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VOLATILITIES OF RUTHENIUM, IODINE, AND TECHNETIUM ON CALCINING FISSION PRODUCT NITRATE WASTES

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Abstract

Various high-level nitrate wastes were subjected to formic acid denitration. Formic acid reacts with the nitrate anion to yield non-condensable, inert gases according to the following equation:

$$4\ HCOOH + 2\ HNO_3 \rightarrow N_2O + 4\ CO_2 + 5\ H_2O\ .$$

These gases can be scrubbed free of ^{106}Ru, ^{131}I, and ^{99}Tc radioactivities prior to elimination from the plant by passage through HEPA filters. The formation of deleterious NO_x fumes is avoided. Moreover, formic acid reduces ruthenium to a lower valence state with a sharp reduction in RuO_4 volatility during subsequent calcination of the pretreated waste. Comparative tests showed that on calcining an acidic thorium nitrate at 250 and 350°C, the percent ^{106}Ru volatilities were 35.6 and 26.0% for the untreated waste, and only 0.07 and 0.15%, respectively, for the same waste pretreated with 2.0 moles of formic acid per mole of nitrate. Other acidic nitrate wastes containing aluminum nitrate or (Zr, Al) fluoride-nitrate showed a substantial decrease in RuO_4 volatility on pretreatment with formic acid. The percent ^{106}Ru volatility is relatively low ($\sim$1.0%) on calcining untreated acidic wastes at high calcination temperatures of 600°C or on calcining alkaline wastes (sludge and sodium nitrate supernate). It is shown that a minimum of 3% of RuO_4 in an off-gas stream reacts with Davison silica gel (Grade 40) to give a fine RuO_2 aerosol having a particle size of 0.5 µ. This RuO_2 aerosol passes through water or weak acid scrub solutions but is trapped by a caustic scrub solution. Iodine volatilizes almost completely on calcining an acidic waste, and the iodine volatility increases with increasing calcination temperature. On calcining an alkaline sodium nitrate waste the iodine volatility is about an order of magnitude lower, with a relatively low iodine volatility of 0.39% at a calcination temperature of 250°C and a moderate volatility of 9.5% at 600°C. Volatilities of ^{99}Tc were generally <1% on calcining acidic or basic wastes at temperatures of 250 to 600°C. Data are presented to indicate that ^{99}Tc concentrates in the alkaline sodium nitrate supernatant waste, with $\sim$10 mg ^{99}Tc being associated with each curie of ^{137}Cs present in the waste. It is shown that lutidine (2,4 dimethyl-pyridine) extracts Tc(VII) quantitatively from alkaline supernatant wastes. The distribution coefficient (K_D) for Tc(VII) going into the organic phase in the above system is 102 for a simulated West Valley waste and 191 for a simulated Savannah River Plant (SRP) waste.

I. Introduction

Denitration

The nitrate anion is the predominant constituent in most, high-level, liquid wastes. In (1) it is shown that the most satisfactory

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method of decomposing HNO_3 and minimizing toxic NO_x production involves addition of the acidic fission-product nitrate solution to formic acid. Formic acid is a reducing agent that reacts with nitric acid at 80 to 100°C to form CO_2, N_2O, and H_2O according to the following equation:

$$4\ HCOOH + 2\ HNO_3 \rightarrow N_2O + 4\ CO_2 + 5\ H_2O \qquad (1)$$

Because of the possible presence of volatile radioactive compounds such as I_2, Tc_2O_7, and RuO_4 in the off-gas stream, it is desirable that the gaseous byproducts (CO_2 and N_2O) be subjected to aqueous scrubbing prior to passage through HEPA filters and elimination from the plant. This process was developed and carried to the pilot plant stage at Karlsruhe, Germany.(2,3) Continuous chemical denitration can be carried out by premixing the formic acid with the high-level waste prior to injection into a spray calciner. In this case N_2 is likely to be formed rather than the N_2O that is formed by reaction of nitric acid with excess formic acid in aqueous solution.

When formic acid is added to the acidic nitrate solution in the presence of excess nitric acid, Orebaugh and Healy(4,5) show that the main reactions are as follows:

$$2\ HNO_3 + HCOOH \rightarrow CO_2 + 2\ NO_2 + 2\ H_2O \text{ at } HNO_3 > 4\ M \qquad (2)$$

and

$$2\ HNO_3 + 3\ HCOOH \rightarrow 3\ CO_2 + 2\ NO + 4\ H_2O \text{ at } HNO_3 < 2\ M \qquad (3)$$

Healy urged the application of these reactions to the removal and recycle of nitric acid from fission-product waste solutions. However, the recovery of NO_x gases introduces engineering and processing difficulties because of the slow absorption kinetics of hydrating the NO_x vapors to produce HNO_3 and HNO_2. The escaping NO_x vapors have an adverse environmental effect, with the threshold limiting value (TLV) for nitrogen dioxide being set at 0.05 ppm (0.10 mg/m^3) as an average annual value(6) because of the deleterious effects of NO_x vapors on lung function. Thus, the present technology has moved toward NO_x abatement rather than to HNO_3 recovery and recycle. Pence and Thomas(7,8) introduce ammonia gas, which reduces NO_2 to N_2 or N_2O according to the following reactions:

$$4\ NH_3 + 3\ NO_2 \rightarrow 7/2\ N_2 + 6\ H_2O + \text{heat} \qquad (4)$$

and

$$6\ NH_3 + 8\ NO_2 \rightarrow 7\ N_2O + 9\ H_2O \qquad (5)$$

Because of the inert nature of the reaction products (N_2 or N_2O gases), these gases can be scrubbed and filtered through HEPA filters before being eliminated from the plant. It should be noted that these same gases are produced by reacting nitrate in the presence of excess formic acid. The harmless inert, noncondensable gases (N_2 and N_2O) produced in both cases serve the goal of NO_x abatement.

Ruthenium Behavior

The high volatility of ruthenium when calcining HNO_3 solutions can be explained(1) by the existence of a highly nitrated ruthenium complex that decomposes at higher temperatures with RuO_4 volatilization.(9,10,11) Formic acid interacts with the nitrated octahedral complexes of ruthenium to yield formate complexes that decompose and form nonvolatile RuO_2, or possibly ruthenium metal, instead of the volatile RuO_4. On calcining a 4.0 *N* HNO_3 solution the RuO_4 volatility is decreased from ~35% to 0.007% after pretreatment with a 15% excess above two moles of formic acid per mole of nitrate.(1) Thus, formic acid decreases the intrinsic volatility by reacting with and removing nitrato and nitro groups from ruthenium complexes.

