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TRIOXANE-INITIATED FORMIC ACID DENITRATION

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PREPARED FOR THE U. S. DEPARTMENT OF ENERGY UNDER CONTRACT DE-AC09-76SR00001

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July 1983

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ABSTRACT

The Savannah River Laboratory has developed a procedure for controlled low-temperature chemical denitration of acidic solutions. The procedure can be used in semi-continuous denitration facilities and can also be directly applied to nitric acid solutions in a storage tank (in situ denitration) if there is some provision for moderate heating (up to 80°C) and cooling. The procedure works well for both highly acidic (~11M) and moderately acidic (~3M) solutions. Trioxane, the cyclic trimer of formaldehyde, is used to initiate the reaction, while the bulk of the denitration is effected by the formic acid. Once initiated, the off-gas rate is controlled by the formic acid addition rate and can easily be maintained within the capacity limits of the off-gas system. The procedure was successfully applied to a plant-scale in situ denitration at the Savannah River Plant.

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TRIOXANE INITIATED FORMIC ACID DENITRATION

INTRODUCTION

Excess acidity in high molarity nitric acid solutions can be removed by evaporative stripping of the nitric acid. However, this technique is inefficient and wasteful of energy when the solution acidity drops below 4M.¹ An alternative to evaporative stripping, particularly for acid concentrations below 4M, is denitration with a suitable organic reductant. The organic reductant converts nitric acid to nitrogen oxides, NO_x, and various organic substrates have been evaluated for this purpose including sucrose²⁻⁴, formaldehyde,⁵⁻⁸ paraformaldehyde,⁹ and formic acid.^{1,10-13} Formic acid has the advantage of being relatively fast reacting, introducing no salts to the solution, and only very slightly increasing solution volume. The principal disadvantage of formic acid is its variable induction period preceding reaction. This induction period can lead to large, difficult-to-control evolutions of gas and heat in a short period of time. This report describes a method to initiate denitration promptly, so that formic acid can be used for lowering acidity without the poorly controlled induction period.

SUMMARY

A safe, controlled initiation of chemical denitration, not normally possible with formic acid alone, can be effected by the use of trioxane, a cyclic trimer of formaldehyde. The procedure can be applied directly to nitric acid solutions contained in a storage tank (in situ denitration) and also can be utilized in semi-continuous denitration facilities. The slow, predictable hydrolysis of trioxane provides formaldehyde, which initiates the denitration reaction. Once initiated, formic acid reacts smoothly and off-gas generation can be controlled by the rate of formic acid addition. Trioxane is not used for the bulk denitration because of its limited solubility in water which would increase solution volume. The trioxane-initiated, formic acid procedure has been shown to work effectively with starting acidities from 2.5 to 11M. A plant-scale demonstration of the in situ procedure successfully reduced the acidity of an acidified plutonium solution from 10.3 to 2.9M smoothly and controllably. The plant test ran as predicted by a pilot laboratory experiment.

Laboratory studies showed that simulated SRP low-activity waste solutions, starting at 2.5 to 3.5M nitric acid, could be smoothly denitrated to about 1M using trioxane initiation. Use of trioxane-initiated formic acid denitration for routine waste streams has potential for significantly reducing plant waste volumes by decreasing the resulting salt content of neutralized waste.

EXPERIMENTAL

All scouting tests on simulated solution were conducted in a chemical hood. Initial small scale tests with SRP plutonium solution were conducted in shielded cells. A 100 mL glass reactor, heated with a controllable electric mantle, was used to carry out the denitrations. The reactor was equipped with a magnetic stirrer, a thermometer, and an off-gas line coupled to an off-gas rate meter. Typically, a 35 mL sample of the test solution was charged to the reactor and heated, and then trioxane was added to initiate denitration. As nitrogen dioxide fumes developed over several minutes, the formic acid feed was started and fed at a controlled rate. As denitration proceeded, the off-gas evolution rate was monitored.

Test conditions and results for the small-scale studies with SRP plutonium solutions are summarized in Table 1. Experiments to define process variables were conducted at rates scaled to plant equipment. For the larger scale experiments using simulated solution (composition given in Table 2), 750 mL of solution was used with scaled chemical feed rates of 7.3 ± 0.7 mL/hr for trioxane, and 1.4 ± 0.2 mL/hr for formic acid. After the solution had equilibrated at the desired temperature, the trioxane was fed for about an hour. Trioxane feed (1M) was then stopped, and the formic acid feed (90%, 23.5M) was started. The off-gas was monitored with a calibrated flowmeter and the total off-gas evolved was measured with a wet-test meter. Figure 1 schematically shows the experimental apparatus.

