Radiolysis Gases from Nitric Acid Solutions Containing HSA and HAN (U)

by

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SUMMARY

The concentration of hydrogen (H_2) in the radiolytically produced off-gas from 2.76-4.25M HNO_3 /Pu solutions has been found to be greatly reduced in the presence of sulfamic acid (HSA) and hydroxylamine nitrate (HAN). The H_2 concentration ($[H_2]$) is reduced from 35 percent to about 4 percent by dilution caused from an increase in the production rates of nitrogen (N_2), nitrous oxide (N_2O), and oxygen (O_2) gases. The generation rate of H_2 was not affected by HSA or HAN giving a measured radiolytic yield, $G(H_2)$, value of 0.201 molecules/100 eV for 2.765M NO_3^- solution (a value of 0.213 is predicted from previous data). The $G(H_2)$ values are dependent on the solution nitrate concentration ($[NO_3^-]$). The generation rates of N_2 , N_2O , and O_2 are not dependent on the $[NO_3^-]$ in this narrow range, but are dependent on the presence of HSA and the concentration of HAN.

The percentage $[H_2]$ for the 2.5 to 3.0M NO_3^- range expected in the off-gas from the FB-Line Pu^{+3} Hold Tanks is conservatively estimated to be about 3.5 to 4.5% for Pu^{+3} solutions initially containing 0.023M HAN/0.165M HSA. The upper limit $[H_2]$ may actually be about 4.1% (4.3% at 90% confidence limits) but more "initial" off-gas rate data is needed at about 2.9M $[NO_3^-]$ in Pu^{+3} solution for verification. Addition of ascorbic acid had no effect on the off-gas rate of Pu^{+3} solutions containing HSA and NO_3^- concentrations higher than those expected in the hold tanks.

The maximum "hold time" for 50 grams/liter Pu^{+3} /0.165M HSA/0.023M HAN/2.5-3.0M HNO_3 solution is 20.3 ± 2.1 days. After this time the HSA initially present will become exhausted and the $[H_2]$ will increase to 35%. This hold time may be longer in $[NO_3^-] < 3.0M$, but again more study is needed.

INTRODUCTION

Bombardment of aqueous solutions by alpha (ionizing) radiation generates broken fragments, radicals and ions, of the water and chemicals in solution^{1,2,3,4,5}. This process, called radiolysis, generates gases such as hydrogen and oxygen which are released as off-gas at a rate equal to their net production rate in solution. The generation rate of the various radiolysis products is proportional to the total dose of alpha energy imparted to the solution. The rate is usually defined in terms of the number of molecules produced per 100 eV of alpha dose, denoted $G(H_2)$ for hydrogen gas.

Many chemicals and certain physical processes can have an effect on the $G(H_2)$ value. Nitrate has a very pronounced effect on the $G(H_2)$ value because of its' ability to scavenge aqueous electrons, $H_2O^\cdot$, generated by radiolysis^{1,2,3,4,5,6}

Aqueous electrons are precursors of hydrogen gas.

As the nitrate concentration in solution increases the $G(H_2)$ value decreases².

Nitrate may also have an effect in minimizing any acid, H^+ , dependence on radiolytic hydrogen formation. High acid concentrations could aid in the production of hydrogen by helping to form hydrogen atoms, $H^\cdot$, which can recombine or react with aqueous electrons to form hydrogen.

Hydrogen atoms react quicker than aqueous electrons with all species to form hydrogen gas⁶. They are also more stable with respect to oxidation by all oxidants, such as nitrate and hydroxyl ions, which could stop it from forming hydrogen gas. The reason hydrogen formation is independent of acid concentration is probably because alpha bombardment of nitrate produces species such as $NO^\cdot$, $NO_2^\cdot$, $\cdot O^-$, and $O_2^\cdot$ which may be able to absorb sufficient H^+ to effectively deplete it from the "recombination zone", approximated by the original alpha track of broken molecules^{6,7}. There are many recombination reactions producing a variety of species. In 2.5M HNO_3 solution the main off-gases are hydrogen, $G(H_2)=.23$, and oxygen, $G(O_2)=.45$.

A physical process which has an effect on the $G(H_2)$ value is mechanical stirring². This is because hydrogen is oxidized in solution by oxidants such as hydroxyl ions. Stirring degasses hydrogen from solution thus limiting its contact with these oxidants. The hydrogen off-gas rate, $G(H_2)$, is therefore increased with stirring.

