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Spontaneous Catalytic Wet Air Oxidation during Pretreatment of High-Level Radioactive Waste Sludge

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ABSTRACT: Savannah River Remediation, LLC (SRR) operates the Defense Waste Processing Facility for the U.S. Department of Energy at the Savannah River Site. This facility immobilizes high-level radioactive waste through vitrification following chemical pretreatment. Catalytic destruction of formate and oxalate ions to carbon dioxide has been observed during qualification testing of non-radioactive analog systems. Carbon dioxide production greatly exceeded hydrogen production, indicating the occurrence of a process other than the catalytic decomposition of formic acid. Statistical modeling was used to relate the new reaction chemistry to partial catalytic wet air oxidation of both formate and oxalate ions driven by the low concentrations of palladium, rhodium, and/or ruthenium in the waste. Variations in process conditions led to increases or decreases in the total oxidative

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destruction, as well as partially shifting the preferred species undergoing destruction from oxalate ion to formate ion.

INTRODUCTION AND BACKGROUND

Fifty-one underground carbon steel tanks, 4000 m³ (million gallon), have been used to store high-level radioactive wastes (HLW) at the U.S. Department of Energy's Savannah River Site (SRS). Most of the radioactive waste mass was generated between 1954 and 1988 in support of production of nuclear materials for the U.S. government (*1*). Closure of the tanks containing the HLW slurries is a critical step in returning the Savannah River Site to something resembling its original, pre-Cold War condition. Savannah River Remediations, LLC (SRR) and Savannah River Nuclear Solutions (SRNS) in Aiken, South Carolina, are in the process of remediating the legacy radioactive nuclear wastes through a vitrification process in which the wastes are incorporated into a borosilicate glass. SRNS is one of two prime contractors at the Savannah River Site and currently administers the Savannah River National Laboratory (SRNL) where the testing described in this paper was performed.

The waste tanks contain three components, which include supernate, salt cake, and sludge slurry. Caustic soluble species, such as cesium, either remain in the aqueous phase or as potentially water-soluble salt cake. The waste slurries were created by caustic treatment of byproduct and purge waste solutions formed during the purification and isotopic enrichment of uranium and plutonium at SRS. Waste slurries are rich in iron, aluminum, manganese, nickel, calcium, and numerous other lesser species including many stable products of the radioactive decay of uranium (²³⁵U by thermal neutron fission) and plutonium. The waste slurries are similar to the red mud waste generated from the caustic leaching of bauxite ore.

Vitrification has been designated the Best Demonstrated Available Technology (BDAT) by the U.S. Environmental Protection Agency for immobilizing large masses of HLW for safe, long term storage. The HLW slurries undergo batch chemical pretreatment including blending with glass forming frit prior

to vitrification in the SRS Defense Waste Processing Facility (DWPF). Molten glass from the DWPF melter is poured into stainless steel canisters which are then sealed. The canisters have been designed to meet the requirements for the national nuclear waste repository. DWPF began processing HLW in 1996. Supporting lab-scale experimentation by the SRNL on the pretreatment process has characterized the typical processing chemistry. To date, wastes from a number of different tanks have been treated and vitrified. Two of the 51 tanks have been formally closed, that is, cleaned and entombed with grout to stabilize any remaining potentially hazardous constituents.

Chemical treatment of the HLW occurs in the DWPF Sludge Receipt and Adjustment Tank (SRAT). Nitric and formic acids are added consecutively at 93 °C to the waste sludge slurry (2). The pH is adjusted from about 12 down to about 4.5. Chemical treatment is intended to:

1. Reduce Hg(II) to elemental mercury that can be removed by steam stripping, since minimal mercury can be incorporated into the final waste glass form.
2. Partially reduce Mn(IV), as MnO₂, to Mn(II) species in order to mitigate foaming in the vitrification melter (Mn(IV) is thermally unstable at the temperatures of the melt pool and reduces to Mn(II) plus oxygen which bubbles up through the melt pool).
3. Create a balance between oxidizing and reducing species in the melter feed that will lead to approximately 20% Fe(II)-80% Fe(III) in the glass (3).
4. Partially dissolve some of the transition metals to improve rheological properties and permit concentration to higher weight percent solids loadings.

Nitrite ion, introduced into the SRS storage tanks as a corrosion inhibitor, is simultaneously reduced during treatment. It was found during the development of the DWPF vitrification process that destruction of the nitrite ion led to the formation of active transition metal catalyst species within the sludge waste (4, 5). These catalysts were found to produce hydrogen through the catalytic decomposition of formic acid to carbon dioxide and hydrogen (6, 7). Research at SRNL has continued with the goals of better understanding the hydrogen generation process and of finding ways to cope with the formation of hydrogen-oxygen mixtures in the air-purged reactor vessel and downstream equipment

(8, 9, 10). The program focused primarily on formic acid chemistry. Potential feeds for the DWPF are expected to include oxalate ion as both dissolved sodium oxalate and as insoluble oxalate salts such as calcium oxalate. These systems had not been investigated previously to determine what impacts the presence of oxalate ion would have on the catalytic species present in the waste.