The scaled SRP plutonium solution experiment was run similarly, except that 188 mL of solution was charged to a 500 mL reaction vessel. Daily, 1 mL samples were removed from the vessel for analysis after hand mixing of the solution.

For the corrosion study, a 6 x 6 x 3/8-inch piece of 304L stainless steel was cut in half and then welded back together. The sample was then cut into equal sized coupons (Figure 2). Two welded and two unwelded coupons were used in the corrosion test. The coupons were cleaned according to ASTM procedure A-380 and weighed. Then each coupon was charged to a separate vessel containing a volume of simulated solution having the same surface-to-

volume ratio expected in full scale equipment. The solutions were heated to 80° to 85°C and kept in a constant temperature bath for 16 days. The samples were then cleaned and reweighed.

Low activity waste (LAW) studies were conducted in the apparatus shown in Figure 1, except for the flow rate-meter which was replaced by a wet-test meter to measure total off-gas volume evolved. In all studies, a 200 mL portion of solution was used for denitration. Trioxane (1.4M) was added as a single charge. Nitrite was delivered in a single addition, either with the trioxane solution or by direct addition to the reaction flask. Formic acid was added at a rate of 0.5 mL/min using a fluid metering pump. The reaction mixture was agitated with a magnetic stirrer. All tests were made at 90°C.

DISCUSSION

Denitration Initiation

Formic acid denitration proceeds via radical intermediate pathways. Once formic acid denitration has initiated and the required combination of nitrous acid, formate radicals, and HNO radicals have formed, formic acid reacts smoothly, and NO_x/CO₂ evolution can be controlled by the rate of formic acid addition. A similar mechanism is proposed for formaldehyde denitration.¹¹ Because formaldehyde reacts rapidly with nitric acid, it would then provide reaction intermediates which would react rapidly with formic acid, and hence eliminate the induction time normally required with formic acid. Trioxane is an easily managed source of formaldehyde.

Trioxane, the cyclic trimer of formaldehyde, is a low-melting, crystalline solid, stable in aqueous alkaline solutions but hydrolyzed by aqueous acids to the monomeric formaldehyde.¹⁴ For a given temperature and acid concentration, the rate of hydrolysis is comparable with the rate of denitration of nitric acid. Initiation of the reaction was achieved with trioxane at the level of 10⁻⁴ to 10⁻³ mole per mole of nitric acid. Similar results were obtained when trioxane was added either as a single addition or by metering in over a period of minutes.

The formic acid can be introduced either immediately following addition of the trioxane or after some delay. Tests with simulated solution showed that delaying the onset of formic acid addition up to one hour had no effect and the formic acid again reacted positively and smoothly. The simulated solution contained nitric acid, iron, chromium, and nickel nitrates; ceric nitrate served as surrogate for plutonium nitrate.

Final acidity is dependent upon the molar ratios of formic acid to nitric acid and must be less than 1.16 if the precipitation of solids is to be avoided. Final acidity decreased with increasing molar ratio through a value of approximately 1.4 (Table 1). Beyond this ratio, final acidity increased due to the accumulation of unreacted formic acid as shown in Figure 3. Off-gas rates followed, and were controlled by, the addition rate of formic acid (Figure 4).

Process Studies for Plant In Situ Denitration

Background

About 18,500 liters of plutonium solution, approximately 11M in nitric acid, had to be stored for several years. In order to slow the corrosive attack on the storage tank cooling coils, it was necessary to lower the acidity to about 3M. Equipment limitations required that the acid reduction be carried out in the storage tank. This imposed the following constraints on the acid reduction:

- Vessel had limited heating capability with a maximum temperature of 80°C
- Vessel was >80% full
- No reflux condenser was present
- Off-gas vent capacity was about 40 cfm.

The trioxane-initiated, formic acid denitration process was selected for acid reduction because it appeared capable of meeting the tight reaction requirements. In addition, good off-gas evolution control was needed to avoid loss of solution, and thus would be a good demonstration of the initiated formic acid system.