The energy of a 5 MeV alpha particle is imparted to the solution along a nearly linear path defined by a column approximately 100 angstroms wide⁷ and 0.0034 cm long⁸ ($2.0E-8$

cm³). It is within this column that most of the fragments recombine. The literature points out that in nitric acid solutions of moderate strength as much as 90% of the radiolysis generated nitrite (NO₂⁻) and hydrogen peroxide (H₂O₂) recombine to reform nitric acid and water⁴. Using a G(H₂O₂) value of 1, about 50,000 molecules will be produced in the column giving an initial concentration of 0.03M. Scoping studies⁹ had shown that H₂O₂ reaction with NO₂⁻ was about 25% faster than for 80% sulfamic acid (HSA) - 20% hydroxylamine nitrate (HAN) solution in 2.5M HNO₃. Calculations predicted the HSA and HAN would effectively compete for nitrite in a solution 0.165M HSA/0.023M HAN/2.5M HNO₃ since these two compounds would be in much greater concentration than H₂O₂ in the recombination zone. Reaction of HSA and HAN with the radiolysis generated nitrite produces large amounts of N₂ (nitrogen) and N₂O (nitrous oxide) gases by the reactions

The G(O₂) value also increases with HSA and HAN in solution since the unreacted H₂O₂ eventually decomposes to form O₂ and water. The radiolysis hydrogen concentration in the off-gas from nitric acid solutions containing HSA and HAN will therefore be much lower than the 35% normally seen, not because of a change in G(H₂), but through dilution by released N₂, N₂O, and O₂ gases.

EXPERIMENTAL

A Scoping Study incorporating nonradioactive and radioactive experiments determined further work feasible. A Task Study^{10,11} was then performed guided by the earlier findings. The Task was divided into two portions, denoted Tasks #1 and #2¹¹, which were performed concurrently. The necessity for performing two sets of experiments was the relatively small amount of Pu⁺³ that could be produced and cleaned from a "column run"¹², about 5 grams in 110 ml solution. In a column run the Pu is reduced to the +3 state with ascorbic acid/HAN, absorbed onto a cation exchange resin, rinsed clean of contaminants, and then eluted to give concentrations of about 50 grams per liter. This small amount of Pu limited the total amount of radiolysis gases that could be generated per week. All column runs were performed, producing Pu⁺³ solutions, in Task #2. Task #1 used 20.59 grams of Pu⁺⁴ in 475 ml of solution to generate the large amount of gas required, over 300 ml, to purge the gas sample tube sufficiently to obtain weekly gas samples for analysis. Task #2 was performed to compare the Pu⁺³ and Pu⁺⁴ off-gas generation rates. A correlation could then be made for the %H₂ concentration in the Pu⁺³ off-gas, assuming that the hydrogen production rate is unaffected by the Pu charge. Performing both was fortuitous in that differences were found to be associated with the charge of Pu and also with high [HNO₃]. These findings will be discussed later. The experimentally generated data and calculations from this study are documented in a Calculation Note¹³.

Scoping Study (Nonradioactive and Pu⁺⁴ Experiments)

Scoping Studies were performed to determine the feasibility of further work into the effects of HSA and HAN on reducing the hydrogen concentration in the off-gas of plutonium solutions. First a comparison of the relative reaction rates for nitrous acid reacting with H₂O₂ (hydrogen peroxide) and a combination of HSA and HAN was performed. As mentioned earlier nitrous acid was found to react 25% faster with H₂O₂ than with an equivalent combined concentration of HSA and HAN under the same conditions. Calculations revealed⁹ that the HSA and HAN might very possibly compete for the nitrite produced from nitrate radiolysis.

A decision was made to further investigate the effects of these compounds using Pu⁺⁴ in nitric acid solution at concentrations similar to those expected in the FB-Line Pu⁺³ hold tanks¹⁴. The experimental system (general design) used for all radioactive work is shown in Figure 1 (most resembles Task #1 apparatus). An attempt was made to set the [NO₃⁻] for the solution at the lower limit for the tanks, 2.5M, to give a conservative %H₂ in the off-gas. The G(H₂) value, molecules of H₂ formed per 100 eV of alpha dose, increases with decreasing [NO₃⁻]². The analysis of the solution used gave 2.38M NO₃⁻. This conservatism was lost when the next four analyses of the "same" solution, during Task #1, resulted in an average of 2.765 ± .112M (Table 1). This didn't produce a problem since the G(H₂) values are well known for [NO₃⁻] from zero to 10M allowing extrapolation to the low nitrate concentration region². The concentration of HSA and HAN was set at half that expected initially from processing to allow depletion of the HSA and HAN, and completion of the experiment, in only a few weeks.

