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HYDROGEN PRODUCTION IN RADIOACTIVE SOLUTIONS IN THE DEFENSE WASTE PROCESSING FACILITY (U)

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Authorized Derivative Classifier

Westinghouse Savannah River Co.
Savannah River Site
Aiken, SC 29808

PREPARED FOR THE U. S. DEPARTMENT OF ENERGY
UNDER CONTRACT DE-AC09-89SR18035

3. Sludge Receipt Adjustment Tank (SRAT)
   Product: G(H2) = 0.39±0.08 molecules/ 100eV
4. Slurry Mix Evaporator (SME)
   Product: $G(H_2)$ = 0.36±0.01 molecules/ 100eV.

The latter three slurries listed above contain formic acid and/or formate ions that can increase the value $G(H_2)$ above the 0.45 molecules/ 100eV.[3] However, 0.45 is still applicable for the sludge feedstream that does not contain formic acid and/or formate.[2]

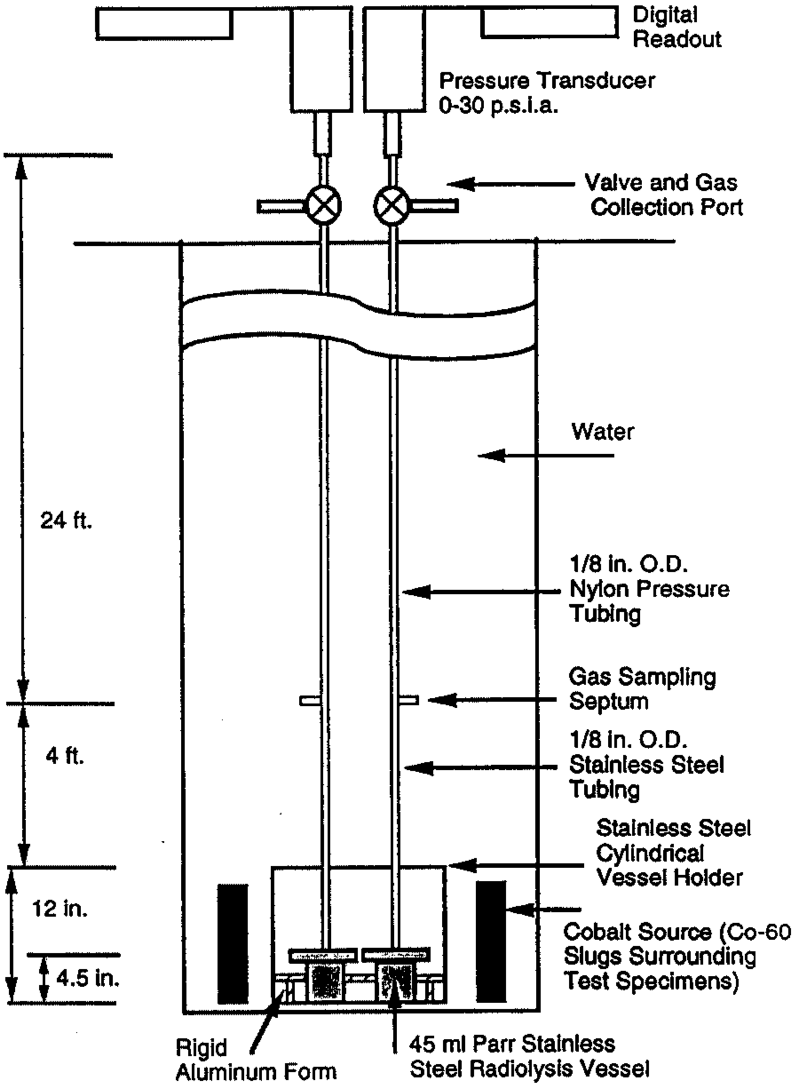
To determine a maximum value for $G(H_2)$ in the presence of formic acid, several formic acid/formate solutions were irradiated in this study. The maximum value obtained for $G(H_2)$ when 0.5, 1, 2, or 3M formic acid solutions were irradiated and when a 0.5M formate solution or a 0.5M formate and 0.5M nitrate solution was irradiated was 2.0±0.1 molecules/100eV. This value is much greater than any of the values obtained for the DWPF process streams. In these tests it was also shown that the NO_3^- in the solution effectively lowers $G(H_2)$ as it does in sludge slurries.[4]

The above G values can be used to determine the required air purge volumes or flow rates needed to prevent flammable atmospheres from occurring in the various process tanks used in the DWPF during radioactive operations.[5,6]

EXPERIMENTAL SECTION

Irradiation Apparatus

Irradiations were carried out in a Co-60 gamma ray source submerged beneath 30 ft. of water for shielding purposes. The radiation dose rates during this study were in the range 6.1E+05 to 6.9E+05 rads/hr due to the decay of the Co-60 ($t_{1/2}$ = 5.3y). This range was determined using standard radiation dosimeters that will be discussed later. The temperature of slurries during the irradiations was ~40°C due to gamma heating. A diagram of the irradiation apparatus is shown in Figure 1. Two samples could be irradiated simultaneously. For each experiment, a known amount of slurry or solution was placed in a 45 ml stainless steel vessel (1 in. diameter and 4.5 in. length). The vessel was connected via 4 ft. of 1/8 in. O.D. stainless steel tubing and 24 ft. of 1/8 inch O.D. nylon pressure tubing to a calibrated pressure transducer located outside of the radiation field. A gas sampling septum was located ~4 ft. above the steel vessel at the stainless steel/nylon pressure tube interface. This gas sampling septum was used to calibrate the void volume of the apparatus before the irradiations and for injection of air for



Gas Production Radiolysis Apparatus

Figure 1. Diagram of irradiation apparatus used to measure radiolytic pressure production.

leak testing the apparatus. For the leak testing, ~40 cc of air was injected into the sealed apparatus. The pressure increased to nominally 25 PSIA. This pressure was then monitored for typically 1-2 hours to ensure that it remained constant and thus indicated that the apparatus was air-tight. To determine the void volume in the free gas in the system, four 10 cc additions of air were added and the pressures noted after each addition. Using the ideal gas law and the pressure increases, the void volume in the apparatus could be calculated.

After the apparatus was leak checked and its void volume determined, the apparatus was opened and the gas sampling septum used for the void volume determination and leak testing was replaced with a new septum. The apparatus was then resealed and was ready for irradiation. As shown in Figure 1, two vessels could be irradiated simultaneously in the source. For irradiation, both vessels had to be placed in a larger stainless steel cylindrical vessel (4" diameter and 12" long) which was attached to a cable used to lower them into the Co-60 source. An aluminum insert was placed in the large vessel to ensure reproducible placement of the two 45 ml stainless steel vessels within the larger cylinder. The slurries were irradiated for typically 1 to 2 days. During this time, the gas pressure generated in each apparatus was recorded periodically throughout the irradiation time.