Simulated Solutions

Simulated plant solutions were denitrated to establish the effect of scaled process variables. Figure 5 shows the total integrated off-gas as a function of time for 5 hour formic acid denitrations of simulated solutions at 80°C, 70°C, and 50°C. For all runs, the feed rate for both trioxane and formic acid was scaled to the expected plant feed rates. Trioxane was added from time zero to 60 minutes, at which time the trioxane feed was turned off and the formic acid feed was started. Figure 5 also shows that for temperatures of 70° and 80°C, the reaction initiated (as indicated by increasing off-gas volume) while the trioxane was

being fed. However, at 50°C, the reaction did not initiate until about 12 minutes after formic acid feed was started. This delayed reaction (induction period) with formic acid at 50°C is shown more clearly in Figure 6 in which only the first 90 minutes of the reaction is plotted. The off-gas rate, in mL/min for the 70° and 80°C runs, is given in Figure 7. Notice the rapidly increasing rate just after formic acid is introduced, and then the constant rate after about 2 hours.

As expected, the off-gas rate is greater for higher temperatures. The off-gas rate equivalent to the 40 cfm off-gas limit in the plant, scaled down to the laboratory apparatus, is 45 mL/minute.

The effect of trioxane initiation is shown in Figure 8. For the trioxane initiated curve, trioxane was added for the first 60 minutes, then formic acid was added until the end of the run. For the no trioxane case, formic acid feed was started at time zero and continued for 240 minutes at which point it was turned off. Once initiated, the formic acid takes control of the reaction and the reaction rate is the same whether the reaction was first initiated with trioxane or not. The figure shows how the reaction can be easily controlled, as indicated by the decrease in reaction immediately upon interrupting the formic acid feed. However, as Figures 9 and 10 show, the uninitiated reaction exhibits a more erratic off-gas rate, whereas the trioxane initiated reaction is much smoother. Again, note the rapid decrease in off-gas rate when the formic acid feed is interrupted.

The need to reinitiate if formic acid feed is interrupted depends on the reaction conditions. If no air sweep is present, the reaction reinitiates without an induction period when the formic acid addition is interrupted for up to 48 hours. In these tests, the reaction was first initiated with trioxane, and the formic acid was added for four hours. Then, the feed was stopped for 48 hours and the vessel was maintained at 80°C. In cases where there is an air sweep over the liquid, scaled to the 40 cfm air sweep for the SRP tank, the allowable delay time is drastically reduced to only a few hours. The first reaction initiation, however, is unaffected by the air sweep.

Laboratory Denitration of SRP Solution

A single run was made on actual SRP plutonium solution at scaled feed rates. This run was carried out in a glove box for seven continuous days. Over this period, the acidity of 188 mL of solution was reduced from 10.1M to 2.6M. Figure 11 shows the decrease in acid with time (the solution was left in the vessel unheated for an additional three days). During the first two days, the formic acid feed rate was about a factor of 2.5 times too high.

This excessive feed rate was corrected by feeding a measured quantity of formic acid to the reaction vessel with a volumetric pipet every 30 to 35 minutes for the duration of the experiment. The desired scaled rate was, however, achieved for the overall run. The more rapid decrease in acidity for the first two days, was due to a combination of this high feed rate, and the more rapid reaction rate at higher nitric acid concentrations. Table 3 summarizes the results of this experiment. The decrease in volume from 188 mL to 148 mL takes into account the solution removed during sampling. However, the major reason for the volume reduction is attributed to evaporation of water during the 10 days. The final molar ratio of formic acid to reacted nitric acid was 0.97. There was no residual formate in solution, it being totally consumed in the denitration. Table 4 gives the major radioisotopes in the initial and denitrated solutions and shows that no radioactivity was lost during denitration. No solids appeared in the denitrated solution after 60 days.

Corrosion Study

Figure 2 is a photograph of the 12 coupons cut from a 3/8-inch thick piece of 304L stainless steel. The four dark pieces were used in the corrosion test, the other eight pieces were spares. This photograph was taken after the samples had been exposed to the simulated tank solution for 16 days, but before the film of Cr_2O_3 was removed. This film was easily removed by treating the coupon for one hour in dilute 80°C nitric acid. Table 5 summarizes the results of this study. The last column of this table gives the corrosion in mils expected for an eleven-day denitration at 80 to 85°C if the acidity remained at 1M. The actual corrosion will be substantially less than this 0.073 mil, since the corrosion rate will be continuously decreasing as the acidity is lowered. This table also shows that there is no difference in corrosion between welded and non-welded samples. The results of this study indicated that corrosion during denitration would not be a problem.