The principal noble metals formed from uranium fission products are Pd, Rh, and Ru. Ru is present at about four times the concentration of Rh due to the relative fission yields. Pd is present at less than half the concentration of Rh for similar reasons plus a greater solubility in the aqueous phase of the waste. Pd has been preferentially depleted below its fission yield relative to Rh and Ru in the HLW sludge tanks due to tank farm operations such as decanting and transferring the aqueous phase to create space for more insoluble HLW in the sludge tanks. The aqueous phase is concentrated in one of several evaporators to remove water or fed to the Saltstone Processing Facility where it is converted into a cementitious waste form. Rh and Ru have been established as the primary catalysts for hydrogen generation in DWPF waste processing, while Pd and Rh have been established as the primary catalysts for catalytic decomposition of nitrite ion by formic acid.

Limits on hydrogen generation rates during chemical pretreatment of waste sludge became part of the safety basis for the DWPF design. A qualification process is followed for each new batch of waste that is to be processed to ensure the design basis is met. A batch typically consists of the waste slurry from one or more storage tanks that undergoes washing to reduce the soluble sodium salts from ~20% to ~2-6% by mass in the slurry (~1M Na). An approximately one dm³ (one-liter) sample of actual waste is used to demonstrate the feasibility of the chemical pretreatment process for each new batch. This lab-scale process simulation is done in the Shielded Cells facility at SRNL. This facility is capable of handling highly radioactive materials using remote manipulator arms and extensive radiation shielding. Scoping work is done prior to each Shielded Cells test using non-radioactive analog wastes called “simulants”. Simulant wastes are prepared by a generally similar process to that which formed the radioactive waste, but the simulant waste is free of the radioactive species. Simulant waste testing can

be conducted in both conventional laboratory hoods and pilot plant equipment at much lower cost for materials, labor, and waste disposal compared to the radioactive testing.

During normal SRAT processing, whether radioactive or simulated, a fraction of the formate ion is destroyed. Formic acid reacts with Hg(II), NaNO₂, and Mn(IV) oxide in a series of chemical reduction reactions that produce elemental Hg, liberate various oxides of nitrogen, and produce soluble Mn(II) formates and nitrates. All of these reduction reactions convert some formate ion into carbon dioxide gas. Consequently, carbon dioxide evolution and formate loss are normally seen during lab-scale processing experiments. Carbon monoxide is not observed, unless the concentration of oxygen in the air purge drops to very low levels. Methane was observed in process development testing prior to DWPF start-up using an inert gas purge. DWPF elected to use an air purge, however, and methane is no longer observed in analogous experiments.

While most DWPF process simulations are used to support sludge batch qualification, some simulant based lab-scale simulations are also performed in support of special projects, for example to prepare material for melter performance testing. It was noted during an early test sequence that the molar production rate of carbon dioxide was 5-10 times greater than that of hydrogen during the latter part of the SRAT cycle. Supporting data indicated that this was past the time when waste carbonate was converted to CO₂, nitrite was being chemically reduced by formic acid, Hg(II) was being reduced to elemental Hg, and Mn(IV) was being converted to Mn(II). Minimal evidence for the hydrogenation of nitrate ion to ammonium ion has been found in the SRS waste processing data (11). SRAT product slurry samples and SRAT off-gas condensate samples are both monitored for ammonium ion by cation chromatography. Consequently this reaction path is unable to explain the difference between the CO₂ and H₂ generation rates.

One or more chemical reactions in addition to catalytic decomposition of formic acid to hydrogen and carbon dioxide must be occurring based on the early test data based on a process of elimination, but the nature of the reaction(s) was still unresolved at the completion of the earlier project. A later SRNL

paper study on noble metal catalyzed formation of hydrogen located a number of papers on catalytic wet air oxidation (CWAO) of organic species in aqueous wastes exposed to air (12-19).

EXPERIMENTAL

Lab-scale SRAT simulations were performed on the projected Tank 7F composition of the washed waste slurry. Tank 7F waste was the main component of Sludge Batch 3 (SB3) feed to DWPF and was expected to have significant quantities of sodium oxalate present in addition to the typical by-products of the actinide separations processes. SRNL was requested to investigate the impact of the sodium oxalate on the chemical treatment and vitrification processes. Two simulated waste streams were prepared, Table 1.