Gas Analyses

After the sample vessels were removed from the radiation field, a 1L evacuated glass bulb was connected to the valve (gas collection port) of each apparatus just in front of its pressure transducer (see Figure 1). The gas contained in the void volume (~55cc) of each apparatus was then expanded into each bulb. These bulbs were purposely made much larger than the void volume in each apparatus to ensure that at least 95% of the gas was removed from each irradiation apparatus. The 1 L glass bulb was then disconnected from the radiation vessel and connected to an evacuated sampling loop of a Varian Model 3400 gas chromatograph (GC). The chromatograph was equipped two detectors - a thermal conductivity detector and a flame ionization detector. Two detectors were necessary to analyze all the gases produced. The columns used were a Chromosorb-101 column and a molecular sieve 13X column with argon as the carrier gas. Multiple GC analyses were made at different pressures, typically between 0.2 and 1.5 psia within the GC sampling loop, to obtain integrated peak area vs. pressure plots for all of the components of the gas collected from each of the irradiated slurries. The linear least squares slopes of these plots were then compared to similar plots obtained for a standard gas (Scott Specialty Gas Co.; 4.04% H_2, 3.99% O_2, 75.99% N_2, 4.00% CH_4, 4.00% CO, 3.99% CO_2, 3.99% C_2H_4) and atmospheric gas (20.8% O_2, 78.2% N_2) in order to calculate the volume percent of the various components in each gas after the irradiations.

Radiation Dosimetry

The radiation dose rate was measured by two methods. In one, thin film nylon dosimeters were placed in the vessels and the radiation intensity determined. The method for using these dosimeters has been described elsewhere.[7] Based on the nylon film dosimeters, the dose rate was 6.9E+5 rads/hr.

The second standard dosimetry method that was used is based on measuring gas production from radiolytic decomposition of water. The dosimeter solution is 0.0001M KI. The KI prevents the radiolytic products H_2 and O_2 from recombining in the radiation field. Figure 2 shows the pressures produced when two identical 0.0001M KI systems were irradiated in the sealed vessels. The pressure production rates are essentially identical. The data show that after an induction period of ~3 hrs, the pressures increase linearly and then may start to level off at large doses. This leveling may be due to back reactions becoming significant at the higher doses. The induction period is the time necessary for the rates of the radiation induced reactions to reach a steady state and the rates of gas evolution to become constant.[8] Compositions of the gases produced and experimental details are given in Table 1. Table 2 shows the G values for H_2 and O_2 calculated from the total dose (determined from the total radiation time and the dose rate measured by the thin film dosimeters) and the final gas composition. The measured values, 0.37 for H_2 and 0.19 for O_2, agree very well with the published values, 0.38 for H2 and 0.19 for O_2.[9] This agreement confirms that the irradiation apparatuses and gas sampling systems were performing properly and that the gas analyses and dose rate determinations were accurate. From the slope of the linear portion of the data in Figure 1 (calculated by a least squares fit of the data) and the published G values, a dose rate could be calculated. As shown in Table 2, this rate is in excellent agreement with that determined using the thin film dosimeters.

Methods of Calculation of G Values for the Test Slurries and Solutions

For the slurries and solutions being tested, radiolytic G values were calculated by two methods. In one method G values were calculated for the individual gaseous components. These G values are based on the number of molecules of each gas produced or depleted. For the individual gaseous components, the G values were calculated from the initial gas composition (air with a nominal composition of 78.2% N_2 and

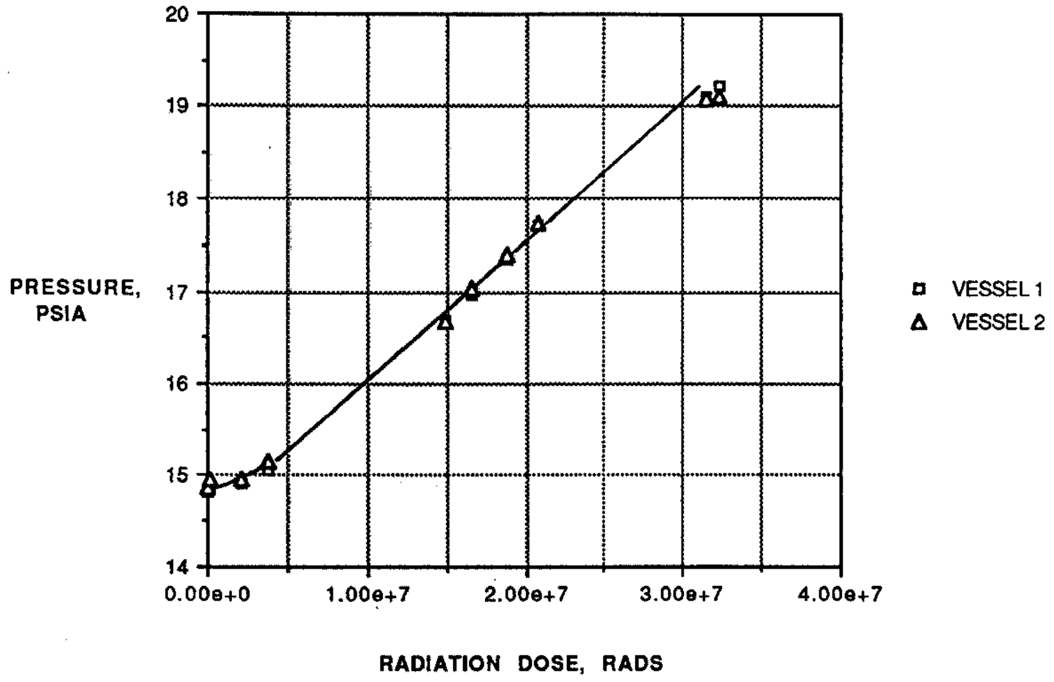


Figure 2. Pressures produced from radiolysis of aerated 0.001 M KI aqueous solutions. This solution is a standard dosimeter for determining gamma radiation dose rates. Solutions in two vessels were irradiated simultaneously in the Co-60 source.

Table 1. Final Gas Composition from Radiolysis of 0.0001 M KI Dosimeter Solutions

Experimental Details

	Vessel 1	Vessel 2
Final Dose, Mrad	31.8	31.8
Init. Press., PSIA	14.8	14.9
Final Press., PSIA	19.2	19.1
Irradiation Time, hr	46.1	46.1
Mass Solution, g	40.0	40.0
Void Volume, cc	55.7	55.8

Final Gas Compositions

Component	Volume Percent				
	Vessel 1	Vessel 2	Avg.	St.Dev.	% R.S.D.[a]
H_2	15.0	15.8	15.4	0.48	3.1
O_2	23.0	23.5	23.2	0.44	1.9
N_2	59.32	56.9	58.1	1.72	3.0

---

[a] Relative Standard Deviation (RSD) = (St. Dev./Avg.)*100

Table 2. Calculated G Values and Dose Rate for 0.0001 M KI Dosimeter Solutions.

Experimental Details

	Vessel 1	Vessel 2
Final Dose, Mrad	31.8	31.8
Init. Press., PSIA	14.8	14.9
Final Press., PSIA	19.2	19.1
Irradiation Time, hr	46.1	46.1
Mass Solution, g	40.0	40.0
Void Volume, cc	55.7	55.8

Calculated G Values

Component	G value, Molecules/100 eV[a]				
	Vessel 1	Vessel 2	Avg.	St.Dev.	% RSD
H_2	0.365	0.380	0.372[b]	0.010	2.70
O_2	0.182	0.198	0.190[b]	0.011	5.83
N_2	0.042[c]	-0.016[c]	0.013[c]	0.040	NA
(H_2+O_2)	0.547	0.578	0.563[b]	0.022	3.90
Dose rate[d] (rads/hr)	7.05E+5	6.80E+5	6.93E+5	0.18E+5	2.54

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[a] All G-values calculated from the final pressure, final gas composition, and final dose.