The volatilized RuO_4 has a high solubility (0.07 to 0.10 mol/liter) in weak acid solutions(12) and is easily scrubbed from an off-gas stream, with 99.9% trapping of RuO_4 in the first two scrubbers of an all-glass system.(1) The RuO_4 is reduced to a nonvolatile, lower-valence state by hydrogen peroxide or nitrous acid present in the scrub solution.(13,14) In studying the vapor pressure of RuO_4, Myuller and Nikol'skii(15) found it necessary to work in all-glass equipment and to remove any grease film by pretreating the glass surfaces with strong oxidizing agents. Because of its reactivity, RuO_4 reacts with stainless steel to form black deposits of RuO_2.(16) This reaction is rapid and complete even at room temperature. The author has observed the immediate coating of stainless steel surfaces with a black RuO_2 deposit after a strong oxidant is added to an acidic ruthenium solution contained in a Pyrex glass vessel fitted with a stainless steel head and stainless steel lines. Special precautions must be taken to eliminate vapor condensation because it is possible for RuO_4 to react with H_2O_2 or HNO_2 in the condensate. Hence, in addition to the use of glass equipment, the off-gas stream is passed through a filter enclosed in an electric heating mantle to prevent vapor condensation. Under these conditions, where precautions are taken to avoid reaction of RuO_4 with stainless steel or other materials, it is possible to define an intrinsic RuO_4 volatility, and to break down the problem of RuO_4 volatility into its component parts. Thus, for example, in (1) we have shown that the intrinsic volatility of RuO_4 is much greater on calcining nitric acid solutions than on calcining formic acid solutions. In this study the intrinsic volatilities of RuO_4 are compared between acidic nitrate wastes and the same wastes pretreated with formic acid. A low intrinsic RuO_4 volatility is desirable for the safe operation of a calcination plant.

Little light has been shed on the characteristics of RuO_2 aerosols formed by decomposition of RuO_4 in the gas phase or by interaction of RuO_4 with stainless steel or silica gel. Feber(17) has observed the formation of particulate RuO_2 with a mean diameter of 0.05 μ or less as a result of RuO_4 decomposition in the gas phase. In this study, gaseous RuO_4 is reacted with silica to form a fine RuO_2 aerosol, which can pass through a series of four acid scrubbers without significant absorption, but which can be scrubbed from the off-gas stream by caustic scrubbing. Agglomerated particles of RuO_2 were observed in the acid traps after 15 to 30 min. This behavior indicates that ruthenium can spread throughout an off-gas system in the form of an RuO_2 aerosol as well as in the form of gaseous RuO_4.

Actually, ruthenium may be present predominantly in the off-gas system as a RuO_2 aerosol. Our observations in (1) and in this study show that it is possible to distinguish between gaseous RuO_4 and particulate RuO_2 in an off-gas stream by passing the gas through a series of four scrubbers with weak acid in the first two scrubbers and caustic in the last two scrubbers.

Rapid denitration of a salt at high temperatures leads to lower RuO_4 volatilities in a number of nitrate systems.(1) The nitrate salt decomposes to an acid vapor (NO_x fumes) with formation of an alkaline residual calcine (the metal oxide). The alkaline oxide matrix fixes ruthenium as the ruthenate, and thus the formation of volatile RuO_4 is suppressed. Calcination of alkaline solutions also yields low ruthenium volatilities because of the fixation of ruthenium as ruthenate in an alkaline oxide matrix. In this study we report on the denitration of acidic solutions containing high concentrations of thorium nitrate, aluminum nitrate, and (Zr, Al) nitrate-fluoride mixture. On calcining the thorium nitrate and aluminum nitrate wastes, the intrinsic RuO_4 volatility is high (20 to 60%) at temperatures of 250 to 450°C, but decreases to a low value of 0.5 to 1.0% at the higher calcination temperature of 600°C. However, the (Zr, Al) fluoride-nitrate waste yields high RuO_4 volatilities (55 to 99%) at all temperatures from 250 to 600°C. Pretreatment of all acidic wastes with two moles of formic acid per mole of nitrate led to low intrinsic RuO_4 volatilities of 0.1 to 3.0% at calcination temperatures of 250 to 600°C. Calcination of alkaline wastes from the Savannah River Plant gave low RuO_4 volatilities.

A number of incidents involving the emission of particulate RuO_2 activity at various reprocessing sites have been reviewed.(18) In these cases, the ruthenium was initially evolved as RuO_4, which reacted with the stainless steel equipment to form RuO_2. Caustic solutions were more effective than acid solutions in solubilizing the black RuO_2 deposits and in scrubbing RuO_2 aerosols from the off-gas stream. Because of the safety hazards, the processes involving the evolution of RuO_4 were evaluated, and then modified to decrease the risk of dealing with large amounts of volatile radioactive RuO_4. Usually the addition of a strong oxidant to an acid solution was eliminated to avoid the formation of volatile RuO_4. Idaho personnel have had extensive experience in operating a waste calcinator. Christian(16,19) has described the difficulties encountered in controlling RuO_4 volatility. Since RuO_4 is formed during the calcination process and is converted to particulate RuO_2 by interaction of volatile RuO_4 with the stainless steel equipment, a final caustic scrubber at the end of the off-gas system in front of the HEPA filters of the off-gas system should be included to trap RuO_2 particulate activity. Giraud and LeBlaye(20) report on the use of efficient caustic scrubbers in the off-gas system of a pilot plant calcining high-level waste with a high RuO_4 volatility of 15%. High decontamination factors (DF) for ^{106}Ru on the order of 10^9 to 10^{10} were obtained in spite of the high intrinsic RuO_4 volatility. Even higher DFs are obtainable at lower intrinsic RuO_4 volatilities.

Technetium Behavior

Smith, Cobble, and Boyd(21) report vapor pressures so high for technetium heptoxide (Tc_2O_7), pertechnic ($HTcO_4$), and aqueous solutions of $HTcO_4$ that almost complete volatility of ^{99}Tc would be expected on calcining an acid solution at 350°C. The boiling point of Tc_2O_7 is estimated to be 311°C, and the melting point is 118°C. The volatilities of Tc_2O_7 and $HTcO_4$ have been widely used to concentrate and isolate the long-lived ^{99}Tc by distillation from concentrated H_2SO_4 or perchloric acid at 200°C.(22,23) However, our study(1) shows less than 1% ^{99}Tc volatilization on calcining a fission-product HNO_3 solution over a range of temperatures from 250 to 600°C. These unexpectedly low ^{99}Tc volatilities can be correlated to the high thermal stability limits of various metal pertechnetates and technetates reported in (24) and which are presented in Table I.

Table I. High melting technetium oxide compounds.[a]

Compounds	Thermal stability limit (°C)	Comment
$Ba(TcO_4)_2$	700	
$Ba_3(TcO_5)_2$	850	
$Ba_5(TcO_6)_2$	850	Mixed oxide with BaO
$Sr(TcO_4)_2$	680	
$Sr_5(TcO_6)_2$	850	Mixed oxide with SrO
$Ca(TcO_4)_2$	650	
$Ca_5(TcO_6)_2$	800	Mixed oxide with CaO
Sr_2LiTcO_6	900	
$BaTcO_3$	800	
$SrTcO_3$	1200	

[a] Source: KFK-341 (July 1965).

