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ORNL-5562

**Volatility of Ruthenium-106,
Technetium-99, and Iodine-129,
and the Evolution of Nitrogen
Oxide Compounds During the
Calcination of High-Level,
Radioactive Nitric Acid Waste**

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Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A04 Microfiche A01

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ORNL-5562
Dist. Category UC-70

Contract No. W-7405-eng-26

OPERATIONS DIVISION 21

Nuclear Fuel and Waste Programs
High-Level Waste Process Test
(Subtask ON 33 0 9 A)

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AND THE EVOLUTION OF NITROGEN OXIDE COMPOUNDS DURING THE
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Date Published: February 1980

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ABSTRACT

The nitrate anion is the predominant constituent in all high-level nuclear wastes. Formic acid reacts with the nitrate anion to yield noncondensable, inert gases (N_2 or N_2O), which can be scrubbed free of ^{106}Ru , ^{129}I , and ^{99}Tc radioactivities prior to elimination from the plant by passing through HEPA filters. Treatment of a high-level authentic radioactive waste with two moles of formic acid per mole of nitrate anion leads to a low RuO_4 volatility of about 0.1%, which can be reduced to an even lower level of 0.007% on adding a 15% excess of formic acid. Without pretreatment of the nitrate waste with formic acid, a high RuO_4 volatility of $\sim 35\%$ is observed on calcining a 4.0 *N* HNO_3 solution in quartz equipment at 350°C. The RuO_4 volatility falls to $\sim 1.0\%$ on decreasing the initial HNO_3 concentration to 1.0 *N* or lower. It is postulated that thermal denitration of a highly nitrated ruthenium complex leads to the formation of volatile RuO_4 , while decarboxylation of a ruthenium-formate complex leads to the formation of non-volatile RuO_2 . Wet scrubbing with water is used to remove RuO_4 from the off-gas stream. In all glass equipment, small amounts of particulate RuO_2 are formed in the gas phase by decomposition of RuO_4 . The ^{99}Tc volatility was found to vary from 0.2 to 1.4% on calcining HNO_3 and $HCOOH$ (formic acid) solutions over the temperature range of 250 to 600°C. These unexpectedly low volatilities of ^{99}Tc are correlated to the high thermal stability limits of various metal pertechnetates and technetates. Iodine volatilities were high, varying from a low of 30% at 350°C to a high of 97% at 650°C. It is concluded that with a proper selection of pretreatment and operating conditions the ^{106}Ru and ^{99}Tc activities can be retained in the calcined solid with recycle of the wet scrubbing solution. However, because of its high volatility, the iodine concentrates in the first scrub solution, which should be segregated and treated separately.

INTRODUCTION

Reprocessing of spent fuel rods from atomic reactors to recover uranium and plutonium has resulted in the accumulation of large quantities of high-level, radioactive liquid wastes in the form of nitric acid

(HNO₃) solutions of fission products, stainless steel corrosion products, and extraneous chemicals added during processing. Research and development work is being conducted to convert these liquid, fission product wastes to an insoluble form for ultimate disposal in a geologic waste repository.

Nitrate, the predominant constituent of high-level waste, can be eliminated in many chemical forms. The most common form of nitrogen elimination is as a mixture of NO and NO₂ (NO_x) vapors, which are evolved during the thermal denitration of metal nitrate salts at high temperatures or on adding various reducing agents (sugar, hydrazine, formaldehyde, phosphorous acid, etc.) to HNO₃ solutions to control RuO₄ volatility. Because of the possible presence of volatile radioactive compounds such as I₂, Tc₂O₇, and RuO₄ in the off-gas stream, it is preferable to convert the nitrate anion to a more inert form such as N₂ or N₂O, from which the radioactive constituents can be readily scrubbed. A survey of the literature showed that N₂ or N₂O is formed on adding a fission product nitrate solution to a formic acid solution. Data are presented on the wet scrubbing of volatile radioactivities. The purpose of this study is to gather data concerning the volatility of ¹⁰⁶Ru, ⁹⁹Tc, and ¹²⁹I under denitration conditions where NO_x vapors are evolved and where N₂ or N₂O are evolved with the use of formic acid as a reducing agent.