[b] Reference G-values for H2, O2, and (H2+O2) are 0.383, 0.192, and 0.575, respectively.[8,9]

[c] These G-values in the range of ±0.04 indicate insignificant change in the N_2 component of the atmospheric gas that was present in the sealed system prior to the start of irradiation.

[d] Calculated from the least squares determination of the slopes of the linear portion of the curves in Figure 2. A reference dose rate determined from thin film nylon dosimetry is = 6.87E+5 rads/hr.[7] This value is an average of two dose rates determined at different levels within the stainless steel cylindrical vessel holder (1 ft length and 3.75 in. diameter) used to lower samples down into the Co-60 source.

20.8% O_2), the final gas composition, and the total dose received by the solution or slurry. In the second method a G value for the total gas produced was calculated. This G value was determined from the linear rate of pressure increase in the apparatus due to radiolysis and from the radiation dose rate to the slurry or solution. If all the individual G values are accurate, this total G value should be equal to the sum of the G values for the individual gaseous components. However this will only be true if the changes in the partial pressures of all the components vary linearly with dose.

RESULTS AND DISCUSSION

Radiolysis of Simulated Potassium Tetraphenylborate (KTPB) and Precipitate Hydrolysis Aqueous (PHA) Slurries

Slurries were prepared to simulate the KTPB feed to the DWPF and the aqueous product (PHA) slurries from hydrolysis of the KTPB feed. The KTPB slurry was ~10 wt % solids that had been irradiated to a dose of ~200 megarads to simulate the radiolysis that would occur during storage in the tank farm in the late wash process prior to the precipitate being sent to the DWPF. The KTPB slurry had also been washed to simulate the late wash process. The PHA was produced from hydrolysis of a KTPB precipitate simulant that had also been irradiated to simulate storage in the tank farm. This simulant contained nominally 2 wt % solids. Figures 3 and 4 show the pressures produced when these slurries were irradiated in sealed vessels. The data in Figure 3 are from three identical experiments for each slurry in which 40 ml samples were irradiated. The lines were drawn by hand and indicate the good reproducibility of the results for identical experiments. Figure 4 shows similar results for single samples of PHA and KTPB irradiated to a higher dose. Both figures show that the pressure increases at a faster rate for the PHA solution than for the KTPB simulant. This may be due to the presence of formic acid/formate in the PHA. (The KTPB simulant did not contain formic acid or formate). Compositions of the measured gas components for the higher dose tests are given in Table 3 along with the experimental details. If all the gases are detected and measured accurately, the sum of the volume percents should be 100. Throughout this study, these sums were normally 95% or better. We feel that the difference from 100% probably results from experimental error in the gas analyses and is not indicating that some major gas component was not detected. Table 4 shows the G values calculated from the data - both for the individual gases and for the total gas produced.

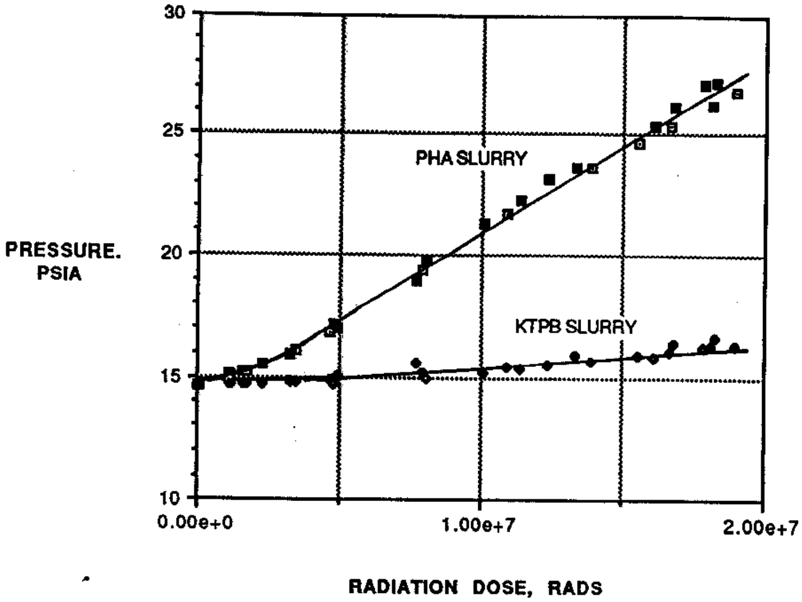

Figure 3. Pressures produced from radiolysis of simulated PHA and KTPB slurries. Results are shown for irradiation of three separate samples of each in the same configuration (40 mL of slurry were irradiated in each case). Single lines are drawn for each data set indicating the good reproducibility of the pressures produced.

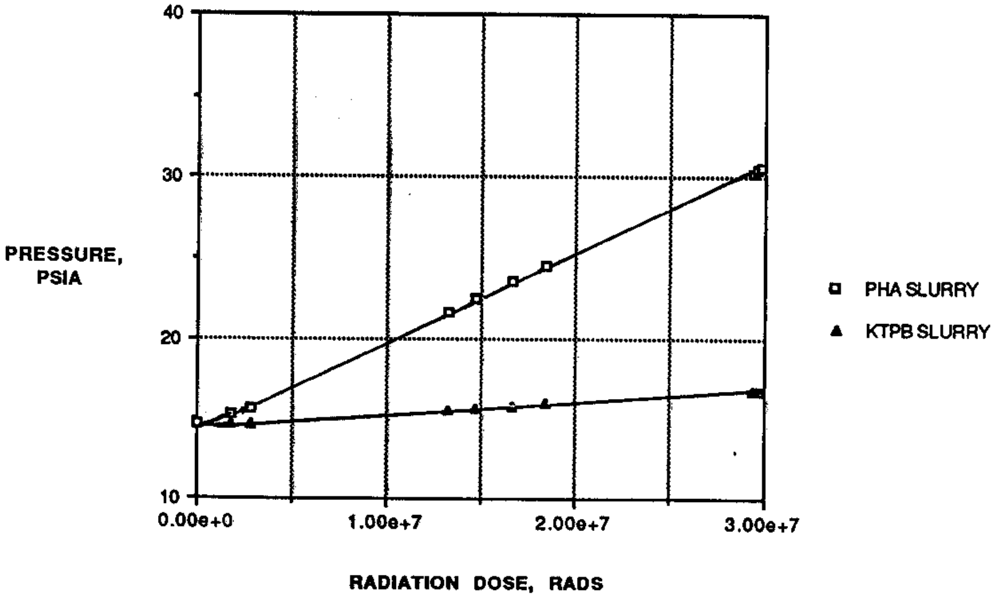

Figure 4. Pressures produced from radiolysis of simulated PHA and KTPB slurries irradiated to a higher dose than those in Figure 2.

Table 3. Final Gas Compositions from Radiolysis of Simulated KTPB and PHA Slurries.

Experimental Details

	KTPB Slurry	PHA Slurry
Final Dose, Mrad	31.1	31.1
Init. Press., PSIA	14.8	14.9
Final Press., PSIA	16.8	30.8
Irradiation Time, hr	45.1	45.1
Mass Solution, g	37.0	30.2
Void Volume, cc	59.5	66.3

Final Gas Compositions

Component	Volume Percent	
	KTPB Slurry	PHA Slurry
H_2	13.5	12.4
O_2	16.7	9.4
N_2	64.3	36.7
CO	ND[a]	3.65
CO_2	ND	37.1
N2O	NS[b]	NS
Sum	94.5	99.8

[a] ND = Not Detected

[b] NS = Not Analyzed For

Table 4. Calculated G Values for Gas Production in Radiolysis of Simulated KTPB and PHA Solutions.