It can be calculated that 10 μg of ^{99}Tc are associated with each mCi of ^{137}Cs as a result of ^{235}U fission. A total of 80 to 90% of fission ^{99}Tc is found associated with ^{137}Cs in alkaline sodium nitrate supernatant waste. Kelley(25) notes that the alkaline SRP supernate contains 200 megacuries of ^{137}Cs in 100 megaliters of solution. Thus, the total amount of ^{99}Tc in the SRP alkaline supernate is 2000 kg. It is estimated that the solids would contain 865 nCi of ^{99}Tc per gram of solids.

It would be desirable to remove the long-lived ^{99}Tc (half-life of 2.05 × 10^5 y) from the alkaline sodium nitrate supernate. The removal of ^{99}Tc from alkaline solutions by solvent extraction with lutidine (2,4-dimethylpyridine) is described in (26,27). The distribution coefficient (K_D) for the extraction of Tc(VII) by lutidine is 102 for a simulated West Valley waste and 191 for a simulated SRP alkaline sodium nitrate waste. Lutidine can be used to recover or remove Tc(VII) from liquid alkaline wastes.

Iodine Behavior

Iodine is readily volatilized from acid solution during dissolution of fuel elements in heated acid. Thus, Yarbro(28,29) reports that 98 to 99% of the iodine is evolved during dissolution and feed adjustment. With NO injection and reflux(30), it is possible to evolve 99.8% of the iodine during dissolution. Thus, the main fission product liquid waste will contain only a small fraction of the iodine formed in fission, which is 0.10 Ci of ^{129}I per metric ton of uranium irradiated at 30,000 Mwd. The volatilized iodine can be trapped by wet scrubbing(1,31) at a yield of 95 to 99% (DF of 20 to 100). Wet scrubbing has been used to trace the fate of iodine during calcination.(1) Iodine volatility is lower on evaporating an alkaline solution than on evaporating an acid solution.(32) Iodine can also react with stainless steel equipment at elevated temperatures.(33) On calcining a HNO_3 waste the iodine volatility increases with increasing temperature,(1) as shown in Fig. 1 and Table II. An appreciable fraction of the iodine is retained in the solid residue only at the lower temperatures (350°C and lower). Almost all the iodine is volatilized at the higher temperatures (650°C and higher). Wastes containing a high fraction of the iodine should be segregated and treated separately.

Table II. Iodine distribution in the pot calciner off-gas scrubber system.

	Calcination temperature (°C)						Row[b]
	350	450	550	650	350[a]	650[a]	
Total distribution of iodine (%)							
Residues	70.2	44.6	41.2	22.6	37.0	2.3	A
Particulates[d]	1.2	9.7	2.3	2.6	3.3	1.0	B
Volatiles	28.6	45.7	56.5	74.8	59.7	96.7	C
Distribution of volatiles (%)							
Formic acid scrubber							
Trap 1	19.2	33.0	52.6	63.9	48.3	76.1	D
Trap 2	7.8	10.2	3.5	9.9	9.6	19.5	E
Trap 3	1.1	0.8	0.2	0.6	0.5	0.7	F
Trap 4	0.3	0.2	0.07	0.2	0.2	0.2	G
NaOH scrubber	0.03	1.3	0.06	0.1	0.1	0.02	H
HEPA							I
Adsorbents							
1st charcoal filter	0.17	0.2	0.07	0.2	1.0	0.18	J
2nd charcoal filter							K
Silica gel				0.08[c]			L

[a] Pretreated with formic acid (2 moles per mole of nitrate).
[b] Rows A–C total 100%; rows D–L total to line C.
[c] The silica gel was placed ahead of the charcoal filter.
[d] Iodine found on rinsing the filter in front of the wet scrubbers.

II. Description of Equipment and Experimental Procedure

A small quartz pot calciner is mounted inside a 10×10×10-cm cavity in a laboratory furnace. The solution to be calcined is added dropwise to the calciner, which is held at a constant temperature. Evaporation takes place by flash evaporation. The vapors are drawn off through a sidearm and passed through a 9-cm-diam fritted glass disk of medium porosity (10- to 15-μ pore size) encased in a heating mantle to prevent condensation of RuO_4. The off-gas is also pulled through four water (weak acid) scrubbers filled with glass Rashig rings and connected to each other with glass ball joints. Since the equipment is of all quartz and Pyrex construction and no grease was used in the ball joints, no black deposits of RuO_2 were ever observed. A caustic scrubber, a silica gel column, and a HEPA filter followed by a vacuum pump complete the off-gas scrubbing train. More details are given in (1). A sketch of the equipment is shown in Fig. 2.

Fig. 1. Iodine-131 volatilization (%) vs temperature (°C).

The solution in the first two water scrubbers was sampled and gamma-emitting radioactivities were analyzed by gamma scanning to determine ^{106}Ru or ^{103}Ru, ^{95m}Tc and ^{131}I, ^{134}Cs, ^{144}Ce, and ^{152}Eu, as well as ^{106}Ru were routinely determined in a mixture of aged fission products by gamma scanning. Strontium-90 and ^{99}Tc were determined radiochemically after addition of a carrier. Nitrate was determined by reduction to ammonia with the use of Devarda's alloy. Other cations were determined by emission spectroscopy.(1)

A highly radioactive nitric acid waste was prepared as described in (1). The composition of waste constituents and radioactivity concentrations is given in Table III. This high-level radioactive waste was used in the preparation of other highly radioactive wastes. Generally, one part of this waste was added to nine parts of a waste containing the major stable components in order to prepare a simulated high-level waste. The composition and activity concentrations of the waste are given in the section in which the waste is discussed. The results of tracer level activity runs were generally confirmed by the results obtained in the high-level activity runs.

Fig. 2. Quartz pot calciner and off-gas scrubber train.

Table III. Composition of actual and simulated HNO_3 waste (100 gallons waste per 1000 kg of U)

Constituent	Formula	Concentration, molar	
Nitric acid	HNO_3	4.0	
Uranium nitrate	$UO_2(NO_3)_2$	0.123	(1% of original U)
Ruthenium nitrate	$Ru(NO_3)_3$	0.061	
Cesium nitrate	$Cs(NO_3)$	0.062	
Rare earth nitrates	$M(NO_3)_3$	0.1608	
Gadolinium nitrate	$Gd(NO_3)_3$	0.1512	(added as a neutron poison)
Strontium nitrate	$Sr(NO_3)_2$	0.0246	
Barium nitrate	$Ba(NO_3)_2$	0.0336	
Cerium nitrate	$Ce(NO_3)_3$	0.0477	
Sodium nitrate	$NaNO_3$	0.0114	
Iron nitrate	$Fe(NO_3)_3$	0.0945	(Stainless steel corrosion products)
Nickel nitrate	$Ni(NO_3)_2$	0.0036	
Chromium nitrate	$Cr(NO_3)_3$	0.0102	
Zirconium nitrate	$Zr(NO_3)_4$	0.1074	
Molybdenum oxide	MoO_3	0.0981	

Activity concentrations

Isotope	Activity curies/liter
Ruthenium-106	120
Cesium-137	177
Cesium-134	75.3
Strontium-90	158
Cerium-144	159
Europium-154	9.1
Technetium-99	86.9 (mg)