During the scoping work much of the analytical methodology was developed. A technique for freezing the radiolytic and acidic decomposition of HSA during sampling was developed. The ability to analyze for HSA (sulfamate) by Ion Chromatography (IC) was tested and found satisfactory. A satisfactory analysis for HAN could not be found. Other techniques were also developed. A systematic error was found in total off-gas rate measurements when inverted burette readings were taken initially in the morning and final readings were taken in the afternoon (gave a high value). This was probably caused by changes in the ventilation system during the day. Taking readings over near 24 hour periods gave more consistent data and this technique was used for the Task studies.

The Scoping study ended with the depletion of the HSA and HAN, when the off-gas rate dropped to about a tenth of that observed earlier. The nitrite generated from radiolysis completely scavenged any remaining traces of these two reducing agents. The first gas analysis of the scoping study detected N₂O, which is a product of HAN reaction with HNO₂ (nitrous acid). The second gas analysis observed very little N₂O. There was no observed change in the total off-gas rate observed; therefore it was assumed that the HAN acted in the same manner as the HSA. Since there was no analytical method for HAN, only HSA was added in Task #1. Also the Scoping study had been performed with HAN present in the appropriate concentration. The only data generated during the Scoping Study that was used for calculation of results¹³ was the [Pu] data obtained at the beginning of the Scoping Study. This data was acquired with the same level of control as the data generated in the Task portions of this study and averaged, after a small correction for dilution, with the other [Pu] data obtained for Task #1.

Task #1 (Pu^{+4})

The Task #1 solution was generated by adding 4.029 grams of HSA (sulfamic acid) to the Scoping study solution. Sampling of the Task #1 solution just after generation (and later samplings for nitrate) determined the initial solution to be 2.2M H^+ /2.765M NO_3^- /0.1325M HSA/0.181M Pu. The time of addition of HSA defined time zero for the experimental data. The reaction system is shown in Figure 1. Once the system was sealed the radiolytically generated off-gases purged the gas space of the reaction bottle and the gas sample tube. The total amount of off-gas needed to adequately flush the gas space was about 300 ml requiring about one week of gas generation per gas sample¹³. A total of three samples were transferred to the Shielded Cells (SRTC) area for gas chromatogram (GC) analysis. Adequate analysis for hydrogen was not obtained with the first sample. The GC was calibrated just prior to analysis¹⁰ to $\pm 2\%$. The GC system measured the concentrations of hydrogen, oxygen, nitrous oxide, and carbon dioxide to a quoted precision of $\pm 10\%$.

When the gas sample tube was removed for GC analysis solution samples were taken for analysis of nitrate, sulfamate, sulfate, and ammonium ion by Ion Chromatography (IC). In order to minimize removal of reaction solution, 100 lambda samples were taken and diluted into a known weight of deionized water¹³. This dilution was also used to freeze the radiolytic destruction of nitrate and sulfamate since the fraction of nitrite formed per unit of alpha dose is very small in dilute nitric acid solutions^{2,4}. This dilution also essentially stopped the chemical hydrolysis of sulfamate since the hydrolysis rate is acid dependent¹⁵. Quadruplicate samples were taken to determine the error in sample preparation and in analysis by ADS on a given day (assuming the instrument is calibrated daily).

The production rate of radiolysis gases were measured using an inverted burette (Figure 1). The temperature from day to day stayed fairly constant, $\pm 2^\circ\text{C}$, and averaged about 23°C . The pressure at times changed rapidly with the passage of a weather front. Therefore atmospheric pressure readings were taken for the initial and final volume measurements and normalized to one atmosphere pressure¹³. A correction was also included for the reduction in pressure of the collected off-gas for the column height of the water above the water level in the beaker.

Task #2 (Pu^{+3})

For Task #2 column runs, described earlier, were performed¹² to produce solutions of Pu^{+3} containing H^+ , NO_3^- , HSA, and HAN in concentrations similar to those expected in the Pu^{+3} Hold Tanks of FB-Line. The nitrate and HSA concentrations for these column runs was higher than the range expected for the Pu^{+3} hold tanks. This difference was probably due to a difference in the cuts to produce the "hearts" solution used¹⁶. The reaction solutions were sampled initially after production and at the end of study prior to depletion of the HSA. Sampling was performed as in Task #1.

The experimental apparatus used was similar to that shown in Figure 1 but used a 100 ml graduated cylinder fit with a ground glass joint (120 ml total volume) as the reaction vessel and a 25 ml titration burette (inverted) to catch and measure the off-gas. Off-gas volume measurements (rates) and data processing was performed in the same manner as in Task #1. Because of the small amount of Pu that could be processed in each column run, gas sample analysis (GC) of the generated off-gas was not performed.

RESULTS AND DISCUSSION

The raw data from this work is tabulated and processed in a Calculation Note¹³. The reaction solution component concentrations are given in Table 1. The errors listed in this report are at the 90% confidence limit¹³, unless stated otherwise.