Table 1
Air-dried elemental composition
of simulants and Sludge Batch 3

	Simulant 1 Wt. %	Simulant 2 Wt. %	Sludge Batch 3 Wt. %
Al	9.6	9.8	5.1
Ba	0.3	0.2	0.1
Ca	2.2	2.6	1.3
Cr	0.2	0.0	0.1
Cu	0.1	0.2	<0.1
Fe	25.4	28.6	13.8
Mg	0.1	0.2	1.5
Mn	2.9	5.3	4.0
Na	5.3	2.3	14.1
Ni	2.9	1.2	0.9
Si	0.8	1.0	1.1
U	0.0	0.0	5.7
Zn	0.2	0.3	Not reported
Zr	0.6	0.6	Not reported

The simulated wastes were tested in a 4-dm³ (4-L) lab-scale version of the chemical treatment process, Figure 1. Supporting data were obtained at 0.5 and 22 dm³ scales. Data from successful tests are summarized in Table 2.

Table 2

Experimental summary data table

Run ID	Fraction HCO ₂ ⁻ Lost	Fraction C ₂ O ₄ ⁼ Lost	C ₂ O ₄ ⁼ Adj Noble metals, %	HCO ₂ ⁻ added, M	Initial C ₂ O ₄ ⁼ , M	Excess acid, M
SB3-1	0.366	0	100	0.797	0	0.356
SB3-2	0.396	0	100	0.797	0	0.356
SB3-3	0.225	0	0	0.797	0	0.356
SB3-3s-1	0.253	0	10	0.745	0	0.269
SB3-4	0.416	0	100	0.797	0	0.356
SB3-6	0.259	0.164	84.65	0.773	0.244	0.067
SB3-7	0.178	0.088	73.39	0.552	0.391	-0.066
SB3-8	0.197	0.202	73.39	0.552	0.391	-0.066
SB3-9	0.057	0.153	73.39	0.647	0.391	0
SB3-10	0.042	0.308	73.39	0.688	0.391	0
SB3-11	-0.060	0.312	7.34	0.688	0.391	0
SB3-12	-0.056	0.289	7.34	0.647	0.391	0
SB3-13	-0.060	0.366	7.34	0.647	0.391	0
SB3-14	0.016	0.230	73.39	0.688	0.391	0
SB3-15	-0.112	0.298	7.34	0.688	0.391	0
SB3-16	0.032	0.188	73.39	0.647	0.391	0
SB3-17	0.040	0.317	73.39	0.688	0.391	0
SB3-18	0.334	0	100	0.908	0	0.587
SB3-20	0.132	0.032	6.48	0.819	0.533	0.243
SB3-20s-2	0.290	0.056	6.48	0.659	0.533	0.049
SB3-21	0.254	-0.012	64.77	0.819	0.533	0.243
SB3-22	0.136	0.100	7.34	0.798	0.391	0.218
SB3-23	0.333	0.066	84.65	0.745	0.226	0.350
SB3-23s-2	0.321	0.147	8.47	0.632	0.226	0.146
SB3A-1s-2	0.231	0.320	6.66	0.797	0.534	0
SB3A-2	0.027	0.121	7.75	0.702	0.382	0.259
SB3A-2s-1	0.199	0.085	7.75	0.644	0.382	0.165
SB3A-2s-3	0.177	0.122	7.75	0.561	0.382	0.047
SB3A-3	0.027	0.159	7.26	0.704	0.422	0.074
SB3A-3s-1	0.249	0.083	7.26	0.693	0.422	0.105
SB3A-4	0.167	0	9.79	0.796	0.026	0.342
SB3A-4s-1	0.335	0	9.79	0.741	0.026	0.250
D-O 1a	0.077	0.308	6.63	0.877	0.546	0.084
D-O 2b	0.213	0.278	6.7	0.651	0.524	0.063
D-O 3a	0.401	0	9.79	0.26	0.026	0.081
SB3A-8	0.361	0.224	66.65	1.002	0.51	0.293
SB3A-9	0.225	0.139	77.51	0.912	0.292	0.542

The two HLW simulants were generally close to SB3 in elemental composition after the appropriate sodium salts were added and an allowance was made for missing radionuclides. Various concentrations

of sodium salts were studied to assess the impact of washing on the SRAT chemistry. Most of the non-sodium species in HLW sludge per Table 1 are fairly insensitive to washing at pH 12-14. Many other species are present in HLW at small concentrations, including Ag, Hg, Pd, Rh, Ru, Pb, La, Cs, and Pu. Ag, Hg, Pd, Rh, and Ru salts are added directly to the lab-scale SRAT to ensure that their concentrations are controlled as close to target levels as possible.