III. Calcining Acidic Thorium Nitrate Waste

At present a total of 45,000 liters of this waste is stored at the West Valley site in New York. The waste composition is as follows: $Th(NO_3)_4 = 1.46\ M$; $Al(NO_3)_3 = 0.36\ M$; $HNO_3 = 1.03\ M$; $F = 0.10\ M$; and $P = 0.04\ M$. Two series of calcination experiments were run at 250, 350, 450, and 600°C. In one series the simulated liquid waste was converted to a solid by adding the liquid at a controlled rate to the quartz pot calciner held at the indicated temperature without any pretreatment. In the second series the nitrate in the waste was subjected to the reducing action of formic acid by adding the nitrate waste to 90% formic acid held at 80 to 100°C. Then this pretreated waste (two moles of formic acid per mole of nitrate) was converted to a dry solid by flash evaporation in the quartz pot calciner. The results of these two series of experiments are presented in Fig. 3 and Table IV. The simulated waste was made up by adding one part of acid waste in Table III to nine parts of acid thorium nitrate waste. Only tracer-level experiments were run. No high-level experiments were performed with the acidic thorium nitrate waste.

Table IV. Tracer studies of ruthenium volatility as a function of temperature on calcining acidic thorium nitrate waste with and without formic acid pretreatment.

Temperature (°C)	^{106}Ru volatility (%)		Nitrate in residual solid (%)	
	Untreated[a]	Treated with formic acid[b]	Untreated	Treated with formic acid
250	26.2	0.07	1.6	0.5
350	27.5	0.15	1.1	0.1
450	0.6	0.10	0.2	0.1
600	0.5	0.18	0.1	0.07

[a] Composition of initial thorium nitrate waste: $Th(NO_3)_4 = 1.46\ M$; $Al(NO_3)_3 = 0.36\ M$; $HNO_3 = 1.03\ M$; $F = 0.10\ M$; and $P = 0.04\ M$.

[b] Thorium nitrate waste was added to a formic acid solution heated to 80 to 100°C and containing two moles of formic acid per mole of nitrate in the waste.

One tracer level experiment with ^{131}I, on calcining an untreated thorium nitrate waste at 250°C, showed a high iodine volatility of 28.0%.

Fig. 3. Ruthenium volatility on calcining thorium nitrate waste (tracer studies).

Thermal denitration precedes ruthenium fixation in an alkaline oxide matrix. The thermal decomposition of thorium nitrate is discussed in (34), where it is noted that thorium nitrate decomposes directly to thorium oxide without the formation of an intermediate basic nitrate salt. The equation for the decomposition of the anhydrous thorium nitrate salt is as follows: $Th(NO_3)_4 = ThO_2 + 4\ NO_2 + O_2$. The decomposition pressure is 119 torr at 134°C, 199 torr at 145°C, and 359 torr at 161°C.

In this case the ThO_2 serves as the alkaline oxide matrix. If denitration is rapid, the incoming acid waste is neutralized, and ruthenium is fixed in the alkaline oxide matrix as ruthenate. If the denitration is slow, insufficient ThO_2 is formed and RuO_4 can evolve under the conditions of high local acidity. Thus, high RuO_4 volatilities of 26.2 and 27.5% are noted at 250 and 350°C, even though the nitrate contents of the residual salt are low (1.6 and 1.1%, respectively). In contrast, the pretreatment of the acidic thorium nitrate waste with formic acid gives low RuO_4 volatilities at all calcination temperatures. Formic acid reduces ruthenium to a lower valence state and interacts with nitrato and nitro groups of the octahedral ruthenium complexes. Decarboxylation at higher temperatures then gives RuO_2 or ruthenium metal rather than volatile RuO_4.

IV. Calcining Acidic Aluminum Nitrate Waste

Acidic aluminum nitrate waste is produced at the Idaho reprocessing plant from aluminum-clad, spent fuel. Its composition is given by Christian(16) as follows: $Al(NO_3)_3 = 2.1\ M$; $HNO_3 = 1.3\ M$; and $NaNO_3 = 0.15\ M$. The volume of this waste is only 10% of the total volume of high-level waste generated at the Idaho plant. This waste is usually blended with the zirconium fluoride waste to decrease the fluoride corrosion on the equipment.

Simulated high-level waste was made up by adding one part of waste having a composition given in Table III to nine parts of aluminum nitrate waste. The radioactivity levels were a factor of 20 to 100 times higher for our simulated high-level waste than they were for an authentic aluminum-zirconium blend given in (35). Tracer-level and high-level runs were carried out at calcination temperatures of 250, 350, 450, and 600°C on the untreated waste and on the aluminum nitrate waste pretreated with two moles of formic acid per mole of nitrate. The results of ^{106}Ru and ^{99}Tc volatilities from these runs are presented in Tables V, VI, and VII, and in Fig. 4.

Table V. Tracer-level experiments to determine ^{106}Ru volatility as a function of temperature from the pot calcination of aluminum nitrate waste with and without formic acid pretreatment.[a]

Temperature (°C)	^{106}Ru volatility (%)		Nitrate in residual salt (%)	
	Untreated	Pretreated with formic acid[b]	Untreated	Pretreated with formic acid[b]
250	31.6	0.06	3.6	2.7
350	21.0	0.20	13.5	4.2
450	57.2	0.09	4.1	1.0
600	0.9	0.13	2.6	7.5

[a] Composition of initial aluminum nitrate waste: $Al(NO_3)_3$ = 2.1 *M*; $NaNO_3$ = 0.15 *M*; HNO_3 = 1.3 *M*.

[b] Aluminum nitrate waste was added to formic acid solution that was heated to 80 to 100°C and that contained two moles of formic acid per mole of nitrate.

Table VI. High-level experiments to determine ^{106}Ru volatility as a function of temperature from the pot calcination of aluminum nitrate waste.[a]

Temperature (°C)	^{106}Ru volatility (%)		Nitrate in residual salt (%)	
	Untreated	Pretreated with formic acid[b]	Untreated	Pretreated with formic acid[b]
250	11.0	1.5	25.4	14.5
350		1.0		7.9
450	45.3	0.8	0.2	9.0
600	17.5	2.8	0.6	3.1

[a] Composition of initial aluminum nitrate waste: $Al(NO_3)_3$ = 2.1 *M*; $NaNO_3$ = 0.15 *M*; HNO_3 = 1.3 *M*.

[b] Aluminum nitrate waste was added to formic acid solution that was heated to 80 to 100°C and that contained two moles of formic acid per mole of nitrate.

Fig. 4. Ruthenium volatility vs temperature on calcining aluminum nitrate waste.

Table VII. Results of high-level experiments to determine ^{99}Tc volatility as a function of temperature and pretreatment conditions during the pot calcination of aluminum nitrate waste.[a]

Temperature (°C)	^{99}Tc volatility (%)	
	Untreated	Treated with formic acid[b]
250	<1.1	<0.1
350		<0.1
450	<0.7	<0.2
600	<1.0	<0.1

[a] Composition of initial aluminum nitrate waste: $Al(NO_3)_3$ = 2.1 *M*; $NaNO_3$ = 0.15 *M*; HNO_3 = 1.3 *M*.

