytic generation. The oxygen yields were adjusted downward assuming the nitrogen present represented air contamination. In all cases this correction was minor and represented less than a 5 % change in the oxygen yield. The copper foil did not completely prevent contamination of the samples with variable minor amounts (0.1 to 4%) of CH₄, C₂H₆, and

CO from the radiolytic degradation of the silicone septa. Control tests in the absence of salt solution or IONSIV™ IE-911 demonstrated these gases originated from the septa. No useful data was obtained from tests using the low dose rate source. The irradiation vessels leaked air during the test so the data was discarded.

Researchers calculated the gas generation rates as G values (molecules/100 eV) assuming ideal gas behavior and 1 atm pressure in the apparatus. No correction was made for water vapor in the samples. The vapor pressure of water at 25 °C is 23 mm Hg (i.e., approximately 3 vol %) and will be less over salt solutions. The gas generation rate (in mL/h/g) was corrected for loss of solution displaced from the sealed section of the apparatus. No correction was made for the recombination of gases in the radiation field.

The calculation of the dose to the solution requires knowledge of the masses of IONSIV™ IE-911 and simulated waste solution in the packed bed. Researchers assume the dose to the liquid phase is the fraction of the total dose equal to the mass fraction of the liquid phase. The previous calculation of gas generation rates¹ assumed the bed contained 50 vol % particles, the IONSIV™ IE-911 particles were 24 vol % void space, the packed dry particle density was 1.0 g/mL, the solution density was 1.26 g/mL, and the IONSIV™ IE-911 solid phase density was 2.6 g/mL. These assumptions yield a calculated dose to the liquid phase equal to 44% of the total dose (or, alternatively, the IONSIV™ IE-911 absorbs 56% of the radiation). In this task, researchers measured the volume and weight fraction of IONSIV™ IE-911 in slurries with salt solutions. A portion of IONSIV™ IE-911 dried to constant weight at 100 °C was added to a measured volume of water in a graduated cylinder. The void fraction in a packed column of dried IONSIV™ IE-911 equaled 63 vol %. The particle density of the dried IONSIV™ IE-911 equaled 2.66 g/mL. In the irradiation experiments, a small amount of excess liquid phase present above the packed bed reduced the calculated liquid weight fraction to 54%.

Analytical Methods

Analytical Development Section (ADS) personnel performed routine analyses to verify the composition of the salt solutions. ADS personnel analyzed gas compositions with a Hewlett-Packard Model 5890 gas chromatograph with a Hewlett-Packard Model 5971 mass spectrometer. A 30 m x 0.53 mm Carboxen-1006 porous layer open tubular capillary column separated the gas components.

Waste Processing Technology Section personnel analyzed gas compositions with a Varian Model 3400 gas chromatograph containing thermal conductivity and flame ionization detectors. Chromosorb-106 and molecular sieve 13X columns separated the gas components. Researchers calibrated the detector response for H₂, O₂, N₂, CO, and CO₂ with NIST traceable gas standards (Scott Specialty Gases, ±5% accuracy).

Figure A-1. Apparatus for Gas Generation Rate Measurements