Lab-scale simulant processing parallels that in the 42 m³ (11,000 gallon) SRAT in the DWPF. Specifically, the approximate ratio of radius to height is maintained; the appropriate scaled working volume is used; the same cycle steps are performed in the same sequence with the same durations; and acid feed rates, air purge rates, and water boil-up rates are appropriately scaled for the working volume in the 4-dm³ vessel. The full-scale SRAT process proceeds as follows:

1. Sludge is received and chemically characterized.
2. A total acid requirement calculation is performed.
3. A glass iron reduction-oxidation state model is used to divide the total acid requirement between nitric and formic acids.
4. Waste is heated to 93 °C.
5. 50% nitric acid is added to the SRAT at about 2 gallons per minute (about 1-2 hours).
6. 90% formic acid is added to the SRAT at about 2 gallons per minute (about 2-8 hours).
7. Waste is taken to boiling.
8. A volume reduction is made by withdrawing condensate (about 3-4 hours).
9. Boiling continues at approximately constant volume by refluxing the condensate back to the SRAT (about 12-40 hours). Elemental mercury is steam-stripped and separated.
10. The vessel contents are cooled to 50 °C and sampled for acceptability.
11. The SRAT contents are transferred to the Slurry Mix Evaporator

Glass frit is added to the waste slurry in the Slurry Mix Evaporator to produce a suitable melter feed composition, the slurry is further concentrated, and the waste is chemically characterized to predict the

properties of the glass that will be poured by the melter. A typical lab-scale SRAT cycle process simulation, including steps 4 through 11, takes about 20 hours.

Thirty SRAT cycle simulations were completed in 4-dm³ vessels as part of the evaluation of the impact of oxalate ion on processing. An additional 26 SRAT cycles were completed in 0.5-dm³ vessels (no off-gas composition data). Eight SRAT cycles were completed in 22-dm³ vessels. The primary variables in the simulations were:

1. The total moles of acid added per liter of starting waste slurry.
2. The percentage of the total acid added that was nitric acid (typically 20-35% by mole).
3. The concentrations of the noble metals Pd, Rh, and Ru added with the sludge waste slurry.
4. The fraction of the simulated waste slurry that was displaced by a sodium oxalate slurry.

Most SRAT starting sludges were about 82 wt. % water. When sodium oxalate was added, it was added with sufficient water to maintain the water content at roughly 82 wt. %. Sodium oxalate made up anywhere from zero to 47 wt. % of the non-aqueous portion of the slurry. Due to project constraints, increasing sodium oxalate content was accompanied by decreasing noble metal concentrations. (Noble metals are linked to the radioactive waste on a sodium oxalate free basis.) Several levels of noble metals were studied. This was permitted because of uncertainty in the noble metal content of the Tank 7 solids. The noble metal concentrations in air-dried waste solids (110 °C oven), free of sodium oxalate, are given in Table 3. The 100% Rh case is roughly 100 mg Rh/kg slurry. The three primary noble metals in SRS radioactive waste sludge have been reported as potentially active for catalytic wet air oxidation (*16, 17, and others*).

Table 3

Noble Metal Concentrations in Air-dried, Oxalate-free Solids

% nominal	wt. % Pd	wt. % Rh	wt. % Ru
0%	0.0	0.0	0.0
10%	0.003 ± 0.0002	0.0055 ± 0.0004	0.0197 ± 0.0013
100%	0.030 ± 0.002	0.055 ± 0.004	0.197 ± 0.013

Gas chromatography (GC) was used to monitor the composition of hydrogen, carbon dioxide, nitrous oxide (N₂O), nitrogen, and oxygen in the 10 °C exhaust gas stream. The instrument was checked against a standard calibration gas before and after each SRAT simulation. Good quality GC data was obtained for 26 4-dm³ SRAT runs and two 22-dm³ SRAT runs. The gas sampling rate was once every three minutes, or about 360 points per SRAT simulation. An internal standard flow was created using a known flow of helium mixed with the purge air (nominally 0.5 vol% He). Helium concentration was monitored by the GC. The combination of GC data with the internal standard flow permitted conversion of off-gas volume percents into molar flowrates. The molar flowrates were integrated numerically using Simpson's Rule to obtain the total moles of various gases evolved.

Ion chromatography (IC) was used to monitor the slurry concentrations of nitrite, nitrate, formate, and oxalate anions. A 100-fold water dilution of the slurry sample was used to bring nitrate, nitrite, and formate into solution prior to filtration. This preparation was not adequate for oxalate. Only about 50-70% of the oxalate was recovered by this technique. An alternative sample preparation method was developed using a strong acid dissolution. This permitted recovery of roughly 95% of the oxalate, although the prepared samples appeared to be mildly time and/or light sensitive (20, 21). Sample reproducibility was not as good for oxalate as for the other anions, roughly ±20% compared to ±10% for the other anions. NIST traceable standards were used to check nitrite and nitrate IC analyses. In-house standards were used to confirm formate and oxalate analysis calibrations. Starting waste simulants were analyzed to determine concentrations of ions prior to processing.