[b] Aluminum nitrate waste was added to a formic acid solution that was heated to 80 to 100°C and contained two moles of formic acid per mole of nitrate.

The ^{99}Tc volatilities are all low (<1.0%) on calcining the aluminum nitrate waste over a temperature range of 250 to 600°C, whether or not the waste has been pretreated with formic acid. Although no experiments with ^{131}I tracer were run, our previous experience in calcining acidic nitrate wastes(1) indicates that the ^{131}I volatility should be high and should increase with temperature on calcining an acidic aluminum nitrate waste.

As can be seen from Fig. 4, the calcination of acidic $Al(NO_3)_3$ waste pretreated with formic acid gives much lower RuO_4 volatilities than those obtained on calcining the untreated $Al(NO_3)_3$ waste. The formic acid serves a double function. It reacts directly with the nitrate anion to give N_2 or N_2O. It also reduces ruthenium to a lower valence state and prevents the formation of volatile RuO_4 during calcination.

Thermal denitration of the untreated $Al(NO_3)_3$ waste proceeds with the formation of lower basic aluminum nitrates and the evolution of NO_x fumes(36). Under calcination conditions ruthenium forms a highly nitrated complex that decomposes with RuO_4 volatilization. In this case moderate amounts of RuO_4 are evolved at 250 and 350°C, with a maximum at 450°C. At a higher temperature of 600°C the alkaline oxide matrix fixes ruthenium as the ruthenate,(1) and the amount of evolved RuO_4 is decreased.(1) Our results agree with those of Christian,(16) who reports a RuO_4 volatility of 65% at 400°C and 2% at 500°C on calcining an $Al(NO_3)_3$ waste in a fluidized bed reactor.

V. Calcining (Zr,Al) Fluoride-Nitrate Waste

The bulk of the high-level waste produced at the Idaho Falls plant is (Zr, Al) fluoride-nitrate waste. Its composition is given in (16) as follows: $Al(NO_3)_3 = 0.6$ *M*; $Zr(NO_3)_4 = 0.35$ *M*; $HNO_3 = 3.2$ *M*; HF = 3.0 *M*. This waste was calcined directly without adding a calcium salt to fix fluoride. A simulated high-level waste was prepared by blending nine parts of waste of the above composition with one part of waste of a composition given in Table III. The activity levels in the simulated high-level waste were a factor of 20 to 100 higher than in the actual waste. Tracer-level and high-level experiments were performed by flash evaporation of the untreated and formic-acid treated wastes in the quartz pot calciner at temperatures of 250, 350, 450, and 600°C. The results of these experiments are presented in Tables VIII, IX, and X, and in Fig. 5.

Table VIII. Results of high-level experiments to determine ^{99}Tc volatility as a function of temperature and pretreatment conditions during the pot calcination of (Zr,Al) fluoride-nitrate waste[a]

Temperature (°C)	^{99}Tc volatility (%)	
	Untreated	Treated with formic acid[b]
250	<2.6	8.1
350	1.3	5.1
450	9.2	3.0
600	21.1	12.9

[a] Composition of initial (Zr,Al) fluoride-nitrate waste: $Al(NO_3)_3 = 0.6$ *M*; $Zr(NO_3)_4 = 0.35$ *M*; $HNO_3 = 3.2$ *M*; HF = 3.0 *M*.

[b] (Zr,Al) fluoride-nitrate waste was added to a formic acid solution containing two moles of formic acid per mole of nitrate, heated to 80 to 100°C.

Fig. 5. Ruthenium volatility vs temperature on calcining a (Zr,Al) fluoride-nitrate waste.

Table IX. Tracer-level experiments to determine ^{106}Ru volatility as a function of temperature and pretreatment conditions during the flash evaporation of (Zr,Al) fluoride-nitrate waste.[a]

Temperature (°C)	Ru volatility (%)		Nitrate in residual salt (%)	
	Untreated	Treated with formic acid[b]	Untreated	Treated with formic acid[b]
250	83.4	0.7	0.16	0.026
350	61.0	0.5	0.13	0.012
450	60.6	0.5	0.024	0.018
600	55.4	12.5	0.024	0.012

[a] Composition of initial (Zr,Al) fluoride-nitrate waste: $Al(NO_3)_3$ = 0.6 *M*; $Zr(NO_3)_4$ = 0.35 *M*; HNO_3 = 3.2 *M*; HF = 3.0 *M*.

[b] (Zr,Al) fluoride-nitrate waste was added to a formic acid solution containing two moles of formic acid per mole of nitrate, heated to 80 to 100°C.

From Tables IX and X and Fig. 5, it can be seen that the use of formic acid dramatically reduces the volatility of ruthenium. From an almost quantitative evolution of ruthenium of 50 to 99%, the volatility of ruthenium is decreased to a percent or two on pretreating the (Zr,Al) fluoride-nitrate waste with two moles of formic acid per mole of nitrate. The percent nitrate in the residual salt remains low regardless of the calcination temperature or the pretreatment conditions. The low nitrate content of the salt would seem to point to a reaction between HNO_3 and HF under calcination conditions, but it is not clear at the present stage of investigation what this reaction

Table X. High-level experiments to determine ^{106}Ru volatility as a function of temperature and pretreatment conditions during the flash evaporation of a (Zr,Al) fluoride-nitrate waste in a quartz pot calciner.[a]

Temperature (°C)	^{106}Ru volatility (%)		Nitrate in residual salt (%)	
	Untreated	Treated with formic acid[b]	Untreated	Treated with formic acid[b]
250		1.8		1.9
350	99.1	2.2	0.5	0.7
450	80.0	1.3	1.8	0.7
600	93.1	0.8	0.65	1.9

[a] Composition of initial (Zr,Al) fluoride-nitrate waste: $Al(NO_3)_3$ = 0.6 *M*; $Zr(NO_3)_4$ = 0.35 *M*; HNO_3 = 3.2 *M*; HF – 3.0 *M*.

[b] (Zr,Al) fluoride-nitrate waste was added to a formic acid solution containing two moles of formic acid per mole of nitrate, heated to 80 to 100°C.

would be. It is possible that ruthenium is being volatilized as RuF_5 and that ruthenium is reduced to a lower valence state by formic acid to prevent volatilization of RuF_5. It was found that 5 to 20% of the initial fluoride was volatilized during calcination of the acid fluoride waste. Fluoride is usually tied up by previous addition of a calcium salt to the acid fluoride waste.

VI. Calcining Alkaline Sodium Nitrate Supernate and Sludge

Alkaline Sodium Nitrate Waste

At present megaliters of alkaline sodium nitrate supernate are stored in mild steel tanks at Hanford, Savannah River, and West Valley.(37,38) The compositions of this waste stored at the Savannah River Plant (SRP) and the West Valley plant are given in Tables XI and XII, respectively.