Table 1. Radiolysis Conditions Versus Time (Component Concentrations).

Date	[H ⁺] (Molar)	[NO ₃ ⁻] (Molar)	[HSA] (Molar)	[SO ₄ ⁻²] (Molar)	[HAN] (Molar)	Pu (grams)
Scoping Study						
11/17/93	~2.2	~2.38	.0878±.0004	~0	.0122±.0000	20.59±.47
12/10/93	"	2.38±.36	.0187±.0028	.0865±.013	~0	"
Task #1						
1/11/94	2.2±.14	2.43±.15	.132±.031	.110±.010	~0	20.59±.47
1/24/94	"	2.85±.27	.0857±.008	.148±.011	"	"
1/31/94	"	2.74±.20	.0538±.0044	.147±.021	"	"
2/7/94	"	2.81±.13	.0320±.0065	.152±.028	"	"
[NO ₃ ⁻] average = 2.77±.11						
Task #2 - Column Run #1						
1/20/94	3.52±.14	4.086±.057	.315±.008	.0421±.0012	~.023	5.80±.17
with Ascorbic acid						
2/7/94	"	4.29±.19	.153±.010	.081±.024	~0	"
[NO ₃ ⁻] average = 4.25±.17						
Column Run #2						
2/15/94	3.045±.077	3.35±.21	.254±.007	.065±.006	~.203	4.75±.10
[NO ₃ ⁻] average = 3.75±.16 (all column run #2 values averaged together)						
Column Run #2, Attempted Dilution to 2.9M NO ₃ ⁻						
2/23/94	~2.64	3.45±.23	.231±.011	.0714±.0061	.203	4.13±.09
2nd Analysis	"	3.56±.15	.174±.015	.0636±.0078	"	"
3/29/94	"	2.86±.12	.0523±.0036	.149±.0063	"	"
[NO ₃ ⁻] average = 3.26±.14 (all column run #2 values averaged together)						

Pu⁺⁴ Solutions (Scoping Study and Task #1)

The off-gas rate data corrected to one atmosphere pressure and 23°C for the Scoping and Task #1 studies is plotted versus time in Figure 2. The linear fit data to Figure 2 is given in Table 2. The plot of "HSA only" is the data from Task #1. The data from the Scoping Study ("HSA and HAN") is higher due to the systematic error described earlier. Both sets of data point out that the off-gas rate is nearly linear and constant with time up to depletion of the sulfamic acid. Initially, during the first day, the off-gas rate is higher probably due to the reaction of HAN with either Pu⁺⁴ or nitric acid (or a combination). This idea was tested by adding HAN to a Pu⁺⁴ solution not containing HSA. The off-gas rate was initially very high, 39 ml/day/gram at 0.44 days¹³, but then quickly fell to zero. The dip below zero is attributed to the reaction of generated NO (now formed because of the lack of a reducing agent, HSA or HAN) with O₂ to form NO₂ which is quickly reabsorbed. Without HSA or HAN the total off-gas rate is about an order of magnitude lower^{2,4} (and 35% H₂).

The off-gas component concentrations for the various gas samples analyzed are given in Table 3. The measured H₂ concentration from the Scoping and Task Studies averages 3.57±.10%¹³ (statistically the same). There is a marked difference in oxygen concentration between the two studies. The presence of HAN in solution for the first gas sample in the

Table 2. Linear Fits to Off-Gas Rate Versus Time Data

	Plot Description	Intercept	slope	Rate at (ml/g Pu/day) 3.0 days	Rate at (ml/g Pu/day) 15.0 days
Pu ⁺⁴	HAN only	36.922	-27.873	-	-
(Scoping & Task #1)	HSA only (without 14.45 day data)	2.762	2.219E-3	-	2.795
	HSA & HAN	3.278	5.901E-4	-	-
Pu ⁺³ (Task #2)					
0 - 4.5 days	4.245M NO ₃ ⁻	2.294	.0100	2.324	-
"	3.750M NO ₃ ⁻	2.366	-.0267	2.286	-
"	3.255M NO ₃ ⁻	2.406	.0294	2.494	-
4.5 -12 days	4.245M NO ₃ ⁻	2.179	.0441	-	-
"	3.750M NO ₃ ⁻	2.088	.0709	-	-
"	3.255M NO ₃ ⁻	2.546	7.98E-3	-	-
over 12 days	4.245M NO ₃ ⁻	2.822	-5.18E-3	-	2.745
"	3.255M NO ₃ ⁻	2.705	-2.80E-3	-	2.663
				average = 2.73±.11	