Calcination involves the rapid dehydration of a radioactive liquid waste with the evolution of volatile radioactive compounds and the production of a radioactive solid calcined material. The objective is to incorporate maximum amounts of volatile radioactive elements in the solid oxide mixture. Hence, wherever feasible, recycle of volatile radioactive components is provided for. The calcination and denitration steps can be carried out in a spray dryer, a fluidized bed, a rotary calciner, or a pot calciner. Because of operational simplicity and small scale of processing, for the high-level waste tests we selected a quartz pot calciner with a heated fritted-glass filter to retain particulate matter and a wet scrubbing train to remove volatile species from the off-gas stream. Tracer studies were also performed in a small stainless steel spray calciner. Data are given on the volatilities of ¹⁰⁶Ru, ¹²⁹I, and ⁹⁹Tc, and the extent of salt denitration at temperatures

of 250, 350, 450, and 600°C with and without the use of formic acid as a reductant for the nitrate anion.

EXECUTIVE SUMMARY

The reprocessing of spent fuel rods from power reactors results in the formation of two waste fractions. One fraction consists of the main fission product mixture (less most of the ^{129}I), approximately 1% of the plutonium and uranium, stainless steel corrosion products (iron, nickel, and chromium), and the gadolinium that has been added for criticality control during processing. This fraction is usually contained in an HNO_3 solution. The second waste fraction consists mainly of HNO_3 and most of the ^{129}I (>99%), which is evolved along with a mixture of NO and NO_2 during dissolution of UO_2 in nitric acid.

The research and development effort is being concentrated on converting the fission product fraction of this waste to an insoluble form that will retain long-lived radionuclides for hundreds or thousands of years. The purpose of this study is to relate the volatility of radionuclides and other components of the waste mixture to process conditions (temperature and nitrate concentration) and to determine the mechanism and chemical forms involved. Both authentic and synthetic wastes are used.

Calcination of high-level liquid waste (HLLW) involves rapid dehydration with some volatilization of components such as RuO_4 , Tc_2O_7 , and I_2 , and thermal denitration of metal nitrate salts at high temperatures with evolution of NO_x vapors. This process has been carried out in a spray calciner, a heated fluidized bed, a rotary calciner, and a pot calciner. Because of operational simplicity and small scale of processing, we selected a quartz pot calciner with a heated fritted-glass filter to retain particulate matter and wet scrubbing to remove volatile species from the off-gas stream for the early studies. A small spray calciner was also operated and will be used extensively in later stages of the study.

Although the nitrate anion is a predominant constituent in all high-level, radioactive, liquid wastes, little attention has been paid

to the mechanism for its elimination from the waste and the form in which nitrogen is eliminated. At high nitrate concentrations ^{106}Ru is oxidized to RuO_4 having a high vapor pressure.

These studies have shown that the most satisfactory method of decomposing HNO_3 and thereby minimizing RuO_4 volatility and toxic NO_x production involves the addition of the HNO_3 solution of fission product nitrates to formic acid.

Formic acid is a reducing agent that reacts with nitric acid to form the gases CO_2 , N_2 , and N_2O , which may be released to the atmosphere after scrubbing and filtration to remove volatile radionuclides. In addition, a ruthenium formate complex is formed that decomposes at calcination temperatures to form very small quantities of volatile RuO_4 . With efficient wet scrubbing essentially all the ruthenium can be recycled back to the primary waste stream and eventually incorporated into a glass. High off-gas decontamination factors ($\sim 10^5$) for ruthenium have been demonstrated with wet scrubbing in these studies.

Technetium forms high-melting oxide compounds that can be incorporated into glass; however, a small amount of technetium ($\sim 1\%$) volatilizes as Tc_2O_7 . This material is trapped in scrubber solution and can be recycled back to the primary waste stream.

A large fraction of the iodine compounds present in HLLW are decomposed during calcination and must be trapped in the wet scrubbers from which an iodine concentrate can be withdrawn if necessary. Recycling of this fraction does not appear to be a promising method for disposal.