Table XI. Composition of alkaline sodium nitrate supernatant waste at Savannah River Plant, South Carolina

Constituent	Formula	Concentration (moles)	Constituent	Formula	Concentration (moles)
Sodium nitrate	$NaNO_3$	2.2	Sodium sulfate	Na_2SO_4	0.3
Sodium nitrite	$NaNO_2$	1.1	Sodium chloride	NaCl	0.022
Sodium aluminate	$NaAlO_2$	0.5	Sodium fluoride	NaF	0.002
Sodium hydroxide	NaOH	0.75	Mercury	Hg	0.001
Sodium carbonate	Na_2CO_3	0.3			

Table XII. Composition of alkaline sodium nitrate waste at West Valley, New York

Constituent	Formula	Concentration (moles)
Sodium nitrate	$NaNO_3$	6.0
Sodium sulfate	Na_2SO_4	0.32
Disodium phosphate	Na_2HPO_4	0.10
Sodium oxalate	$Na_2C_2O_4$	0.09
Aluminum nitrate	$Al(NO_3)_3$	0.11
Sodium molybdate	Na_2MoO_4	0.01
Sodium fluoride	NaF	0.01
Sodium chloride	NaCl	0.01
Sodium hydroxide	NaOH	1.0

A simulated high-level waste was prepared by blending nine parts of alkaline sodium nitrate waste with one part of highly radioactive waste having a composition given in Table III. The activity levels in the simulated high-level waste are approximately the same as those found in the actual waste. Tracer-level and high-level experiments were performed by flash evaporation of the waste in a quartz pot calciner at temperatures of 250, 350, 450, and 600°C.

Metal Hydroxide Sludge

The sludge composition was a composite of a number of sludges analyzed at the Savannah River Plant.(39) The average SRP sludge consists of 31.6 wt % Fe_2O_3, 46.4 wt % Al_2O_3, 10.3 wt % MnO_2, 6.1 wt % U_3O_8, 3.3 wt % CaO, and 2.3 wt % NiO. The sludge was prepared by making up a HNO_3 solution of the metal elements and precipitating the metal hydroxides by neutralizing the acid solution with caustic. The sludge also contained other elements up to the following amounts: 4.1 wt % Hg, 0.1 wt % Ru, 0.02 wt % I, and 0.0033 wt % Ag. Sludge tagged with tracer was prepared by adding tracer to the acid solution just prior to caustic neutralization. Silver was added only in a few experiments involving iodine tracing. The sludge was washed twice with water to remove most of the sodium salts, resuspended in water, and fed to the calciner as a 3.3% (dry basis) oxide-water slurry. The centrifuged volume of hydrous hydroxides in the hydroxide-water slurry was 50% of the total volume.

Ruthenium Behavior

Alkaline sodium nitrate supernate (simulated West Valley waste) was pretreated with two moles of formic acid per mole of nitrate to determine the completeness of denitration. The tracer-level experiments are in essential agreement with the high-level experiments, as can be seen from Table XIII. Because of hydroxide substitution in the octahedral ruthenium complex, the ruthenium volatilities are low at all temperatures. Considerable denitration of sodium nitrate is achieved at relatively low temperatures with the use of formic acid.

Tracer-level RuO_4 volatility determinations were performed on a simulated SRP sludge recovered from an alkaline solution 6.0 *N* in sodium nitrate and 1.0 *N* in sodium nitrite after aging for one week.

Table XIII. Ruthenium volatility as a function of temperature on calcining a West Valley alkaline sodium nitrate supernate pretreated with two moles of formic acid per mole of nitrate

Temperature (°C)	^{103}Ru volatility (%)		Nitrate in residual calcine (%)	
	Tracer-level	High-level	Tracer-level	High-level
250	0.034	0.17	2.4	10.1
350	0.037	0.32	3.0	
450	0.26	0.37	1.2	11.7
600	0.055	0.22	0.6	5.9

Table XIV. Tracer-level RuO_4 volatility as a function of temperature on calcining a simulated SRP sludge recovered from an alkaline solution 6.0 *N* in $NaNO_3$ and 1.0 *N* in $NaNO_2$ after aging for one week.[a]

Temperature (°C)	RuO_4 volatility (%)
250	0.004
350	0.001
450	0.175
600	0.30

[a] Centrifuged volume of hydrous metal hydroxides was 50%. Sludge composition: 31.6 wt % Fe_2O_3, 46.4 wt % Al_2O_3, 10.3 wt % MnO_2, 6.1 wt % U_3O_8, 3.3 wt % CaO, 2.3 wt % NiO, and 0.03 wt % RuO_2. Sludge was washed twice with distilled water.

As can be seen from Table XIV, the RuO_4 volatilities were low at all temperatures, and increased slightly with increasing temperature.

Iodine Behavior

Stable iodine was added to SRP processing solutions to control the valence state of plutonium during its separation from uranium. Most of this stable iodine was added to the alkaline waste. Our studies showed that 75% of the iodine reports to the alkaline supernate, while 25% coprecipitates with the sludge. If the sludge is treated with boiling 5 *N* NaOH to remove aluminum,(38) most of the iodine (>95%) will be found in the alkaline supernate after processing.

A simulated West Valley alkaline supernate tagged with tracer ^{131}I was rapidly evaporated to dryness in the quartz calciner held at 250, 350, 450, and 600°C. The results presented in Table XV and Fig. 6 show that the iodine volatility increases linearly with temperature. Iodine volatilities on calcining an alkaline solution are lower than those obtained on calcining an acid solution.(1)

Fig. 6. Iodine volatility as a function of temperature on calcining simulated alkaline sodium nitrate supernate from West Valley, New York.

Table XV. Iodine volatility as a function of temperature during the flash evaporation of West Valley alkaline sodium nitrate supernate in a quartz pot calciner

Temperature (°C)	^{131}I volatility (%)
250	0.4
350	2.1
450	6.7
600	9.5

Iodine volatility was also determined on a simulated SRP sludge containing both mercury and silver. The results are presented in Table XVI and Fig. 7. The iodine volatility increases with increasing temperature of calcination.

Difficulties were encountered in determining ^{131}I material balances on calcining a simulated SRP sludge tagged with ^{131}I in a stainless steel spray calciner having wall temperatures of 650 to 775°C. Only 3 to 7% of the ^{131}I reported to the solid residue in the calciner. A total of 50 to 65% of the ^{131}I was recovered in rinse solutions (6 *N* HNO_3 and 1.0 *N* NaOH – 0.05 *M* sodium persulfate) used to remove iodine from the stainless steel walls. A total of 25 to 50% of the ^{131}I was still unaccounted for in the stainless steel equipment. Iodine appears to react with stainless steel at elevated temperatures.(33)

Fig. 7. Iodine volatility as a function of temperature on calcining simulated SRP sludge containing mercury and silver and tagged with ^{131}I.

Table XVI. Iodine volatility as a function of temperature on calcining a simulated SRP sludge containing mercury and silver tagged with ^{131}I.[a]

Temperature (°C)	Iodine volatility (%)
250	10.8
350	12.5
450	17.2
600	43.7

[a] Sludge composition (dry oxides): 31.6 wt % Fe_2O_3; 46.4 wt % Al_2O_3, 10.3 wt % MnO_2, 6.1 wt % U_3O_8, 3.3 wt % CaO, 2.3 wt % NiO, and up to 4.1 wt % Hg, 0.11 wt % Ru, 0.02 wt % I, and 0.0033 wt % Ag.