Experimental Details

	KTPB Slurry	PHA Slurry
Final Dose, Mrad	31.1	31.1
Init. Press., PSIA	14.8	14.9
Final Press., PSIA	16.8	30.8
Irradiation Time, hr	45.1	45.1
Mass Solution, g	37.0	30.2
Void Volume, cc	59.5	66.3

Calculated G Values

Component	G value, Molecules/100 eV	
	KTPB Slurry	PHA Slurry
Total Gas[a]	0.31	3.08
H_2	0.34	0.77
O_2	-0.01[b]	-0.03[b]
N_2	0.01[b]	-0.02[b]
CO	---	0.23
CO_2	---	2.33
N_2O	---	---
Sum	0.34	3.29

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[a] Calculated from the least squares determination of the slopes of the linear portion of the curves in Figure 4. All other G-values calculated from the final pressure, final gas composition, and final dose.

[b] These G-values in the range of ±0.03 indicate insignificant changes in the O_2 and N_2 components of the atmospheric gas that was present in the sealed system prior to the start of irradiation.

Simulated, Preirradiated KTPB Slurry

The only gas produced from radiolysis of the pre-irradiated KTPB slurry was H_2 with a G value of 0.34 molecules/100eV. The G value for the total gas produced based on the least squares determined slope of the data in Figure 4 is 0.31 which is within experimental error the value for $G(H_2)$. The detailed composition of this slurry is given in Appendix 1. In other radiolysis tests with tetraphenylborate slurries, the only gas produced was H_2. Gupta et al. from radiolysis of millimolar aqueous NaTPB solutions determined a G value of 0.46.[10] In recent tests with 5 wt% NaTPB slurry, Walker measured a G value of 0.074 and 0.011 respectively, in the presence of 0.76 and 1.9M NO_3^-.[11] Nitrate was not present in Gupta's tests. NO_2^-, HCO_2^-, and NO_3^- were present in the slurry irradiated here. These anions are known to decrease the G value for H_2 and thus a value lower than 0.45 was obtained.[12]

Simulated PHA Slurry

The concentrations of the soluble components in the simulated PHA sample irradiated in this study are given in Table 5. The results for the unirradiated PHA are in agreement with analyses of other representative PHA solutions from TNX experiments.[13] The organic compounds result from the radiolysis of the KTPB precipitate prior to the hydrolysis. The table also presents the final concentrations for a majority of the components in the irradiated sample. The insoluble component in the slurry was primarily Ti to simulate that which will be used in the tank farm to adsorb Sr and Pu from the radioactive supernate. Gases produced from radiolysis of the PHA are CO_2, CO, and H_2. Both CO_2 and H_2 have been reported in radiolysis studies with formate/ formic acid solutions.[14-16] CO was not reported as a product in those tests,[14-16] but the doses there were not nearly as large as doses in the present experiments. Carbon dioxide is the main gas produced from the radiolysis of PHA solution. The G value for CO_2 is 2.3 (see Table 4). The G value for H_2 is 0.77, and that for CO is 0.23. The G value for total gas produced was 3.1 in good agreement with the 3.3 which is the sum of the individual G values.

The concentrations in Table 5 are averages of three similar tests involving the radiolysis of ~40 ml of PHA for ~28 hours at a dose rate of 6.9E+05 rads/hr. The precisions of the average concentrations were 10% or better. The concentrations of formate and nitrate decrease significantly and that for oxalate increases slightly as a result of radiolysis. The concentrations differences for the other species are within experimental error. The concentrations of the organic compounds (other than formate and oxalate) were

Table 5. Concentrations of Soluble Species in Unirradiated and Irradiated PHA Solutions and Resulting G Values[a]

Component	Concentrations Unirrad. PHA	 Irrad. PHA	Change	Calculated G values, Molec./100eV
	Concentrations (M)			
Anions, moles/liter				
Chloride	7.4E-4	5.0E-4	-2.4E-4	b
Formate	3.2E-1	2.2E-1	-9.4E-2	-4.7
Oxalate	4.1E-4	1.0E-3	+1.5E-3	+0.08
Nitrate	4.1E-2	7.9E-3	-3.3E-2	-1.6
Nitrite	8.6E-4	6.7E-4	-1.9E-4	-0.01
Sulfate	1.5E-4	1.4E-4	-8.7E-6	b
Cations, ppm[c]				
K	3550	3475		
B	1966	2003		
Na	819	828		
Cu	770	553		
Mn	681	671		
Cs	210	194		
Fe	93	62		
Ca	32	32		
Al	8	7		
Zn	3	3		
pH	3.5	4.2	+0.7	

Organic Compounds Analyzed for in Unirradiated PHA

Compound	Conc., ppm	Compound	Conc., ppm
Phenylboric Acid	7060	diphenylamine	15
phenol	1323	o-terphenyl	9
aniline	244	2-phenylphenol	8
m-terphenyl	39	biphenyl	5
p-terphenyl	10	n-phenyl formamide	<1
nitrobenzene	<1	4-phenylphenol	<1
nitrosobenzene	<1	diphenyl mercury	<1

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[a] Results are averages of three experiments involving the radiolysis of ~ 40 ml of PHA for ~ 28 hours at dose rate of 6.9E+05 rads/hr. Anions analyzed by ion chromatography, cations by inductively coupled atomic emission spectroscopy and organic compounds by high pressure liquid chromatography.

[b] The change in concentration is within experimental error and G values were not calculated.

[c] G values were not calculated for these species.

not measured in the irradiated solution. Both formic acid and the formate anion react rapidly with the hydroxyl radical, OH·, one of the reactive species formed by the radiolysis of water.[14-16] This reaction eventually leads to the formation of CO_2 gas and the oxalate anion, $C_2O_4^{2-}$ which were observed in these tests. Nitrate is readily reduced by H atoms and the aqueous electron which are the other reactive intermediates produced by the radiolysis of water.[12] Nitrite ion can be a product, however, we observe no significant increase in the nitrite concentration in the irradiated PHA solutions. In fact there is a slight decrease in nitrite. It is likely that the nitrite ion undergoes reduction.[17] Possible final reduction products include N_2O, N_2, and NH_3.[18,19] Nitrous oxide, N_2O, has been detected in the three PHA irradiations at ~0.1 volume percent but this does account for all the reduction of nitrate. Nitrogen does not appear to be a product from the radiolysis of PHA solutions (see Table 4). Analyses for ammonium ion in the irradiated PHA solutions indicate that a small amount of ammonium is produced with a $G(NH_4^+) = 0.08$. The ammonium ion has been shown to be a major product formed ($G(NH_4^+) = 0.1\text{-}0.4$) from the radiolysis of both millimolar nitrate and nitrite solutions containing excess ~0.1 M formate as a hydroxyl radical scavenger.[19] Another possibility is that formate reacts with the intermediate in the nitrate reduction prior to nitrite formation. This intermediate is probably NO_2.[20]

The other two species whose concentrations change are Fe and Cu. Radiolysis caused the pH to increase ~0.5 units, thus, this decrease in Fe and Cu concentrations may be due to precipitation of these ions. As a possible indication of precipitation, the color of the PHA solutions changed from a light green for the unirradiated solution to a dark green for the irradiated solution.