As expected, the starting waste simulants were free of formate ion. All SRAT product slurries were analyzed to determine the concentrations of key anions following processing. The analytical information obtained from the SRAT runs was used to create overall material balances, which closed to within 2-3% on the individual runs with GC data. For runs without GC data, material balances closed to within 8-14% due to the absence of the mass lost in the purge gas term. Nevertheless, closure errors for runs without GC data fell in a narrow range when the other analytical data were of good quality, since the majority of the off-gas species are formed routinely during processing. Species material balances

were constructed on formate ion and on oxalate ion. Considerable variation was seen in the results depending on the processing conditions that were selected. These results are discussed further below.

Results from Simulant Process Simulation Experiments

The tests described above were screened to eliminate tests that indicated that insufficient acid was added to meet the processing goals. This judgment was primarily based on the successful destruction of nitrite ion. There were 37 tests where the acid addition was sufficient to meet plant requirements, Table 2, of less than 1,000 mg nitrite/kg product slurry. These formed the basic data set for the statistical analysis below.

The presence of sodium oxalate had a significant impact on processing. The first discovery was that the displacement of significant masses of the 18 wt. % basic simulated waste slurry by equivalent masses of 18 wt. % sodium oxalate slurry did not produce a corresponding reduction in the acid required for successful processing. The combination of oxalate and acid apparently promoted chemical attack on the hydroxide-rich sludge solids. These reactions liberated additional hydroxide groups into the aqueous phase which required additional acid to neutralize. Historically, acid hydrolysis of the sludge insoluble solids has proceeded fairly slowly with only a small percent reacted by the end of the SRAT cycle. In this case, however, the process converted sodium oxalate into various other oxalates, e.g. calcium oxalate, manganese oxalate, and probably some iron oxalate. These species were identified or inferred by various techniques such as X-ray diffraction and scanning electron microscopy. The liberated oxalate ion was apparently also able to tie up some of the available acid protons as the bioxalate ion, HC_2O_4^- .

A second, more surprising, discovery came in a set of four tests containing 24% sodium oxalate slurry-76% waste simulant slurry. This set of tests was at 10% of the nominal noble metals listed in Table 3 and at essentially the minimum total acid requirement for nitrite destruction. In these four runs, more total formate mass was found in the SRAT product than was added. This was the opposite of the historical processing outcome, where there was inevitably a net loss of formate through chemical reduction reactions and catalytic attack. Simultaneously, it was found that approximately 30% of the oxalate added as sodium oxalate could not be accounted for in the product or samples.

A further observation came from other SRAT simulations in this program, where as much as 40% of the added formate was consumed by reduction reactions and through decompositions. This represented a larger than expected formate loss, but was not inconsistent with historical SRAT work coupled with expectations due to the nominal noble metal concentrations, and to the addition of about 25% more acid than was necessary. Additional research on catalytic wet air oxidation was undertaken at this point. The paper by Lee (15) was of particular value, since it showed that the catalytic wet air oxidation of the oxalate ion proceeded with formate ion as an intermediate product. It was hypothesized that oxalate ion was being catalytically converted to formate ion during the SRAT process, which explained how formate ions could be consumed by the waste simulant while simultaneously having more total formate in the SRAT product than was added as formic acid.

The four initial SRAT observations of actual net formate generation at 10% nominal noble metals were subsequently found to be somewhat atypical. Generally, there was enough formate destruction by reduction reactions, combined with catalytic decomposition and oxidation, to more than offset any gain from oxalate oxidation. However, other SRAT simulations produced formate losses that were insufficient to explain the reduction reaction losses (from reactions with Hg, nitrite, and Mn), where oxalate to formate conversion could be inferred. At least eight other SRAT runs in the 4-dm³ vessels (out of 30) exhibited a formate loss that was less than the reduction reaction requirement. The SRAT simulations indicated varying levels of oxalate loss with losses as large as 30% to essentially no loss.

A statistical approach was used to isolate factors affecting formate and oxalate ion concentrations during SRAT processing. This approach was selected due to the complexity of the process (large number of poorly defined species) and lack of independently proven kinetic models for the phenomena in question. The following causal factors were selected for study:

1. Formate ion added, moles/liter
2. Oxalate ion added, moles/liter
3. Relative concentration of noble metals present; % relative to the Table 3, 100% case
4. Excess acid added beyond that required for sludge processing

These were analyzed against the following outcome factors, or responses:

1. Net formate ion lost, moles/liter
2. Net oxalate ion lost, moles/liter

The analysis was made using the JMP statistical software package, professional edition. Factors were selected, and a step-wise linear regression was performed. The regression of net oxalate ion lost gave the following results in Table 4.