Technetium Behavior

Technetium is found associated with ^{137}Cs in the alkaline supernate. An analysis on a West Valley supernate showed 10.0 μg of ^{99}Tc per mCi of ^{137}Cs, which represents 92% of the theoretical amount of ^{99}Tc formed in fission. On the other hand, an analysis of an authentic SRP sludge showed <0.3% of the theoretical amount of ^{99}Tc formed in fission.

A simulated SRP alkaline sodium nitrate supernate containing 100 mg of ^{99}Tc per liter and ^{95m}Tc tracer was calcined by flash evaporation in a quartz pot calciner at 250, 350, 450, and 600°C.

The results are presented in Table XVII along with the results of ^{99}Tc volatility from a simulated high-level SRP alkaline waste pretreated with formic acid. As reported previously,(1) the volatility of ^{99}Tc is low in the presence of large amounts of salts because of the high thermal stability limits of pertechnetate compounds.

Table XVII. Volatility of ^{99}Tc as a function of temperature on calcining a simulated SRP alkaline sodium nitrate supernate containing 100 mg of ^{99}Tc per liter and ^{95m}Tc tracer, and on calcining a simulated high-level SRP alkaline supernate pretreated with formic acid.

Temperature (°C)	^{99}Tc volatility (%) Tracer-level	^{99}Tc volatility (%) High-level[a]
250	0.0025	<2.6
350	0.0033	<3.3
450	0.0044	
600	0.0063	<0.001

[a] Pretreated with two moles of formic acid per mole of nitrate.

The above results indicate that ^{99}Tc will concentrate in the alkaline sodium nitrate supernate. Kelley(25) notes that the alkaline SRP supernate will contain 200 megacuries (MCi) of ^{137}Cs in 100 megaliters (Ml) of solution. If it is assumed that 10 μg of ^{99}Tc are associated with each mCi of ^{137}Cs, it can be calculated that the total amount of ^{99}Tc in the SRP alkaline supernate is 2000 kg. If it is further assumed that each liter of SRP alkaline supernate contains 400 g of solids per liter and that the specific activity of ^{99}Tc is 0.0173 Ci/g of ^{99}Tc, it can be calculated that these solids contain 865 nCi of ^{99}Tc/g of solids, an amount that considerably exceeds 10 nCi/g, which is used as a guide in disposing of waste containing long-lived alpha emitters. In addition to removing ^{137}Cs, ^{90}Sr, and plutonium from SRP alkaline supernate by ion exchange processing,(40) these calculations amd analyses show that it would also be desirable to remove the long-lived ^{99}Tc (half-life of 2.05 × 10^5 y) from the alkaline sodium nitrate supernate.

A suitable method that involves the removal of ^{99}Tc from an alkaline sodium nitrate solution by solvent extraction with lutidine (2,4 dimethylpyridine) is descirbed in (26,27). The distribution coefficient (K_D), which is the ratio of the Tc(VII) concentration in the organic phase divided by the Tc(VII) concentration in the aqueous phase, decreases with increasing sodium nitrate concentration in the alkaline supernate, as can be seen from Table XVIII taken from (27). Lutidine extracts Tc(VII) almost completely even from an alkaline solution containing 2.9 *M* $NaNO_3$ and 0.1 *M* NaOH. The K_D for Tc(VII) is 102 for a simulated West Valley waste and 191 for a simulated SRP waste. Each waste contained 4 mg of ^{99}Tc/liter and ^{95m}Tc tracer.

The distribution of Tc(VII) between the organic and aqueous phases (K_D) was determined as a function of technetium loading of the organic phase (lutidine). The initial solution was a simulated SRP alkaline sodium nitrate supernatant waste containing 0.400 g of ^{99}Tc

Table XVIII. Distribution coefficient of technetium (VII) as a function of nitrate concentration in a mixture of $NaOH + NaNO_3$ at a constant ionic strength of 3.[a]

Nitrate concentration in mole/liter	K_D for Tc(VII) in lutidine
2.9	78.5
2.5	104
2.0	146
1.5	171
1.0	205
0.5	296
0.3	604
0.1	775
zero	1670
$NaNO_3 = 6.0\ N$; $Na_2So_4 = 0.35\ M$	102 (West Valley waste, see Table XII)
$NaNO_3 = 2.2\ N$; $NaNO_3 = 1.1\ N$; $Na_2SO_4 = 0.3\ M$	191 (Savannah River waste, see Table XI)

[a] Data taken from ([27]) except the K_D values for West Valley and Savannah River wastes, which were determined experimentally.

Table XIX. Distribution coefficient (K_D) of ^{99}Tc between lutidine (2,4 dimethylpyridine) and simulated SRP alkaline sodium nitrate waste containing 0.400 g of ^{99}Tc per liter and ^{95m}Tc tracer as a function of ^{99}Tc loading in the organic phase.

Number of extraction	Distribution coefficient of ^{99}Tc (K_D)	^{99}Tc (g/liter)	
		Organic	Aqueous
2	91	0.774	0.008
4	89	1.530	0.017
6	79	2.260	0.029
8	78	2.976	0.038
10	68	3.656	0.053
12	60	4.298	0.072
15	58	5.210	0.090
16	54	5.488	0.102
20	45	6.525	0.145
22	38	6.928	0.182
24	34	7.257	0.213
26	32	7.496	0.234
28	30	7.577	0.253
29	29	7.588	0.262
30	30	7.597	0.263

per liter and ^{95m}Tc tracer. The ^{99}Tc concentration is a factor of 10 higher than the highest ^{99}Tc concentration expected in SRP waste. From the results presented in Table XIX it can be seen that the K_D for ^{99}Tc decreases slowly as the organic phase (lutidine) becomes loaded with ^{99}Tc. This K_D remains high enough to concentrate and recover ^{99}Tc in high yield with high decontamination of the waste from ^{99}Tc. A plot of the technetium distribution between the organic and aqueous phase is presented in Fig. 8.

Fig. 8. Technetium distribution between organic and aqueous phase on contacting an organic lutidine (2,4 dimethylpyridine) phase with successive portions of a simulated SRP alkaline sodium nitrate supernatant waste containing 0.400 g of ^{99}Tc/liter and ^{95m}Tc tracer.

The solvent (lutidine) can be distilled and recycled back to be reused in the process. The sodium technetate can be shipped as a solid for disposal with other wastes by hydraulic fracture, or it can be incorporated into a cement and shipped to an approved site for permanent disposal.