LITERATURE REVIEW

It is not generally recognized that the nitrate anion (NO_3^-), nitrous acid (HNO_2), and the nitrosyl group (NO) can interact with the ruthenium ion to yield a complex series of mixed nitrato-nitro-nitrosyl compounds, which at high temperatures are denitrated with the formation of volatile RuO_4 . The volatility and reactivity of RuO_4 with stainless steel components of the off-gas system and silica gel columns can lead to the accumulation of large amounts of ^{106}Ru activity in inaccessible

parts of the operating system. Thus, it is essential to devise calcination conditions where little or no RuO_4 is formed and to find efficient scrubbing systems for volatile RuO_4 or particulate RuO_2 activity in the event that RuO_4 does volatilize. This literature review selectively summarizes the rather voluminous work done on ruthenium that can shed light on the solution of these problems.

The observations of Fletcher,¹⁻⁴ Brown,⁵⁻⁶ Anderson,⁷ and Powell⁸ are useful in deducing the mechanism for the formation of RuO_4 and in devising pretreatment conditions to decrease the amounts of RuO_4 formed under calcination conditions. The existence of mixed, multiple chemical forms⁹ of ruthenium (Fig. 1) and the slowness of interconversion reactions have been noted frequently.¹⁻¹⁰ The work of Fletcher^{1,2} and Brown⁵ make it possible to explain the high volatility of RuO_4 from HNO_3 solution by the existence of a highly nitrated ruthenium complex that decomposes with RuO_4 volatilization. Because nitrate-complexing is relatively weak,⁵ the RuNO nitrate complexes can be changed to RuNO nitro complexes in the presence of nitrous acid, which can be decomposed at 170°C .³ These nitro complexes are stronger than the nitrate complexes. Although the ruthenium nitrosyl complex is very stable the nitrosyl group can be attacked slowly by reducing agents such as ferrous sulfate or ferrous sulfamate⁸ with gradual removal of the NO group from the ruthenium complex. Since formic acid is a reducing agent and can also react with the nitrate or nitro group, it can be used to promote the removal of nitrate and nitro groups prior to the calcination step with subsequent low volatility of RuO_4 . Thus, in addition to reacting with the nitrate anion to form innocuous gases and water, formic acid also interacts with the nitrated octahedral complexes of ruthenium to yield formate complexes that decompose with the formation of nonvolatile RuO_2 instead of the volatile RuO_4 .

At present the most satisfactory method of decomposing HNO_3 , which minimizes RuO_4 volatility and avoids the necessity for NO_x abatement, involves the addition of the HNO_3 solution of fission product nitrates to formic acid. In a series of reports,¹¹ Drobnick and Hild show that nitrous oxide is evolved according to the following reaction:

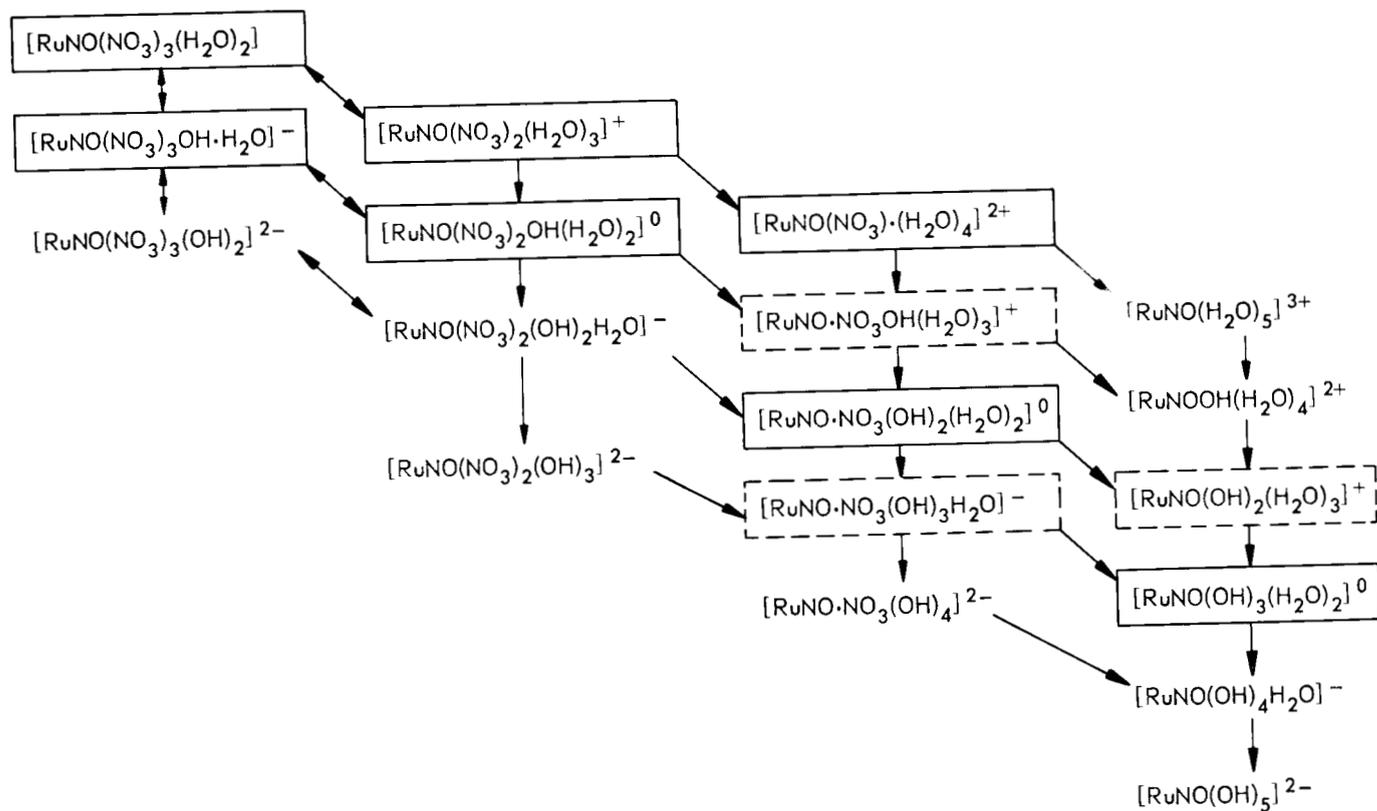
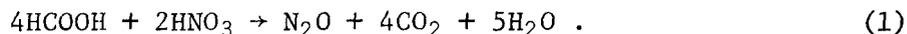
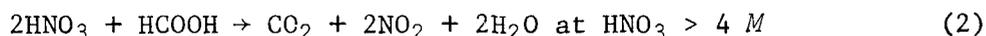


Fig. 1. Formation of mixed complexes of ruthenium.

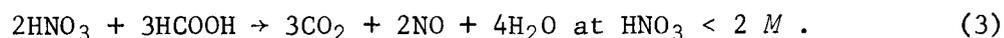


In this reaction the chemical reagent (formic acid) reacts with the predominant nitrate anion to form noncondensable gases (nitrous oxide and carbon dioxide) and water. Very low RuO_4 volatilities were observed during calcination. In addition the noncondensable gases, N_2O and CO_2 are easily scrubbed and decontaminated from volatile radioactivities prior to elimination from the plant by passing through HEPA filters. This process was carried to the pilot plant stage at Karlsruhe, Germany.¹² Inconel was found to be suitable for batch denitration. Continuous chemical denitration can also be carried out by mixing formic acid with high-level waste in the spray nozzle of an Inconel spray calciner directly heated to 650°C (wall temperature) with superheated steam. At the 420°C temperature prevailing in the spray tower N_2 was formed rather than the N_2O that was formed by reaction in the aqueous solution. The nitrate content of the residual calcined oxides is low, only about 2%.