Table 4
Regression Results for Net Oxalate Ion Lost

Term	Estimate	t Ratio	Prob > t
Intercept	-0.072	-1.84	0.075
Formate added	0.221	3.08	0.004
Oxalate added	0.049	1.05	0.302
Noble metals	-0.0001	-0.62	0.537
Excess acid	-0.261	-4.01	0.0003

The regression had an R^2 of 0.626 and adjusted R^2 of 0.579. A small “Prob > |t|” indicates a significant factor. The regression of net formate ion lost gave the results in Table 5. The regression had an R^2 of 0.549 and adjusted R^2 of 0.493. The relatively modest R^2 values are not unusual given the number of phenomena that are being ignored during the modeling.

Table 5
Regression Results for Net Formate Ion Lost

Term	Estimate	t Ratio	Prob > t
Intercept	0.0135	0.15	0.882
Formate added	0.0727	0.44	0.663
Oxalate added	-0.0519	-0.48	0.632
Noble metals	0.0007	1.78	0.085
Excess acid	0.3592	2.40	0.022

The explanation of the net formate loss was dominated by the two factors “excess acid” and “noble metals”. Formate loss increased with increasing excess acid and with increasing noble metal concentrations. Formate loss was relatively insensitive to the total formate and oxalate additions. Levec (16) reported that formic acid oxidation was first-order with respect to both oxygen partial pressure and

formic acid concentration. This is consistent with the observed JMP correlation between net formate lost and excess acid.

Net oxalate loss was also sensitive to “excess acid”, however the dependence regressed with the opposite sign as that for net formate loss. The net oxalate loss was relatively insensitive to “noble metals”. The net oxalate loss tended to increase as the amount of formate added increased and as the amount of excess acid decreased. This is significant since these two factors are themselves correlated, that is they both tend to increase together other effects being equal.

Lee (15) reports that the catalytic oxidation of oxalic acid with Pt catalysts is slower than that of formic acid. Conversion of oxalate to formate is one step ahead of the final step, oxidation of formic acid to carbon dioxide and water. This is consistent with the regression findings above where net formate loss was sensitive to the noble metals concentration. This does not seem to be consistent with the result that the net oxalate loss was not sensitive to the noble metals concentration.

Neither formate nor oxalate oxidation went to completion in the SRAT process simulations. The carbon dioxide generation rates gradually fell as the system pH rose during processing. This trend is consistent with literature results that the oxidation rates of the molecular acids are greater than the oxidation rates of the anions. CWAO is clearly indicated as a likely cause of SRAT formate loss. If CWAO is causing formate loss, then CWAO is the likeliest explanation for the SRAT oxalate loss. The two reactions have been established as occurring together even if there is no statistically significant dependence of oxalate loss on noble metal concentration. It remains possible, if unlikely, that the oxalate was converted to formate by some other process than CWAO, including simple, or thermal, wet air oxidation. This reaction has been studied by Mishra (19) and by Shende (18). The 225-245 °C processing conditions in the Shende paper, however, were considerably more severe than those reached in the SRAT simulations (101-102 °C).

The effect of excess acid was in opposite directions for formate and oxalate losses. Net formate loss was increased by increasing excess acid, while net oxalate loss was reduced by increasing excess acid. This is potentially indicative of a competition between formate and oxalate ions for reaction sites, in

which increased excess acid leads to conditions that favor formate destruction over oxalate destruction. Runs with more excess acid reached lower pH values immediately following acid addition, although they often ended with a slightly higher pH. The slightly higher pH can be traced directly to the greater losses of formic acid that occurred in those runs.

Net oxalate loss had a statistically significant dependence on the formate loss in the absence of other factors. The “prob > |t|” was 0.0022 and the regression coefficient was negative, that is, more net oxalate loss strongly correlated to less net formate loss. A significant statistical dependence between the two net ion losses was also seen during a regression in the presence of the other factors; however the most significant term was the net molarity of “formate added”, “prob |t|” > 0.0025. “Excess acid” was no longer significant to net oxalate loss in this regression analysis; however it was already significant in explaining variations in net formate loss. It would seem that the significance of “excess acid” to net oxalate loss was shifted to net formate loss when the latter was allowed to be an effect factor rather than an outcome variable.

The question of which species in the simulated waste sludge were catalyzing the catalytic wet air oxidation was not systematically investigated due to programmatic constraints. The three primary noble metals form in relatively constant ratios related to their fission product yields, so the individual concentrations were not varied independently of one another. The prior work by King (9) indicated that both Rh and Pd were effective catalysts for formic acid oxidation in a simple aqueous system, while Ru appeared to be an ineffective catalyst. There are other species in the simulated waste that have been associated with catalytic wet air oxidation, including Mn: Andreozzi (12), Levec (16), and Luck (17). The literature has indicated a generally higher temperature requirement for significant reaction rates than occurs during SRAT processing. Conversely, there was a hundred-fold greater concentration of Mn than the individual noble metals.