Full-Scale Denitration

The acidity of 18,500 L of a plutonium solution in an SRP storage tank was reduced by formic acid denitration following the procedure specified in Appendix A. This is a 10^5 scale-up from the laboratory denitration. The trioxane solution (1M) was fed to the tank for 1 hour at 3.4 L/minute. The brown NO_2 vapors were detected after about 30 minutes of trioxane addition. After trioxane addition was complete, formic acid was delivered at 0.6 L/minute for 173 hours. The reaction remained at 75°C throughout the formic acid addition time. The reaction was sampled and checked for acidity level as the denitration proceeded. As seen in Figure 12, the solution acidity was lowered smoothly and dropped as

predicted by laboratory studies. No process problems or upsets were observed during the denitration. Pre- and post-analysis of the vessel revealed no loss of radioactivity to the off-gas.

Low-Activity Waste (LAW) Study

The availability of a controlled process for formic acid denitration opens the way for use of chemical denitration of routine plant streams where reduction of acidity is needed. To demonstrate such an application, a formic acid denitration process was studied for reducing the acidity of a low-activity waste stream from the low enriched uranium process at SRP. The proposed new application of formic acid denitration is to replace a pre-evaporation dilution (which is performed to limit corrosion in the waste reduction evaporators) with a continuous or semi-batch formic acid denitration process. The denitration step would serve the same function as the dilution, but the large amounts of water added for dilution would not have to be evaporated. The substantial amount of time spent in the evaporation step would thus be eliminated.

Process Flowsheet

The process shown in Figure 13 was used for this study. This flowsheet replaces the dilution, evaporation, and steam-stripping portion of the current SRP system with a formic acid denitration step. In addition, 1M HNO_3 would be neutralized (vs. 4.3M acid now) which would reduce the salt volume. The 6M acid obtained by further concentration in the evaporators would be recycled to the denitrator feed. In order to accommodate salt buildup in the 6M recycle stream, a separate denitration without LAW feed would be scheduled as part of the overall denitration routine.

LAW Initiation

The experimental results, discussed earlier, provided the basis for specifying 10^{-4} to 10^{-3} moles of trioxane/mole of nitric acid in the SRP tank denitrator. Since the starting acidity of the SRP tank was much higher (10 to 11M) than LAW (2.5 to 3.5M), the trioxane requirements for initiating lower molarity acid were investigated. The trioxane was added in one charge as a 1.4M aqueous solution. The results (Table 6) show that the lower molarity acid requires at least 5×10^{-3} moles of trioxane/mole of acid to provide initiation of denitration. These results also show that the off-gas evolution rate increases as the trioxane ratio increases. Thus, to provide a smooth initiation, the lowest practical amount of trioxane should be used.

During additional work aimed at further optimization of the trioxane concentration, we observed nonreproducible initiation behavior using a 2×10^{-3} to 2×10^{-2} trioxane ratio which appeared to be related to starting acidity. A 2×10^{-3} trioxane ratio would not initiate 3.5M acid but initiated 11M acid readily. Since hydrolysis of trioxane to the reactive formaldehyde is a function of solution acidity,¹⁴ the degree of trioxane hydrolysis was determined under conditions similar to those used for denitration. Sulfuric acid was used to avoid oxidation of the formaldehyde. The results (Table 7) show that under the denitration conditions, virtually all the trioxane is converted to formaldehyde in 60 minutes. Thus, lack of formaldehyde production was not the reason for inconsistent initiation. This was further confirmed by sampling an actual initiation experiment and measuring formaldehyde concentration (Table 8). Nearly complete hydrolysis was shown in 20 minutes, yet no initiation was detected even after 180 minutes.

Nitrous acid has been shown to be necessary to initiate formic acid reduction of nitric acid.^{10,11} In fact, in the absence of nitrous acid, no reaction was detected.¹⁰ A series of tests were made to establish the level of nitrite needed to initiate 3.5M acid. It was found (Table 9) that if at least 1.4×10^{-6} moles of nitrite/mole of acid were present, initiation would occur readily.