Orebaugh¹³ and Healy¹⁴ have reviewed the reactions involved in formic acid denitration. Orebaugh showed that in the presence of excess HNO_3 the main reactions are



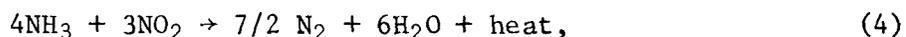
and



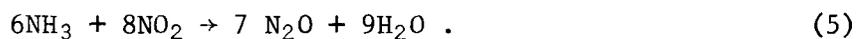
Healy¹⁴ found that concentrated HNO_3 reacts at 100°C with formaldehyde (CH_2O) and with formic acid (HCOOH) to give NO_2 and CO_2 , whereas dilute HNO_3 gives NO and CO_2 . Healy urges the application of these reactions to the removal of nitric acid from fission product waste solutions. It should be noted here that recent quotes indicate a price of \$0.20 per pound or about \$2.00 per gallon for 90% formic acid in drum or tank car lots. This price is moderate and should not bar the application of formic acid for use in the nuclear industry.

The evolution of NO_x gases introduces engineering and processing difficulties. The absorption of these NO_x gases into water and dilute HNO_3 has been reviewed recently by Counce.¹⁵ The absorption kinetics are slow and involve the oxidation of HNO_2 to HNO_3 to recover a dilute

HNO₃ solution which then must be further concentrated to 60% HNO₃ by evaporation. The rate-determining step is the hydration of the NO_x vapors to produce HNO₃ and HNO₂. These reactions are highly exothermic and cooling is required. Absorption rates increase with decreasing operating temperature and with increasing operating pressures (up to 5 atm). Oxygen is added to convert NO to NO₂. Most manufacturers use a pressure process with absorption of NO_x gases in bubble-cap plate towers to produce HNO₃. Hanson¹⁶ notes that only 20 to 45% of the NO_x vapors are usually removed by water scrubbing under ambient conditions. Although the potential for recycling the recovered HNO₃ has been mentioned frequently,¹⁴ operating systems involving HNO₃ recovery and recycle are seldom mentioned in the literature, perhaps because of the problems mentioned above. The escaping NO_x vapors have an adverse environmental effect and the threshold limiting value (TLV) for nitrogen dioxide (NO₂) has been set at 0.05 ppm (0.10 mg/m³) as an average annual value¹⁷ because of the deleterious effects of NO_x vapors on lung function. Thus, technology has evolved towards NO_x abatement rather than to HNO₃ recovery and recycle. Pence¹⁸ and Thomas¹⁹ introduce ammonia gas into the off-gas stream to reduce NO₂ to N₂ or N₂O. The reactions are:



and



The reactions take place on a zeolite catalyst. The harmless, inert, noncondensable gases (N₂ and N₂O) produced in this case admirably serve the goal of NO_x abatement. These gases can be scrubbed and filtered through HEPA filters before being eliminated from the plant. It should be noted that these gases (N₂O and N₂) are the same that are produced directly in reaction 1. Because of the inert nature of these gases every effort should be made towards eliminating nitrogen in this form.

Since nitrate ion is the predominant constituent in high-level waste the possibilities of HNO₃ recycle are limited. As stressed previously, there is accumulating evidence that RuO₄ is formed by denitration of a highly nitrated octahedral complex or polymer of ruthenium. Early efforts to control RuO₄ volatility are reviewed by Christian²⁰ and

in Gmelin's Handbook of Inorganic Chemistry.²¹ With a starting solution of 4.0 *N* HNO₃ or higher, about 30% of the ¹⁰⁶Ru is volatilized on calcining an acid waste. Recently, for example, Mendel²² reported a 30% ¹⁰⁶Ru volatility loss on calcining a high-level nitrate waste prior to the preparation of a radioactive glass. Ruthenium-106 volatilities can be decreased to ~1% by adding various reducing agents (sugar, hydrazine, phosphorous acid, formaldehyde, etc.) to the HNO₃ solution. However, the volatilization of even 1% ¹⁰⁶Ru can represent thousands of curies of activity per ton of heavy metal irradiated at 33,000 Mwd/ton, which can be a serious operating hazard when present in the off-gas stream in volatile form. More study is required on methods of decreasing ¹⁰⁶Ru volatilities far below 1% in order to achieve high decontamination factors of the off-gas stream.²⁰