Radiolysis of the Sludge Receiving and Adjustment Tank (SRAT) and the Slurry Mix Evaporator (SME) Product Slurries from DWPF Cold Run FA.13

In July, 1994, a ~500 mL sample of the SRAT product and a ~500 mL sample of the SME product were delivered from the DWPF to TNX. These slurries were generated in the DWPF during Cold Run FA.13. Analyses at TNX showed that the samples had the compositions given in Table 6. The SRAT product contained sludge and PHA. The SME product contained sludge, PHA, and frit. The SME product had a much greater weight percent solids due to the presence of frit added to the slurry. These slurries were irradiated to determine the gases produced and their respective G values. Figure 5 shows the pressures produced when SRAT and SME product slurries were irradiated in sealed vessels.

Table 6. Composition of SRAT and SME Product Samples from DWPF Cold Run FA.13. These Samples were used in the Radiolysis Tests.

	SRAT Sample	**SME Sample**
Wt.Percent Total Solids	25.4	50.8
Density, g/ml	1.18	1.43
pH	6.3	5.7
Soluble Anions, moles/L		
Formate	0.69	0.86
Nitrite	<0.01	<0.01
Nitrate	0.45	0.44
Sulfate	0.006	0.009
Metals in Dried Solids,ppm[a]		
Al	4.71	2.57
B	1.09	2.02
Ca	1.5	0.73
Cr	0.089	0.11
Cu	0.64	0.35
Fe	16.1	8.5
K	3.99	2.01
Mg	0.27	0.88
Mn	4.09	2.02
Na	6.65	6.03
Ni	1.57	0.84
Si	2.83	22.9
Ti	0.33	0.16

[a] Determined by Peroxide Fusion and Acid Dissolution of the Dried Sample and Analysis of the Resulting Solution by ICP-AES

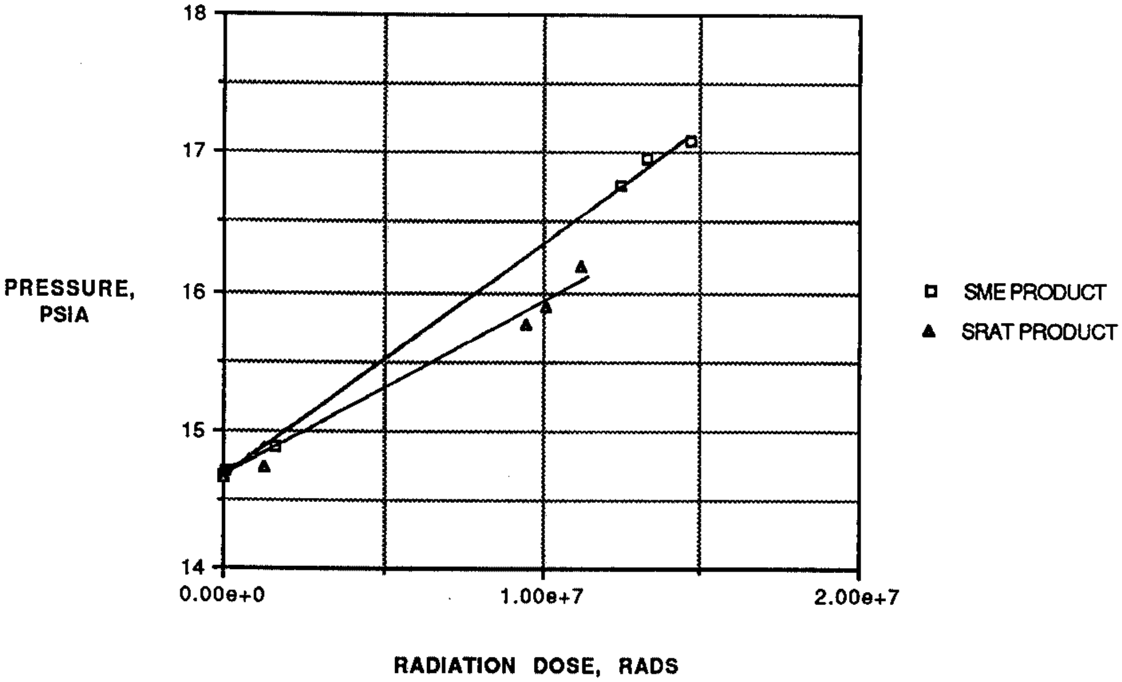

Figure 5. Pressures produced from radiolysis of a sample of SME product and a sample of SRAT product from DWPF cold run FA.13.

Tables 7 and 8 give the experimental details, the final gas compositions, and calculated G values. The sums of the percentages of the individual gases in the SRAT and SME tests were 95 and 98%, respectively, indicating that all the major gases were detected and measured. As with the PHA, the main gases produced were H_2 and CO_2, with a small amount of CO. The values for $G(H_2)$, 0.31 for the SRAT and 0.35 for the SME, are lower than the 0.77 determined or the PHA. This is because the NO_3^- concentration is ~10X higher in the SRAT and SME product than in the PHA solution (0.44M compared to 0.041M). In the test with the SME product, there was a relatively large decrease in the amount of N_2 present following radiolysis. This gave the large G value of (-0.2 to -0.5) molec./100eV for N_2 disappearance. Currently we have no explanation for this. However, the analysis for N_2 does not affect the analysis for H_2 and the subsequent determination of its G value.

Radiolysis of Formic Acid, Formate, and Formate-Nitrate Solutions Prepared at TNX

To determine the effect of pH, nitrate, and formic acid concentration on $G(H_2)$, several solutions of different concentrations were irradiated. These solutions were prepared at TNX with 1.0M formic acid and 0.5M sodium hydroxide stock solutions. Four solutions were prepared - 0.5 and 1.0M formic acid solutions, a 0.5M formate solution, and a 0.5M formate solution containing 0.5M nitrate. Analyses at TNX confirmed that these concentrations were achieved. Each solution was irradiated in duplicate. Figure 6 shows the pressures produced when a set of the solutions was irradiated in sealed vessels. Table 9 gives the experimental details for irradiating this set along with the average compositions of the gases produced from both sets of irradiations. Table 10 gives the average of the calculated G values.

Comparison of the results for $G(H_2)$ for all four solutions confirms that nitrate lowers the yield of hydrogen. There does not appear to be a significant effect on $G(H_2)$ whether the solution is 0.5M formic acid or 0.5M formate. This agrees with the published results of Hart and Draganic.[14,15] The 1 M formic acid to gives a higher value for $G(H_2)$ than the other solutions. The G values for CO_2 are large. With 0.5M nitrate present in the 0.5M formate solution, the CO_2 yield is significantly increased over its value in the other solutions and nitrous oxide, N_2O, is also produced. This suggests that the intermediate from nitrate radiolysis may indeed be reacting with formate to produce CO_2 and N_2O.

Table 7. Final Gas Compositions from Radiolysis of the SRAT and SME Product Samples from DWPF Cold Run FA.13.