Based on these studies, an initiation recipe of 8×10^{-3} moles of trioxane/mole of acid plus at least 3×10^{-6} moles of nitrite/mole of acid was chosen for initiating formic acid denitration. These amounts are about 2 times the minimum amounts needed.

LAW Denitration

Based on the work of Bradley and Goodlett,¹ 1.3 moles of formic acid/mole of nitric acid were used to demonstrate the integrated initiation-denitration process. The trioxane initiator (plus sodium nitrite, if used) was added to the nitric acid solution in one charge. After initiation occurred, formic acid was metered in at a rate of 0.5 mL/minute until the amount necessary to reduce nitric acid acidity to 1.0M was added. Initiation was detected by visual observation of the brown NO_2 gas above the reaction. Total off-gas volume evolved and reaction temperatures were monitored during the run.

Initial work involved only nitric acid solution. The benefit of trioxane initiation was clearly evident when nitric acid was denitrated with and without trioxane addition. The off-gas flow rate for trioxane-initiated denitration (Figure 14) rose rapidly after formic acid addition and remained fairly constant until formic acid addition was complete. When trioxane initiation was not used (Figure 14), a very high off-gas surge (>2 times the

initiated level) was obtained just after initiation. The addition of sodium nitrite without trioxane (Figure 15) did not provide a controlled initiation. Trioxane initiation also provided a more moderate temperature rise than uninitiated denitration. These results show that the denitration is in better control when trioxane initiation is used. A smooth decrease in solution acidity (Figure 16) was found when trioxane initiation was employed.

Denitration of Simulated SRP LAW Solution

A simulated LAW solution (Table 10) was prepared to confirm the process feasibility. Because the LAW contains nitrite, addition of nitrite with the trioxane was unnecessary. Denitration of this LAW with trioxane initiation (Figure 17) proceeded smoothly. No precipitates or foaming were observed. Denitration without trioxane initiation (Figure 17) exhibited the same surge of off-gas described above. The overall results of acidity, volume change, and off-gas volume are given in Table 11. Good reproducibility was found between replicates. The final acidity was obtained with only a small change in volume.

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APPENDIX A

Recommended Full-Scale In Situ Denitration Process Conditions

TEMPERATURE: 70° to 80°C for initiation. Heating/cooling via the tank coils will be needed to maintain 70° to 80°C throughout the addition of formic acid and for at least four hours beyond to complete the reaction.

CHEMICALS: Trioxane — 1.0M aqueous solution.
Formic acid — 90% (23.5M)

INITIATION: A molar ratio of trioxane/nitric acid of 10^{-3} will assure reaction during trioxane feed. This will require about 200 moles of trioxane (40 lb.). The 1M aqueous solution should be fed at a rate of 3.0 ± 0.3 liters/minute for about one hour. This addition rate will assure that the off-gas rate will be less than the vent capacity of 40 cfm.

DENITRATION: A final molar ratio of formic acid to nitric acid in the range of 0.9 to 1.1 will provide final solutions free of precipitates. A formic acid feed rate of 34 ± 3 liters/hour will be commensurate with the 40 cfm off-gas limit. Separate feed tanks and lines should be used for trioxane and formic acid, if possible.

The test will end when the desired 3M acidity is reached. The denitration could be stopped at 4M, thus shortening the test while still achieving the desired corrosion reduction.

If formic acid feed is inadvertently stopped, it should be reinitiated with trioxane.

SAMPLING: Samples should be drawn at least once a day for acid determination, and more frequently as the endpoint is approached. The vessel should be agitated prior to sampling, but need not be agitated during denitration.