Table 3. Pu⁺⁴ Solution Off-Gas Component Concentrations^{17,18}.

date	H ₂ %	O ₂ %	N ₂ O%	CO ₂ %	Balance, N ₂ %
Scoping Study (HSA and HAN)					
11/22/93	3.52	26.6	5.1	0.1	64.68
12/2/93	3.69	23.3	0.2	0.1	72.71
Task #1 (HSA only)					
1/24/94	-	42.1	0.1	0.05	
1/31/94	3.57	48.3	0.06	1.0	52.93
2/7/94	3.51	45.9	0.01	0.05	49.47
average = 3.57±.10					

Scoping Study, representing the first week, may account for this lower oxygen concentration (discussed later) but the second analysis shows no sign of N₂O (from nitrite reaction with HAN) and is still low in oxygen. Interestingly, the total off-gas rate is about the same.

The normally tabulated value for the relative production rate of compounds from radiolysis is the G value, denoted G(H₂) for H₂, and represents the molecules produced per 100 eV of radiation dose (in this case alpha). G(H₂) is given by

$$G(H_2) = \frac{[H_2](R, \text{ ml/gPu} \cdot \text{day})(6.023E23 \text{ mol./mole})}{(1.207E15 \text{ MeV/gPu} \cdot \text{day})(1E4 \text{ 100eV/MeV})(24,287 \text{ ml/mole, 1 atm \& 23}^\circ\text{C})} \quad (7)$$

where [H₂] is the fractional concentration of hydrogen in the off-gas and R is the total off-gas production rate. The dose imparted to the solution per gram of Pu per day, 1.207E15 MeV^{19,20}, is for weapons grade Pu. The average off-gas rate, R, for the Pu⁺³ and ⁴ data is 2.73±.11 ml/gPu·day (Table 2). The average [H₂] in the off-gas for the Pu⁺⁴ solutions is 3.57±.10% (Table 3). This gives a G(H₂) value of .201. the G values for oxygen and nitrogen can be determined by replacing [H₂] by the appropriate fractions for these two compounds.

There is considerable data for G(H₂) values for "stirred" Pu⁺⁴ solutions over a large range of nitrate concentrations^{2,4}. The production rate of hydrogen from radiolysis, proportional to G(H₂), is normally via aqueous electrons and therefore is related to the water concentration in solution. The [H₂O] in nitrate (or HNO₃) solution should therefore be inversely proportional to the [NO₃⁻]. The G(H₂) versus [NO₃⁻] data, including the point from this work, is very well fit¹³ by the simple equation

$$G(H_2) = 1.217/(1+1.702[NO_3^-]) \quad (8)$$

A total of 36 data points were used in this fit, Figure 3, giving a calculated error (90%

confidence limits¹³) of $\pm 3.26\%$ over the full concentration range, 0 to 10M NO_3^- . The value calculated for $G(\text{H}_2)$ using this equation for 2.765M nitrate is 0.213 making the value from this study 5.8% low.

Pu^{+3} Solutions (Task #2)

The radiolysis conditions for the Pu^{+3} solutions (Task #2) are shown in Table 1. The off-gas data are plotted in Figure 4. The line fits to the data, Table 2, extend to the data points included in the fit, note some overlap. There seems to be three distinct regions to the off-gas data versus time for these solutions (Figure 4). There is initially a relatively low off-gas rate region which is generally flat lasting about 4 days. Next there is a transition region lasting about 8 days in which the off-gas rate increases at a constant rate to a level similar to that of the Pu^{+4} /HSA system. At the 15 day point the off-gas rate for the 4.245 and 3.255M nitrate solutions are 2.745 and 2.663 ml/g Pu-day respectively, Table 2. The rate in 2.765M nitrate/ Pu^{+4} solution, 2.795, is within the statistical range of these two values. This shows that the total off-gas rate is very constant in HSA/ Pu^{+3} or $^{+4}$ solution from 2.765 to 4.245M nitrate concentration.

Since there wasn't an analytical test for HAN, the dependence on HAN was tested by adding hydroxylamine-sulfate ($\text{NH}_2\text{OH}\cdot\text{H}_2\text{SO}_4$) into the 3.75M nitrate run (Figure 4) at about 7.5 days, after dilution to 3.255M nitrate. As can be seen from the graph the initial off-gas rate once again was reduced but not as far. An increase in the initial off-gas rate compared to the 4.245M NO_3^- rate was not unexpected since autocatalytic reaction of HAN with nitric acid is sensitive to the nitric acid concentration in the 2.8 to 3.2M region²². The just referenced work has a plot of "Variation of rate of nitrous acid formation in the oxidation of hydroxylamine by nitric acid at 25°C" for 0.01 M HNO_3 , etc., from 2 to 8M HNO_3 which has an inverse plot very similar to Figure 5. Figure 5 is a plot the off-gas rates at day 3 in Figures 2 and 4. If the generation of species such as HNO , by reaction of HAN and nitric acid (discussed later), are reducing the total off-gas rate this "HAN affect" may be lost at $[\text{NO}_3^-]$ less than about 3.0M and therefore wouldn't be of concern for the conditions of the Pu^{+3} Hold Tanks. The 3.255M NO_3^- data was expected to be for 2.9M NO_3^- (this was the expected result from the dilution) and should have resolved this question. Data therefore still needs to be acquired at about 2.9M NO_3^- .