Experimental Details

	SRAT Product		SME Product	
	Test 1	Test 2	Test 1	Test 2
Final Dose, Mrad	11.8	14.8	14.3	18.7
Init. Press.,PSIA	14.7	14.7	14.7	14.7
Final Press., PSIA	16.2	17.6	17.1	18.4
Irradiation Time, hr	15.2	21.3	15.2	21.3
Mass Solution,g	42.9	42.9	55.7	54.1
Void Volume, cc	59.1	58.8	57.1	57.2

Composition of Gases Produced

Component	Volume Percent			
	SRAT Product		SME Product	
	Test 1	Test 2	Test 1	Test 2
H_2	5.5	9.4	10.1	9.2
O_2	17.6	19.2	15.0	19.0
N_2	67.0	64.0	50.5	58.0
CO	0.3	0.5	1.0	0.9
CO_2	4.9	5.1	21.6	14.8
Sum	95.3	98.2	98.2	101.9

Table 8. Calculated G Values for Gas Production from Radiolysis of the SRAT and SME Product Samples from DWPF FA.13 Cold Run.

Experimental Details

	SRAT Product		SME Product	
	Test 1	Test 2	Test 1	Test 2
Final Dose, Mrad	11.8	14.8	14.3	18.7
Init. Press.,PSIA	14.7	14.7	14.7	14.7
Final Press., PSIA	16.2	17.6	17.1	18.4
Irradiation Time, hr	15.2	21.3	15.2	21.3
Mass Solution,g	42.9	42.9	55.7	54.1
Void Volume, cc	59.1	58.8	57.1	57.2

Calculated G Values

Component **G-Values Molecules/100 eV**

	SRAT Product		SME Product	
	Test 1	Test 2	Test 1	Test 2
Total Gas[a]	0.50	0.73	0.49	0.56
H_2	0.33	0.44	0.37	0.35
O_2	-0.05	0.07	-0.09	0.08
N_2	-0.04	0.00	-0.54	-0.22
CO	0.02	0.02	0.04	0.03
CO_2	0.30	0.24	0.78	0.56
Sum	0.56	0.77	0.53	0.81

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[a] Calculated from the least squares determination of the slopes of the linear portion of the curves in Figure 5. All other G-values calculated from the final pressure, final gas composition, and final dose.

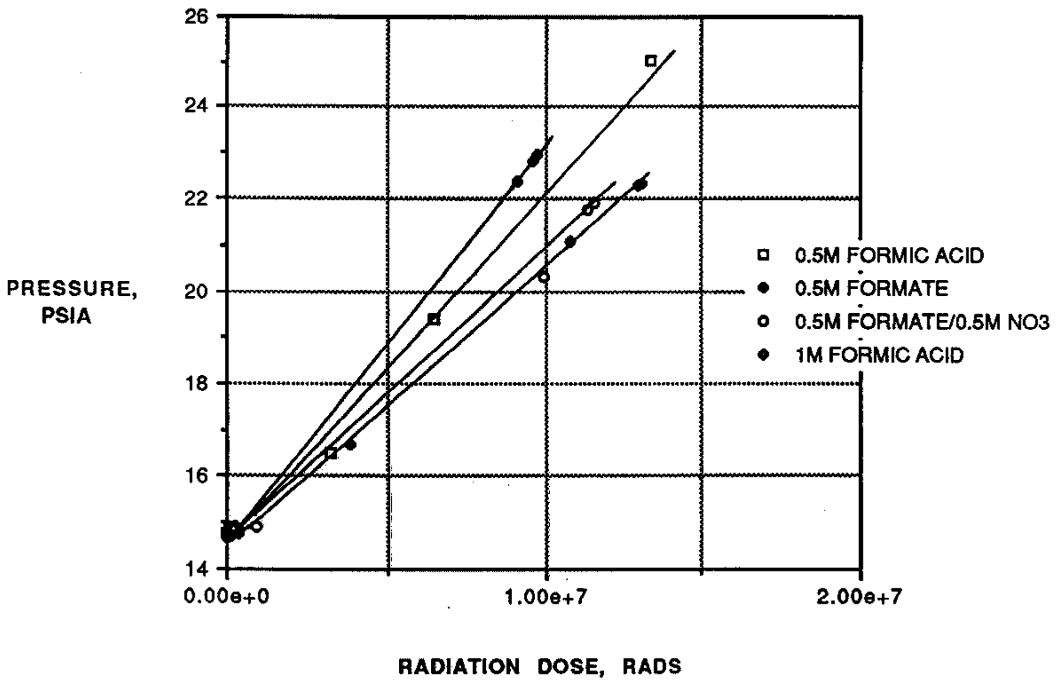

Figure 6. Pressures produced from radiolysis of formic acid, formate, and formate-nitrate solutions prepared at TNX.

Table 9. Final Gas Compositions from Radiolysis of Formic Acid and Formate Solutions. Duplicate Samples Irradiated

Experimental Details for Irradiation of one Set of Samples

	0.5M Formic Acid	**0.5M Formate**	**0.5M Formate 0.5M $NO3^-$**	**1.0 M Formic Acid**
Final Dose, Mrad	13.5	13.1	11.7	9.9
Init. Press., PSIA	14.9	14.7	14.8	15.0
Final Press., PSIA	25.1	22.4	21.9	23.2
Irradiation Time, hr	20.1	19.8	17.5	14.8
Mass Solution, g	35.0	35.0	35.1	35.1
Void Volume, cc	59.4	60.9	61.1	60.3

Average and Standard Deviations of Compositions of Gases Produced

Component		**Volume Percent**		
Formic	**0.5M Formic**	**0.5M Formate Acid**	**0.5M Formate 0.5M NO3-**	**1.0 M Acid**
H_2	19.0±0.30	18.1±0.15	5.5±0.16	15.7±0.70
O_2	10.9±0.05	11.8±0.51	10.7±0.16	11.7±0.04
N_2	41.1±0.49	44.7±2.17	40.7±0.16	44.4±0.37
CO	1.5±0.39	2.1±0.71	0.2±0.00	3.0±1.2
CO_2	23.9±0.01	20.0±2.6	34.1±0.02	23.2±0.57
N_2O	ND[a]	ND	9.4±0.10	ND
Sum	96.4±0.62	96.6±1.00	100.4±0.61	97.9±1.7

[a] ND = Not Detected

Table 10. Calculated G Values for Gas Production from Radiolysis of Formic Acid and Formate Solutions. Duplicate Samples Irradiated.

Experimental Details for Irradiation of one Set of Samples

	0.5M Formic Acid	0.5M Formate	0.5M Formate 0.5M NO3-	1.0 M Formic Acid
Final dose, Mrad	13.5	13.1	11.7	9.9
Init. Press., PSIA	14.9	14.7	14.8	15.0
Final Press., PSIA	25.1	22.4	21.9	23.2
Irradiation Time, hr	20.1	19.8	17.5	14.8
Mass Solution, g	35.0	35.0	35.1	35.1
Void Volume, cc	59.4	60.9	61.1	60.3

Average of Calculated G Values

Component	Average and Standard Deviation of G-Values, Molecules/100 eV			
	0.5M Formic Acid	0.5M Formate	0.5M Formate 0.5M NO3-	1.0 M Formic Acid
Total Gas[a]	3.5±0.07	2.8±0.33	2.9±0.42	3.9±0.26
H_2	1.8±0.00	1.6±0.07	0.52±0.00	1.9±0.13
O_2	-0.10±0.00	-0.12±0.00	-0.33±0.05	-0.17±0.00
N_2	-0.37±0.05	-0.44±0.04	-1.2±0.22	-0.66±0.14
CO	0.14±0.04	0.18±0.05	0.02±0.00	0.35±0.15
CO_2	2.2±0.03	1.7±0.31	3.3±0.11	2.7±0.00
N_2O	ND	ND	0.90±0.02	ND
Sum	3.6±0.13	2.9±0.29	3.2±0.39	4.1±0.43

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[a] Calculated from the least squares determination of the slopes of the linear portion of the curves in Figure 6. All other G-values calculated from the final pressure, final gas composition, and final dose.