TABLE 1

Effect of Formic Acid to Nitric Acid Ratio

	Run No.								
	1	2	3	4	5	6	7	8	9
<u>Additions</u>									
Trioxane (moles)	0.0010*	0.0019	0.0019	0.0019	0.0019	0.0019	0.0019	0.0019	0.0019
HCOOH (moles)	0.549	0.408	0.253	0.363	0.522	0.398	0.372	0.385	0.190
HCOOH/HNO ₃ (moles)	1.61	1.20	0.74	1.06	1.53	1.17	1.09	1.13	0.53
HCOOH rate (mL/hr)	9.6	9.3	8.0	8.7	8.7	9.1	8.2	8.8	7.3
Off-gas (mL/min)	-	140-180	100-120	120-140	120-140	130-160	110-140	130-170	110-130
<u>Final Solution</u>									
[H ⁺] (M)	4.31	0.68	3.99	2.43	0.39	1.44	2.03	1.86	5.48
[NO ₃ ⁻] (M)	0.07	0.60	4.00	2.10	0.60	1.44	2.25	1.81	5.40
[HCO ₂ ⁻] (M)	5.20	0.01	0.001	0.001	0.05	0.001	0.002	0.001	0.002
Solids (g)	0.266	0.170	0	0	0.201	0.058	0	0	0
Volume change (%)	+8.6	-2.9	0	-2.9	+2.9	+2.9	+5.7	+2.9	-1.6

* Sucrose used to initiate reaction.

NOTES:

- (1) All reactions were run at 70 to 80°C with initiation at <70°C.
 (2) [H⁺] initially was 10.54M.

TABLE 2**Composition of Simulated SRP Plutonium Solution**

<u>Compound</u>	<u>Denitration Studies Molarity</u>	<u>Corrosion Study Molarity</u>
HNO ₃	10.5	11.0
NH ₂ SO ₃ H	-	0.0280
Fe(NO ₃) ₃ •9H ₂ O	0.0320	0.0322
Ni(NO ₃) ₂ •6H ₂ O	0.0016	0.0016
Cr(NO ₃) ₃ •9H ₂ O	0.0037	0.0037
Ce(NO ₃) ₃ •6H ₂ O*	0.0101	0.0101

* Ce was used as a surrogate for plutonium.

TABLE 3**Summary of Laboratory Denitration of Actual SRP Plutonium Solution**

Duration: 168 Hours Temperature: 80 ±3°C

Trioxane (1M): 2 mL in 1 hour

Formic Acid (23.5M): 59.6 mL in 167 hours, 0.36 mL/hr

Molar Ratio: (HCOOH)/(HNO₃) = 0.97

	<u>Initial</u>	<u>Final</u>
Volume	188 mL	148 mL
Total acid	10.2M	2.5M
Free acid	9.8M	2.3M
Nitrate	10.5M	2.6M
HCOOH	-	<0.01M

TABLE 4**Gamma Radioactivity of SRP Solution**

<u>Isotope</u>	<u>Initial</u>	<u>Denitrated</u>	<u>Units</u>
Pu-238	4×10^5	4×10^5	$\gamma/\text{m/mL}$
Pu-239	9×10^5	2×10^6	$\gamma/\text{m/mL}$
Pu-240	3×10^4	3×10^4	$\gamma/\text{m/mL}$
Am-241	3×10^5	3×10^5	$\gamma/\text{m/mL}$
U-237	6×10^2	5×10^2	$\gamma/\text{m/mL}$
Pa-233	2×10^3	2×10^3	$\text{d}/\text{m/mL}$
Cs-137	3×10^3	4×10^3	$\text{d}/\text{m/mL}$

TABLE 5**Results of Corrosion Study**

	<u>Wt. Loss, (grams)</u>	<u>Corrosion, (mil)</u>	<u>Corrosion Rate, (mil/day)</u>	<u>Expected Corrosion of SRP Tank (mil)</u>
Sample 1	0.085	0.099	0.006	0.068
Sample 2	0.110	0.127	0.008	0.087
Sample 3W	0.087	0.098	0.006	0.067
Sample 4W	<u>0.088</u>	<u>0.102</u>	<u>0.006</u>	<u>0.070</u>
Average	0.093	0.106	0.007	0.073

TABLE 6**Trioxane Initiation Results**

<u>Moles Trioxane Per Mole HNO₃</u>	<u>Acid Molarity</u>	<u>Reaction Temp. °C</u>	<u>Induction* Time, min.</u>	<u>Off-Gas Evolution Rate, mL/min</u>
5×10^{-4}	3.5	90	>85	-
5×10^{-3}	3.5	90	15-81	8
9×10^{-3}	3.5	90	13	30
1.3×10^{-2}	3.5	90	9	62
2.6×10^{-2}	3.5	90	4	115
5×10^{-2}	3.5	90	8	184
1.3×10^{-2}	2.5	90	18	31

* Time to detect NO₂ coloration in reaction vessel after addition of trioxane.