Affect of Ascorbic Acid on Off-Gas Rate

Ascorbic acid was added to the 4.245M $\text{NO}_3^-/\text{Pu}^{+3}$ solution generated from column run #1 at the 18 day point, Figure 4. The initial [ascorbic acid] was 0.060M. The initial high value may have been due to mechanical vibrations, centrifuge operation, in the glovebox used for the study. Ultrasonic vibrations de-gas solutions in much the same manner as stirring. This would also account for the later low off-gas rates observed as the main product gases (N_2 and O_2) established a new equilibrium. Since the average off-gas rate is close to that observed before the

addition of ascorbic acid there is no significant effect.

Off-Gas Hydrogen Concentrations in Pu⁺³ Hold Tanks

The hydrogen concentration expected in the off-gas can be calculated from its generation rate, $G(H_2)$, and the total off-gas rate, R . The equation is the same as described earlier, equation (7), with some rearrangement and multiplication.

$$\%H_2 = \frac{(G(H_2), \text{ mol./100eV})(48.67, 100\text{eV}\cdot\text{ml/gPu}\cdot\text{day}\cdot\text{mol.})}{(R, \text{ ml/gPu}\cdot\text{day})} \quad (9)$$

The error associated with the $\%H_2$ values are due to the errors in the $G(H_2)$ and R values. The error determined for $G(H_2)$ is 3.26% (90% confidence limits)¹³. This value is produced from more than one study and therefore should be more confident than data from one source which could have an undetected systematic errors. The error associated with R is extracted from the variance in data determining this value. The $\%H_2$ needs to be calculated at two different times. R changes with time from an initially low but constant value to a higher value after about two weeks. The data that most closely represents the "initial" off-gas rate for Pu⁺³ solutions in the nitrate range expected for the Pu⁺³ Hold Tank conditions is for 3.255M NO₃⁻, Figure 4, giving an R value of $2.510 \pm .029$ ¹³. The value for R after 2 weeks is determined at 15 days and is $2.73 \pm .11$ (4.1%), Table 2. Since this value was determined from three different experiments (two different experimental systems) it includes errors associated with volume measurements, calculation of total grams Pu in solution, and burette readings. Since the "initial" rate R value does not include these other sources of error, this percentage error (4.1%) is also used for the initial rate error making it $2.51 \pm .10$. The values for R at the 15 day point show that once the HAN is depleted the total off-gas rate is independent of the Pu charge (at least +3 and 4) and the nitrate concentration. For initial R the $\%H_2$ is¹³

$$\%H_2 = (48.67)\left(\frac{G(H_2)}{R}\right) = (48.67)\left(\frac{1.217/(1+1.701[NO_3^-])}{2.51}\right) \pm 5.24\% \quad (10)$$

The 2 week value is obtained by replacing the 2.51 value with 2.73. Calculations for $\%H_2$ in the off-gas for varying $[NO_3^-]$ and the upper 90% confidence value are given in Table 4.

"Hold Time" of HSA in Pu⁺³ Solutions

The $[H_2]$ in the off-gas is reduced to near 4% only until the HSA in solution is depleted. The rate at which the HSA is destroyed is determined mainly by the total alpha dose, proportional to grams Pu, per unit volume of solution. A smaller contributing factor is

Table 4. % $[H_2]$ in Off-Gas for Pu^{+3} Hold Tank Range of Conditions.