Radiolysis of Formic Acid Solutions Prepared at SRTC

Higher concentrations of formic acid were investigated to determine if they caused a significant increase in $G(H_2)$ or if some bounding value for $G(H_2)$ was obtained. Formic acid solutions were prepared in SRTC using reagent grade 90 wt% formic acid and deionized water. The solutions investigated were 1, 2, and 3M formic acid. Analyses of the solutions confirmed these concentrations were achieved. Figure 7 shows the pressure increases for all three solutions. The increases appear essentially identical. The compositions of the gases produced by radiolysis are in Table 11 and the calculated G values in Table 12. The 1M formic acid was irradiated in duplicate to the same dose. Samples of 2M formic acid were irradiated to two different doses, and only one test was performed with the 3M formic acid. In that test, oxygen and nitrogen could not be determined after the irradiation due to an instrument malfunction. As with the DWPF slurries and the formic acid/formate solutions investigated earlier, the main gases were H_2 and CO_2. A maximum value of 2.0 ± 0.1 was obtained for these solutions. This was in 1M formic acid. At 2 and 3M formic the values are slightly lower. For these solutions then, a value of 2.0 ± 0.1 molecules/100eV is the bounding value for $G(H_2)$.

CONCLUSIONS

The data generated by this study and presented in this report support the following conclusions:

1. During the processing of radioactive slurries in the DWPF, radiolysis will produce H_2. Other gases such as CO_2, CO, and N_2O will also be produced depending on the composition of the slurry.

2. The production rates for hydrogen in terms of G values or molecules produced per 100eV of energy absorbed by the slurry depend upon the composition of the slurry. These production rates are summarized in Table 13.

3. In the DWPF the PHA slurry will produce hydrogen with the highest G value. This is because this slurry has the smallest concentration of nitrate ions which are excellent scavengers for the precursors of H_2.

4. The G values for hydrogen production in the DWPF slurries are smaller than in homogeneous solutions of formic acid or formate. For example, in the absence of nitrate, values as high as 2.0 molecules/100eV were obtained.

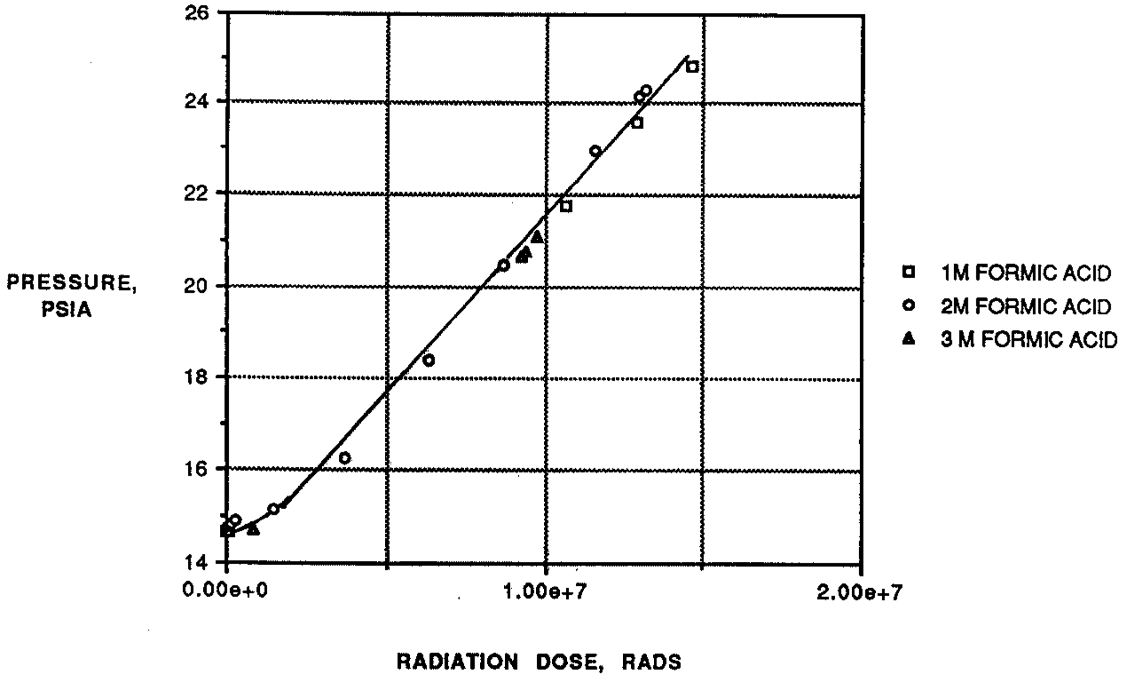

Figure 7. Pressures produced from radiolysis of 1, 2, and 3M formic acid solutions prepared at SRTC.

Table 11. Final Gas Compositions from Radiolysis of Formic Acid Solutions.

Experimental Details for Irradiation of Samples

	1M Formic[a]	2M Formic		3M Formic	
		Test 1[b]	Test 2[b]	Test 1[b]	Test 2[a]
Final Dose, Mrad	12.9	13.7	9.8	9.8	12.0
Init. Press., PSIA	14.7	14.7	14.7	14.7	14.7
Final Press., PSIA	24.7	24.3	21.3	21.1	22.94
Irradiation Time, hr	19.6	19.9	14.8	14.8	19.27
Mass Solution, g	30.0	30.0	30.0	30.0	30.1
Void Volume, mL	66.0	66.8	67.9	66.9	66.4

Compositions of Gases Produced

Component	Volume Percent				
	1M Formic[a]	2M Formic		3M Formic	
		Test 1[b]	Test 2[b]	Test 1[b]	Test 2[a]
H_2	15.9±0.6	13.0	13.0	11.7	13.3±0.3
O_2	12.0±0.7	11.6	13.7	7.5	7.3±0.3
N_2	44.5±1.9	42.9	49.6	27.6	26.8±1.5
CH_4	0.1±0.1	0.1	0.2	0.1	0.1±0.0
CO	1.2±0.0	1.9	1.1	1.6	1.4±0.1
CO_2	23.6±0.7	29.3	20.5	23.5	25.5±3.1
SUM	97.3	98.8	98.1	72.0	74.4

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[a] Average results from two identical solutions irradiated simultaneously.

[b] Results for a single irradiated sample.

Table 12. Calculated G Values for Gas Production from Radiolysis of Formic Acid Solutions.