TABLE 7
Trioxane Hydrolysis — Simulated Reaction
 (3.5N H₂SO₄, 90°C, 1.4M Trioxane)

<u>Reaction Time/min.</u>	<u>Percent Conversion to Formaldehyde</u>
10	37
20	53
30	67
45	80
60	87
90	93
120	93
180	93

TABLE 8**Trioxane Hydrolysis — Actual Reaction**3.5M HNO_3 , 90°C, 1.4M Trioxane

<u>Reaction Time, min</u>	<u>Percent Conversion to Formaldehyde</u>
11	79
20	94
30	95
45	95
60	95
90	93
180	92

NOTE: Denitration was not initiated in this run.

TABLE 9**Nitrite Catalyzed Initiation**0.7 moles HNO_3 , 5.6×10^{-3} moles trioxane

<u>Moles NaNO_2 Added</u>	<u>Moles NaNO_2 / Moles HNO_3</u>	<u>Initiation Time, min.</u>
1×10^{-7}	1.4×10^{-7}	>32
2×10^{-7}	2.9×10^{-7}	>34
5×10^{-7}	7.1×10^{-7}	>64
7.5×10^{-7}	1.1×10^{-6}	>48
1×10^{-6}	1.4×10^{-6}	8
2×10^{-6}	2.9×10^{-6}	6
5×10^{-6}	7.1×10^{-6}	4

TABLE 10**Composition of Simulated Low Activity Waste Solution**

HNO ₃	2.52M
NaNO ₂	0.106M
Fe Sulfamate	0.027M
Hydroxylamine Sulfate	0.015M
KMnO ₄	0.003M
NaNO ₃	0.134M

TABLE 11**Experimental Denitration Runs**

Run No.	Acid Molarity		Solution Vol., mL		Off-Gas Vol., L	
	Start	End	Start	End	Calc.	Observed
FA1B	3.5	1.2	200	204	25.8	22.6
FA3	2.5	0.9	200	202	17.8	17.8
FA4	2.5*	0.9	200	204	17.7	16.8
FA5	2.5*	0.9	200	202	17.8	16.8
FA6	2.5	1.0	200	202	17.1	17.3
FA7	2.5	1.0	200	202	16.9	17.3
FA8	2.5*	1.0	200	198	17.2	18.0
FA9**	2.5*	0.9	200	204	17.6	17.2
FA10***	2.5	1.0	200	204	17.0	17.4

* Simulated LAW

** Repeat of FA5

*** Repeat of FA6

**FIGURE 1. Sketch of Experimental Apparatus in a Chemical Hood
(Not to Scale)**

FIGURE 2. 304L Stainless Steel Coupons Used in the Corrosion Study

FIGURE 3. Effect of the Formic Acid/Nitric Acid Ratio on the Final Acidity

FIGURE 4. Effect of the Formic Acid Feed Rate on the Off-Gas Rate

FIGURE 5. Effect of Temperature on Total Off-Gas During Formic Acid Denitration

FIGURE 6. Effect of Temperature on Total Off-Gas During Formic Acid Denitration (Expanded Scale)

FIGURE 7. Effect of Temperature on Rate of Off-Gas Evolution During Formic Acid Denitration

FIGURE 8. Total Off-Gas for Trioxane-Initiated and Non-Initiated Formic Acid Denitration

FIGURE 9. Off-Gas for Trioxane-Initiated and Non-Initiated Formic Acid Denitration

FIGURE 10. Off-Gas Rate for Trioxane-Initiated and Non-Initiated Formic Acid Denitration (Expanded Scale)

FIGURE 11. Decrease in Total Acidity for Laboratory Denitration of Actual SRP Solution

FIGURE 12. Full-Scale Formic Acid Denitration

FIGURE 13. Proposed Flowsheet for Formic Acid Denitration of Low Activity Waste

FIGURE 14. Trioxane-Initiated Denitration of 2.5M Nitric Acid

FIGURE 15. Denitration of 2.5M Nitric Acid - Nitrite Added - No Trioxane Initiation

FIGURE 16. Trioxane-Initiated Denitration of 3.6M Nitric Acid

FIGURE 17. Trioxane-Initiated Denitration of Simulated Low Activity Waste