$[HNO_3]$ <u>initial</u>	$[NO_3^-]$ <u>Molar</u>	$G(H_2)$ Bibler <u>Savel'ev</u>	$H_2\%$ <u>initial</u>	$H_2\%$ <u>initial(90%)</u>	$H_2\%$ <u>2 weeks</u>	$H_2\%$ <u>2 weeks(90%)</u>
2.50	2.523	0.230	4.460	4.693	4.094	4.308
2.55	2.573	0.226	4.389	4.619	4.029	4.240
2.60	2.623	0.223	4.321	4.547	3.967	4.174
2.65	2.673	0.219	4.254	4.477	3.906	4.110
2.70	2.723	0.216	4.190	4.409	3.847	4.048
2.75	2.773	0.213	4.128	4.344	3.790	3.988
2.80	2.823	0.210	4.067	4.280	3.734	3.929
2.85	2.873	0.207	4.009	4.218	3.680	3.873
2.90	2.923	0.204	3.951	4.158	3.628	3.817
2.95	2.973	0.201	3.896	4.100	3.577	3.764
3.00	3.023	0.198	3.842	4.043	3.527	3.712

hydrolysis but the rate is comparatively low near room temperature and included in the experimentally determined loss rate. The [HSA] versus time for Task #1 and both column runs of Task #2 are plotted in Figure 6. The [Pu] varied from 35 to 51 grams liter of solution (not normalized for [Pu] in Figure 6). Note the very linear drop in [HSA] for the Pu^{+4} solution. This is expected since radiolysis production of nitrite should be the major mechanism for destruction of HSA. The calculated "hold time" for 0.165M HSA and 50 grams/liter Pu^{+3} is given in Table 5, data from Table 1. The hold time is given by

$$H.T. = (\Delta Time)(.165)[Pu]/(\Delta[HSA])(50 \text{ g/l Pu}) \quad (11)$$

Table 5. Hold Time for HSA in Pu^{+3} Solutions.

<u>Initial</u> <u>Sampling Time</u>	<u>Final</u> <u>Sampling Time</u>	<u>[Pu]</u> <u>grams/liter</u>	<u>$\Delta[HSA]$</u> <u>Molar</u>	<u>50 g/l Pu and .165M HSA</u> <u>Days to Depletion</u>
0.00	17.95 days	51.319	0.1617	18.79
0.00	33.87 days	34.805	0.1784	21.81
				average = 20.30
				std dev. = ± 2.14

The value for the Pu^{+4} solution calculated in this manner is 38.4 days. The radiolytic generation rate of HNO_2 , $G(\text{HNO}_2)$, increases with nitrate concentration⁴ but this change must be small over the range of nitrate concentrations measured, 2.765 to 4.245M, since the rate of off-gas production stays nearly constant. The shorter hold time observed for the Pu^{+3} solutions is probably due to HSA reaction with HAN oxidation species (discussed in the next section). The HAN added to the initial Pu^{+3} solution diluted to 3.26M NO_3^- resulted in a [HAN] of 0.0236M. The resulting hold time was 21.81 days. The [HAN] for the 18.79 day value is not known but resulted from column run #1 and should have been in the range of 0.023M. The value of 20.3 days gives a good estimate of the hold time for a Pu^{+3} solution initially 0.165M HSA/0.236M HAN/2.5 to 3.0M HNO_3 .

Solution Chemistry Effect on Off-Gas Rate

The rate of nitrous acid formation should be related to the decrease in off-gas rate because nitrous acid is generated from HNO ^{22, 23, 24}. HNO can react with O_2 in solution producing HNO_3 directly, reducing the total off-gas rate and the dilution of $[\text{H}_2]$. The formation and reaction of HNO varies according to the oxidants in solution and the nitric acid (nitrate) concentration. Below about 2.8M nitrate, the HAN should be mainly oxidized by Pu^{+4} (in Pu^{+4} solution)²³ by reactions of the type.

The HNO can be further oxidized to nitrous acid or nitric oxide²²

At nitric acid (nitrate) concentrations higher than 2.8M, the oxidation by nitric acid will occur in much the same manner²². The nitrous acid generated is quickly reduced to N_2 or N_2O by the HSA or HAN in solution.

The NO produced in reaction (15) also contributes to the production of N_2 and N_2O by reduction of nitric acid to nitrite

The rapid oxidation of HAN by Pu^{+4} and corresponding greatly increased off-gas rate are

observed in Figure 2 at the beginning of the Scoping Study run, "HSA and HAN", and for the "HAN only" run. The oxidation is surmised to be by Pu^{+4} because there isn't an equivalent initial increase in the Pu^{+3} solutions, even at higher nitrate concentrations. The HSA and HAN, both strong reducing agents, are limiting the autocatalytic oxidation behavior of the nitrate (nitric acid) by keeping the concentration of nitrous acid low. Oxygen is abundant in the Pu^{+4} solutions from radiolysis (Table 3) and there isn't any reason for a Pu^{+3} system to be any different. The reduced concentration of oxygen in the off-gas in the Scoping Study is probably due to formation of NO, via HNO, by traces of HAN. The oxygen enters the reaction by

Note how one molecule of N_2 or N_2O is formed, reaction (16) and (17), for each molecule of oxygen consumed. This is how the oxygen concentrations in the Scoping and Task #1 Study can be different but the total off-gas be about the same.