Experimental Details for Irradiation of Samples

	1M Formic[a]	2M Formic		3M Formic	
		Test 1[b]	Test 2[b]	Test 1[b]	Test 2[a]
Final Dose, Mrad	12.9	13.7	9.8	9.8	12.0
Init. Press., PSIA	14.7	14.7	14.7	14.7	14.7
Final Press., PSIA	24.7	24.3	21.3	21.1	22.94
Irradiation Time, hr	19.6	19.9	14.8	14.8	19.27
Mass Solution, g	30.0	30.0	30.0	30.0	30.1
Void Volume, mL	66.0	66.8	67.9	66.9	66.4

Calculated G Values

Component	G Values				
	1M Formic[a]	2M Formic		3M Formic	
		Test 1[b]	Test 2[b]	Test 1[b]	Test 2[a]
Total Gas[c]	4.1±0.2	4.5	4.2	4.0	4.2±0.3
H_2	2.0±0.1	1.5	1.8	1.6	1.6±0.1
O_2	-0.09±0.1	-0.05	-0.05	-0.4	-0.7±0.0
N_2	-0.19±0.07	-0.40	-0.5	-3.6	-2.9±0.1
CH_4	<0.1	<0.1	<0.1	<0.1	<0.1
CO	0.14±0.0	0.16	0.15	0.2	0.2
CO_2	2.9±0.1	3.5	2.9	3.3	3.1±0.5
SUM	4.8±0.1	4.7	4.4	1.12	1.3±0.5

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[a] Average results from two identical solutions irradiated simultaneously.

[b] Results for a single irradiated sample.

[c] Calculated from the least squares determination of the slopes of the linear portion of the curves in Figure 7. All other G-values calculated from the final pressure, final gas composition, and final dose.

Table 13. G Values for Hydrogen Produced by Radiolysis in DWPF Product Slurries and in Formic Acid, Formate, and Formate-Nitrate Solutions.

DWPF Slurries	**G (H2), molecules/100eV** [a]
KTPB Slurry	0.34
PHA Slurry	0.77
SRAT Product	0.39±0.08
SME Product	0.36±0.01
Formic Acid/Formate Solutions	
0.5M Formic Acid	1.8 ± 0.0
0.5M Formate	1.6 ± 0.1
0.5M Formate, 0.5M NO_3^-	0.52± 0.0
1.0M Formic Acid	2.0 ± 0.1
2.0M Formic Acid	1.7 ± 0.2
3.0M Formic Acid	1.6 ± 0.1

[a] Average and standard deviation for duplicate experiments. KTPB and PHA Slurry results from single sample analysis.

QUALIFICATION OF DATA

The data presented in this report were collected using calibrated equipment and gas mixtures. All pressure measurements were taken by pressure transducers that were calibrated by the SRS Standards Laboratory. The transducers were sensitive to pressure fluctuations of ±0.01 PSIA. The gases used to calibrate the gas chromatograph were certified mixtures specially prepared by Scott Specialty Gases of Atlanta, GA. The gas compositions are certified to be within ±2% of the stated values. The general operating procedure for the gas chromatograph is in Reference 21. The amount of gamma ray energy absorbed by the slurries was determined by using two known standard dosimeters. One was a set of commercially available nylon film dosimeters impregnated by a radiochromic dye.[7] The other dosimeter is based on measuring the H_2 and O_2 evolved from radiolytic decomposition of water.[8] Results for this latter technique are singularly important in qualifying the data. The results confirm that the sealed irradiation vessel systems used in this study were operating properly and that the gas analyses and dose rate determinations were correct. The G values for H_2 and O_2 determined in this study for that dosimeter are in excellent agreement with the published G values.[8] All data for this study are recorded in laboratory notebooks, WSRC-94-326 and WSRC-93-148.

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APPENDIX 1. COMPOSITION OF IRRADIATED, KTPB SLURRY SIMULATING PRECIPITATE FEED TO THE DWPF

							PERCENT
SAMPLE #		1	2	3			**RELATIVE**
SAMPLE ID	UNITS	25559	25560	25561	**AVERAGE**	**ST.DEV.**	**ST.DEV.**
RADIATION DOSE	MRAD	190	190	190			
pH		10.2	10.2	10.2	10.2	0.0	0.1
WT% SOLIDS	**WT%**	10.4	10.4	10.3	10.4	0.1	0.6
TETRAPHENYLBORATE	**WT%**	7.7	7.6	8.1	7.8	0.2	3.1
INORGANIC AND ORGANIC CARBON							
TIC	**PPM**	963	908	1130	1000	115.6	11.6
TOC	**PPM**	50911	51521	56890	53107	3290.1	6.2
TIC+TOC	**PPM**	51874	52429	58020	54108	3399.5	6.3
TC	**PPM**	71682	71417	70930	71343	381.4	0.5
SOLUBLE ANIONS (Filtered)							
FLUORIDE	**MG/L**	<5	<5	<5			
FORMATE	**MG/L**	43	43	42	43	0.6	1.4
CHLORIDE	**MG/L**	<16	<16	<16			
NITRITE	**MG/L**	370	369	365	368	2.6	0.7
NITRATE	**MG/L**	5	6	6	6	0.6	10.2
SULFATE	**MG/L**	<14	<14	<14			
OXALATE	**MG/L**	<12	<12	<12			
PHOSPHATE	**MG/L**	<1	<1	<1			
SOLUBLE CATIONS (Filtered)							
AMMONIUM	**MG/L**	61.0	44.0	55.0	53.3	8.6	16.2
K	**PPM**	0.7	0.7	1.0	0.8	0.2	19.1
NA	**PPM**	566	550	547	554	10.2	1.8
B	**PPM**	95.2	96.4	99.2	97.0	2.0	2.1
CR	**PPM**	0.2	0.2	0.2	0.2	0.0	0.5
TOTAL CATIONS (SOLUBLE AND INSOLUBLE)							
HG (AA ANAL)	**PPM**	424	481	472	459	30.6	6.7
K (AA ANAL)	**PPM**	4939	6385	6017	5780	751.5	13.0
CU (ICP ANAL)	**PPM**	1.1	3.0	1.2	1.8	1.0	59.6
MN (ICP ANAL)	**PPM**	106	113	113	111	4.4	4.0
FE (ICP ANAL)	**PPM**	361	377	380	373	10.0	2.7
B (ICP ANAL)	**PPM**	2459	2530	2496	2495	35.8	1.4
TI (ICP ANAL)	**PPM**	837	866	856	853	14.9	1.7
NA (ICP ANAL)	**PPM**	1231	1221	1174	1209	30.4	2.5
K (ICP ANAL)	**PPM**	6812	7075	5876	6587	630.1	9.6
CR (ICP ANAL)	**PPM**	3.5	3.7	3.7	3.6	0.2	4.3
ORGANIC COMPOUNDS							
PHENYLBORONIC ACID	**MG/L**	480	491	534	502	28.5	5.7
ANILINE	**MG/L**	<1	20	23	22	2.1	9.9
PHENOL	**MG/L**	435	585	765	595	165.2	27.8
NITROBENZENE	**MG/L**	60	1	<1	31	41.7	136.8
NITROSOBENZENE	**MG/L**	<1	<1	<1	<1		
4-PHENYLPHENOL	**MG/L**	102	89	18	70	45.2	64.9
2-PHENYLPHENOL	**MG/L**	31	24	32	29	4.4	15.0
DIPHENYLAMINE	**MG/L**	16	19	78	38	35.0	92.8
BIPHENYL	**MG/L**	1020	1035	1353	1136	188.1	16.6
O-TERPHENYL	**MG/L**	28	27	55	37	15.9	43.3
M-TERPHENYL	**MG/L**	84	87	160	110	43.0	39.0
P-TERPHENYL	**MG/L**	41	43	79	54	21.4	39.4
DIPHENYLMERCURY	**MG/L**	272	1000	247	506	427.7	84.5