VII. Generation of a Fine RuO_2 Aerosol

Because of its high vapor pressure,$^{(15)}$ RuO_4 diffuses rapidly throughout the off-gas system. Because of its reactivity, the RuO_4 interacts with stainless steel with the formation of a black shiny deposit of RuO_2.$^{(16)}$ It is not known whether the ruthenium in a practical system of stainless steel equipment is present as RuO_4, RuO_2 or a mixture of both these forms. In an all-glass system, 99.9% of the RuO_4 in an off-gas stream can be trapped in the first two water scrubbers of the train.$^{(1)}$ Black RuO_2 deposits on stainless steel equipment can be dissolved by a 1.0 *N* NaOH—0.05 *M* sodium persulfate solution to give a clear orange solution.(41) Heavy reliance is usually placed on packed columns filled with silica gel as the sorbent material to remove RuO_4.(16,42,43) The DF across the silica gel bed is only 8 for particulate matter and 1000 for volatile RuO_4.(44) This system was chosen as an object of study to distinguish between RuO_4 and RuO_2 in the off-gas effluent from a silica gel column.

The equipment shown in Fig. 2 was modified by replacing the quartz calciner with a 1-liter Pyrex flask, in which gaseous RuO_4 was generated by adding periodic acid or potassium permanganate as an oxidizing agent to an 18 *N* H_2SO_4 solution containing ruthenium. Air was pulled through a dip leg in the 1-liter flask to sweep out the RuO_4. The off-gas laden with gaseous RuO_4 was passed down through a column of Davison 40 silica gel supported on a 10-cm fritted-glass filter having a medium porosity (pore size of 10 to 15 μ). The same filter shown in Fig. 2 next to the quartz calciner, which was used to trap particulate matter formed during calcination, was converted to a silica gel column by removing the glass wool packing, filling with silica gel and mounting vertically in the off-gas line. The equipment was of all-glass construction with ball joints being used for flexibility. The first four traps contained weak acid as the scrubbing medium, while the fifth trap contained a caustic solution.

As the gaseous RuO_4 reacted with the silica gel, a dark green color was noted in the upper part of the silica gel column. At this time the four acid scrubbers remained colorless. This behavior indicated that no significant absorption of RuO_4 from the off-gas stream was taking place. Soon it was noted that a tygon line connecting the fourth acid trap and the fifth caustic trap was starting to turn black. Also, significant amounts of ruthenium, indicated by a color change, were being absorbed in the fifth caustic trap. After 15 to 30 minutes, a small amount of agglomerated black particles was observed in the acid traps. It was concluded that significant quantities of a fine RuO_2 aerosol were formed by reacting RuO_4 with silica gel. This aerosol passed unscathed through the silica gel column, a fritted-glass filter, and four weak acid scrubbers. A caustic solution is a more suitable scrubbing medium than a weak acid solution for removing the RuO_2 aerosol particles from an off-gas stream. Although our previous experiments(1) have shown that 99 to 99.9% of any RuO_4 should have been caught in the first two acid scrubbers, the amount of particulate RuO_2 trapped by acid scrubbing is considerably less.

In order to ascertain some of the physical characteristics of the fine RuO_2 aerosol, samples collected on a millipore filter were examined under a scanning electron microscope. The particles consisted primarily of agglomerated RuO_2 particles having a mean diameter of <0.5 μ. A number of particles having a mean diameter of 0.1 μ were observed in agreement with the particle size reported by Feber(17) who noted an average diameter of 0.05 μ for an RuO_2 aerosol. X-ray diffraction analysis showed that the particles consisted mainly of RuO_2.

Tracer ^{106}Ru was added to the distilling flask, and the previous experiment was repeated in order to determine the amount of fine RuO_2 aerosol that is formed on reacting RuO_4 with silica gel. The first trap contained an acid scrub solution, and the next three traps contained a 1.0 *N* NaOH–0.05 *M* sodium persulfate scrub solution. As can be seen from Table XX, the first acid trap caught very little of the RuO_2 aerosol, while the caustic traps were moderately efficient in trapping the RuO_2 particles. At least 3% of the total ruthenium in the distilling flask reacted with the silica gel and passed out of the bottom of the silica gel column and through the first acid trap in the form of a fine RuO_2 aerosol.

Table XX. Scrubbing of a fine RuO_2 aerosol by a 1.0 *N* NaOH–0.05 *M* sodium persulfate solution after interaction of radioactive RuO_4 with Davison silica gel (grade 40) supported on a 10-cm, fritted-glass filter of medium porosity (pore size of 10 to 15 µ.

Trap number	Percent of initial ruthenium	Type of scrubber
1	0.0037	acid
2	1.95	caustic
3	1.04	caustic
4	0.05	caustic

VIII. Conclusions and Recommendations

Denitration

Chemical denitration with formic acid leads to the formation of noncondensable gases (nitrogen or nitrous oxide), which may be eliminated through HEPA filters after liquid scrubbing to remove gaseous radioactivities. The denitration of HNO_3 and metal nitrate solutions is carried out without the evolution of toxic NO_x vapors, which have an adverse environmental effect and deleterious effects on lung function in man. Formic acid can be advantageously used to reduce the large amounts of nitrate anion that have accumulated in nuclear defense wastes without the necessity of recycling nitric acid.

Ruthenium

The intrinsic volatility of RuO_4 formed by decomposition of a highly nitrated ruthenium complex can be reduced to the vanishing point by the use of two moles of formic acid per mole of nitrate. Formic acid reacts with the nitrated octahedral complexes of ruthenium to yield lower-valence formate complexes of ruthenium that decompose with the formation of nonvolatile RuO_2 instead of the volatile RuO_4. The use of formic acid is recommended whenever it is desirable to decrease the intrinsic volatility of RuO_4 almost to zero (for example, during the calcination of high-level wastes).

Rapid thermal denitration of high-level wastes can also be carried out in a number of cases at a high temperature of 600°C with the evolution of a few percent of the ruthenium in the form of RuO_4. Even though the intrinsic RuO_4 volatility is low in this case, it is recommended that a liquid caustic scrubber be installed in front of the HEPA filters to remove any RuO_2 particulate matter formed as a result of the interaction of RuO_4 with the stainless steel components of the off-gas system.

Finally, it is recommended that the interaction of RuO_4 with silica gel and with stainless steel at high temperatures should be investigated fully to determine how adequately the various components of the off-gas system retain the fine RuO_2 aerosol that may be formed in stainless steel systems under calcination conditions.

Iodine

A high fraction of iodine compounds is decomposed and volatilized on calcining acidic nitrate solutions. The iodine volatility is almost an order of magnitude lower on calcining alkaline wastes than it is on calcining an acid waste. Wet scrubbers are effective in removing iodine from an off-gas stream in concentrated form. It is recommended that methods be developed to withdraw an iodine concentrate from a bubble-cap plate in order to prevent the buildup and breakthrough of iodine activity in the off-gas stream.

Technetium

Generally, less than 1% of the ^{99}Tc volatilizes on calcining either acidic or basic nitrate solutions of fission products over a range of temperatures from 250 to 600°C. Most of the fission product ^{99}Tc can be found associated with ^{137}Cs in the alkaline nitrate supernate. It is recommended that pilot plant studies be initiated to recover ^{99}Tc from the alkaline nitrate supernate by solvent extraction with lutidine (2,4 dimethylpyridine).

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