The Pu^{+3} solutions are interesting because there is an initial decrease in the total off-gas rate in a nitric acid (nitrate) concentration range where oxidation by nitric acid should produce large quantities of nitrous acid²² according to the above equations. The lack of autocatalytic oxidation is once again due to the presence of HSA and HAN. Pu^{+3} is not an oxidizing agent. This should allow the build-up of HNO, as in reaction (13), but with nitric acid as oxidant. The initial reduction in total off-gas rate is probably due to the reaction of HNO with dissolved O_2 ²⁴

Not only does this remove oxygen from the off-gas but eliminates the possibility of production of HNO_2 and subsequent production of N_2 or N_2O . Also the potential off-gas via HNO can be cut in half by²⁴.

This explains the reduction in off-gas rate until the HAN is destroyed in Pu^{+3} solutions.

The shorter hold time observed for Pu^{+3} as compared to Pu^{+4} solutions is probably due to HSA reaction with HAN oxidation species, especially HNO_2 . These reactions would potentially produce extra N_2 off-gas, but this must not make-up for the O_2 lost to HNO reaction. If this mechanism is correct this faster HSA destruction rate would end with the destruction of HAN and may not occur at $[\text{NO}_3^-]$ less than about 2.9M. It is therefore possible that in the $[\text{NO}_3^-]$ range of the Pu^{+3} Hold Tanks the hold time may be closer to 38 days.

The change in oxidation rate of HAN with nitric acid (nitrate) in the 2.8 to 3.2M range is very steep²² and decreases with decreasing $[\text{NO}_3^-]$. The Pu^{+4} value in Figure 5 represents an upper limit off-gas rate (no reaction of HAN with HNO_3). A curve in Figure 5 following the Pu^{+3} values probably would reach this limit at a nitrate concentration higher than 2.8M²². Another data point needs to be obtained at this $[\text{NO}_3^-]$ to verify this prediction.

CONCLUSIONS

The $\%[\text{H}_2]$ in the 2.5 to 3.0M NO_3^- range should be about 3.5 to 4.5%, as shown in Table 5, for Pu^{+3} solutions that initially contain 0.023M HAN/0.165M HSA. In Pu^{+3} solution, $[\text{NO}_3^-] > 3.0\text{M}$, nitric acid oxidation of HAN generates species that probably react with dissolved O_2 to reduce the total off-gas rate. This lower off-gas rate reduces the dilution of radiolytically produced H_2 . The upper limit $\%[\text{H}_2]$ may actually be about 4.1% (4.3% at 90% confidence limits) at $[\text{NO}_3^-] < 3.0\text{M}$ but more "initial" off-gas rate data is needed at about 2.9M NO_3^- for verification. Further work could also include measurement of the effect of urea on the total off-gas rate. Per unit of nitrous acid reacted, urea will produce 50% more gas than HSA or HAN. The products from reaction of urea with nitrous acid are N_2 and CO_2 (no residual sulfate).

HSA is consumed at a constant rate, mainly defined by the radiolytic generation of nitrous acid (nitrite), in Pu^{+4} solutions, and possibly also in Pu^{+3} solutions not containing HAN or with HAN but $[\text{NO}_3^-] < 3.0\text{M}$. Until the reactivity of HAN at $[\text{NO}_3^-] < 3.0\text{M}$ (in the presence of HSA) is better understood, the expected hold time for 50 grams/liter Pu^{+3} /0.165M HSA/0.023M HAN/2.5-3.0M HNO_3 solution is 20.3 ± 2.1 days.

The $G(\text{H}_2)$ value determined in this work at 2.765M NO_3^- is slightly less (5.8%) than predicted from the fit to the published data, equation (8), but falls within expected error. The production rate of H_2 , $G(\text{H}_2)$, therefore seems to be unaffected by the presence of HSA and HAN. Addition of ascorbic acid had no measured effect on the off-gas rate of Pu^{+3} solutions containing HSA and nitrate concentrations higher than those expected in the hold tanks. This test of its effect should be conservative for the range of nitrate concentrations expected presently.

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Figure 1. Experimental Apparatus Design.

Figure 2. Off-Gas rate Versus Time (2.765M $\text{NO}_3^-/\text{Pu}^{+4}$).

Figure 3. $G(H_2)$ Versus $[NO_3]$.

Figure 4. Off-Gas Rate Versus Time (Pu^{+3}).

Figure 5. Initial Off-Gas Rate Versus [NO₃⁻].

Figure 6. [HSA] Depletion (Radiolytic) Versus Time.