Radioactive Processing Data

Actual oxalate levels in the Tank 7 radioactive slurry were found to be less than expected. They were only a few percent of the maximum predicted value. This may indicate either that oxalate destruction

has occurred over time in a radiation environment (SRNL irradiation testing did not indicate this was likely), or that oxalate was transferred with the aqueous phase to other locations within the tank farm. Many such decanting transfers occurred during the history of Tank 7. Two SRAT simulations were performed in the SRNL Shielded Cells facility with Tank 7 samples. The DWPF has subsequently processed this particular waste into glass. Since then, oxalic acid has become the preferred choice for chemically cleaning waste tank heels. The caustic neutralized spent cleaning solution/slurry will potentially be combined with the normal feed to the DWPF. This scenario will present the same processing challenges as were investigated for Tank 7.

The noble metal concentrations of the radioactive waste samples were somewhat greater than the 10% nominal case given in Table 3. The actual waste that was processed in the DWPF corresponded generally to the sample used in Shielded Cells Run 2, Table 6.

Table 6
Noble metal concentrations
in wt% of air-dried solids

	Pd	Rh	Ru
Shielded Cells Run 1	0.0017	0.0071	0.036
Shielded Cells Run 2	0.0014	0.0074	0.035

Formate and oxalate losses were observed during radioactive waste slurry processing. The approximate levels of these losses as a percentage of the respective starting masses are given in Table 7. The DWPF data comes from the first nine full-scale SRAT runs of the SB3 campaign.

Table 7
Anion losses with radioactive HLW

	% formate lost	% oxalate lost
Shielded Cells Run 1	16	39
Shielded Cells Run 2	19	0
DWPF (average)	23	~50

The analytical data are less certain for the two Shielded Cells runs. Sampling and analysis are both more difficult with radioactive samples than with simulants, and the total experimental system size is generally much smaller. The two Cells runs each started with only about 0.3 dm³ of waste slurry. Obtaining accuracy on the oxalate analysis presented some additional difficulty, and the two numbers given for percent oxalate lost have accumulated significant uncertainty. The DWPF pulls multiple samples every SRAT batch using a flow-through sampling system. Formate and oxalate results are generated in quadruplicate for both the starting and ending slurries. A batch is typically about 30,000-35,000 kg of radioactive waste slurry. Total initial formate was about 1350-1700 kg per batch, including the formic acid added plus formate in the heel from the previous batch. Total initial oxalate was about 30-40 kg. Accurate tracking of formate is more feasible than for oxalate, because of the much larger concentrations. (Note that certain minimum dilutions must be performed on the samples in order to reduce the radioactivity to a level that can be tolerated in the vicinity of the ion chromatograph.)

GC data were taken during the two Shielded Cells runs. Both runs detected hydrogen generation. These were well below 1% hydrogen in the air purge exhaust. Both runs also detected a sustained molar generation rate of carbon dioxide that was significantly greater than that of hydrogen, along with a generally rising pH with processing time. These are the markers associated with continuing formate destruction in both simulant and radioactive SRAT cycles that appear to be associated with catalytic wet air oxidation.

Radioactive and non-radioactive simulations of the DWPF – Sludge Receipt and Adjustment Tank process have both shown an unexplained loss of oxalate ion, an unexplained loss of formate ion, occasional formation of new formate ion, and sustained generation of carbon dioxide at levels above those required by catalytic decomposition of formic acid to hydrogen. Supporting data has also been obtained on the full-scale tank. A single, likely explanation has been found for all of these observations. A relatively mild form of catalytic wet air oxidation chemistry is occurring during processing at boiling temperatures. Statistical analysis of available data has shown that the formate loss is strongly correlated with the collective concentrations of Pd, Rh, and Ru in the system. Therefore, the process is presumed

to be catalytic in nature. This is also consistent with previous work establishing noble metal catalysis as the primary source of hydrogen generation during processing (as opposed to radiolytic formation of hydrogen, which is also observed, but at much lower levels). Formate destruction also correlates to the amount of excess acid present in the system. This could be due to a preferential attack on molecular formic acid relative to formate ion (dissolved sodium formate).

Oxalate destruction correlates to both the total formate added and the excess acid present in the system, but in opposite directions. These correlations indicate a general dependence on the quantity of formic acid added, since more excess acid implies more total formate added. The net impact, which is negative, indicates that competition of the oxalate and the formate for the catalyst sites shifts more toward formic acid as the amount of formic acid in the system increases. The apparent lack of sensitivity of net oxalate destruction to the quantity of noble metals present, however, could be taken as an indication that noble metal availability is not limiting the conversion rate. Evidence for simple wet air oxidation of oxalate was not obtained, nor could it be established that more common species in the waste, such as Mn, might not be acting as catalysts for oxalate oxidation. Evidence for simple wet air oxidation of formate, however, is negative under the normal SRAT processing conditions. A general high-level history of legacy radioactive waste at the former U. S. government nuclear weapons sites can be found in the U. S. Department of Energy-Office of Environmental Management publication: *Linking Legacies: Connecting the Cold War Nuclear Weapons Production Processes to Their Environmental Consequences (I)*.

More research is planned on oxalate-rich HLW slurry feeds for the DWPF. Oxalic acid is actively being used to dissolve residual solids in the waste storage tanks as part of the tank closure program. A process to destroy the oxalate prior to DWPF is the preferred option, but that capability has yet to be demonstrated at large scale. Therefore, the interim disposal route is potentially through the DWPF. The capability of handling high oxalate concentrations in the DWPF feed increases the options available for remediating the HLW stored at the Savannah River Site.

BRIEF: Catalytic wet air oxidation chemistry occurs spontaneously during the formic acid pretreatment of high level radioactive waste containing oxalate due to the presence of noble metals formed as fission products of ^{235}U .

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NOMENCLATURE

CWAO	Catalytic wet air oxidation
DWPF	Defense Waste Processing Facility
HLW	High-Level Waste
MWWT	Mercury Water Wash Tank
NIST	National Institute of Standards and Technology
SB3	Sludge Batch 3 (fourth HLW feed campaign in DWPF)
SRAT	Sludge Receipt and Adjustment Tank
SRNS	Savannah River Nuclear Solutions
SRR	Savannah River Remediations
SRS	Savannah River Site

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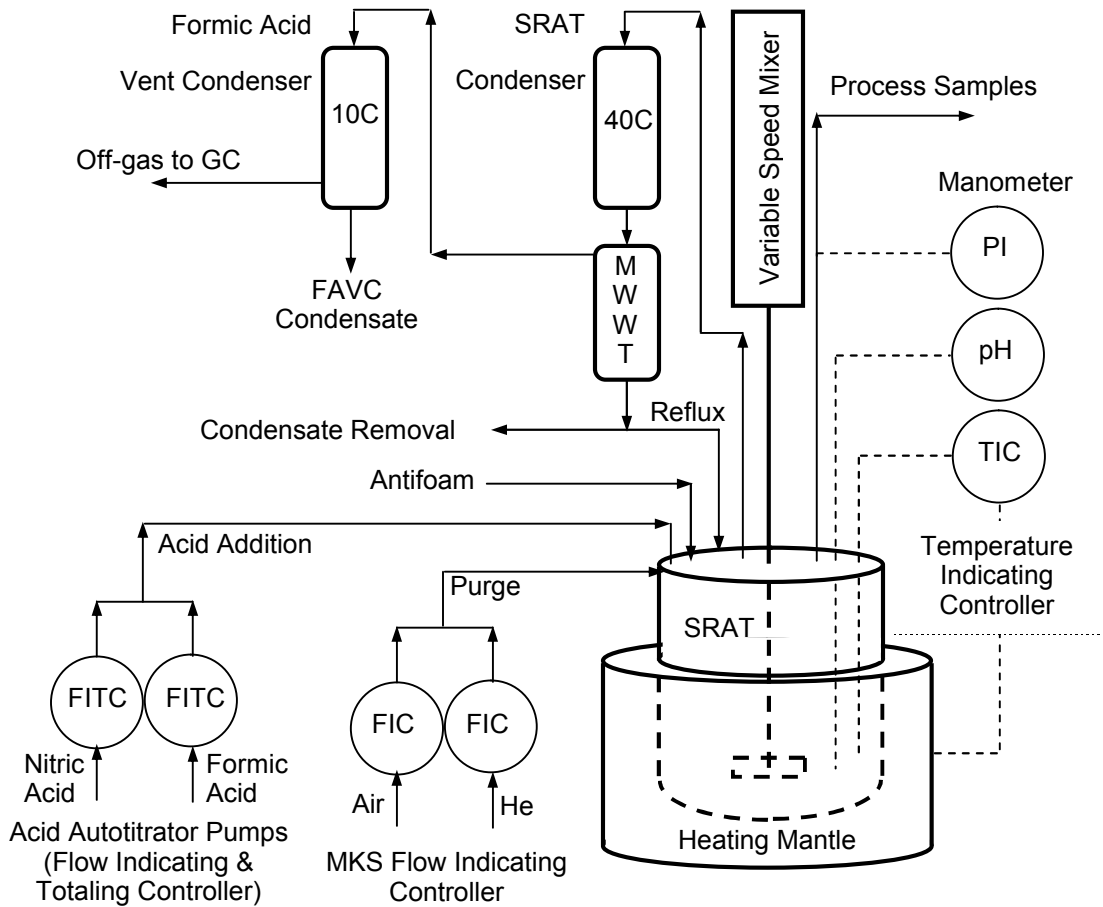


Figure 1. Schematic diagram of the 4-dm³ Sludge Receipt and Adjustment Tank test facility at SRNL.