It is generally recognized that ¹⁰⁶Ru is the radioisotope most likely to create problems in operating a waste calcination plant because of RuO₄ volatility. Idaho personnel have had extensive experience in this area and Christian^{20,23} has described the difficulties encountered in controlling RuO₄ volatility. The RuO₄ interacts with stainless steel walls to give particulate RuO₂ which can accumulate in the off-gas system and be an operating hazard for years. Feber²⁴ notes that RuO₄ is stable for at least 100 h in stainless steel systems in the absence of light and water vapor. However, under process conditions the RuO₄ is reduced to RuO₂ which deposits on the equipment walls. Feber notes that particulate RuO₂ with a mean particle diameter of 0.05 μ or less has been observed as a result of decomposition of RuO₄ in the gas phase. Incidents involving the emission of particulate RuO₂ activity at various reprocessing sites have been reviewed.^{25,26} More data are required on the reactivity of RuO₄ with stainless steel, especially at higher temperatures. The interaction of RuO₄ with stainless steel to give particulate RuO₂ can mask the intrinsic volatility of RuO₄ from nitrate solutions under calcination conditions. For example, many observers^{20,21} have noted the formation of black shiny deposits of RuO₂ which presumably occurred after volatilization of RuO₄.

It should be kept in mind that thermodynamically RuO₄ is a very reactive compound²⁰ (standard free energy of formation ΔF = -33.42 kilocal per mole). In addition, RuO₄ has a high solubility in weak acid

solutions²⁷ (0.07 to 0.10 mole/liter). Thus, the RuO_4 in an off-gas stream is readily dissolved in aqueous scrub solutions which can consist of water condensed from the evaporated waste. Sufficient hydrogen peroxide from the interaction of radiation with water or nitrous acid is present in the scrub solution to reduce RuO_4 to a nonvolatile, lower valence state.^{3,10} Small amounts of oxalic acid or formic acid can also be added to reduce RuO_4 . Most of the water in the scrub solution can be eliminated by evaporation and the concentrated solution can be recycled after blending with fresh incoming waste. High concentration factors can be achieved if the NO_x vapors are not recovered or if nitrogen is present as N_2 or N_2O gases which are insoluble in the scrubbing solution. In small scale equipment it is relatively simple to use all glass equipment and, thus, to achieve efficient scrubbing of RuO_4 from an off-gas stream (99.9% trapping of RuO_4 in the first two scrubbers). However, whenever a process is reduced to industrial practice it is essential that the equipment be built of stainless steel because of its durability and strength. In this case, because of the reactivity of RuO_4 the ruthenium in the off-gas stream will consist of a mixture of RuO_2 and RuO_4 , or even almost entirely of RuO_2 particulate matter. It is known^{20,21} that near the condensation point of water, RuO_4 reacts with stainless steel which becomes coated with a black shiny deposit of RuO_2 . Christian²⁰ has assembled a considerable amount of data on the decontamination factors (DFs) achievable with various scrubbers and filters in off-gas systems. Heavy reliance is usually placed on packed columns filled with silica as the sorbent material to remove RuO_4 .^{20,28,29} The RuO_4 in vapor form reacts with the solid silica gel in the packed column. Later the ruthenium is flushed from the column with a water rinse. It is stated that the DF across the silica gel bed is only 8 for particulate matter and 1000 for volatile RuO_4 .³⁰ It is important to distinguish between RuO_4 and RuO_2 . The DF data are likely to be flawed if it is not known whether ruthenium is present as RuO_4 , RuO_2 or a mixture of both these forms. Postma has recently presented a theoretical study on the nucleation and capture of condensable airborne contaminants.³¹ It is known²¹ that RuO_2 can be dissolved by a 1.0 *N* NaOH-0.05 *M* sodium persulfate

solution to give a clear orange solution. Since RuO_4 volatilizes from the calcination process itself and is subsequently converted to particulate RuO_2 , the preferred design of an off-gas system would have a weak acid, plate scrubber near the calciner to trap RuO_4 with a final caustic scrubber at the end of the off-gas system to trap RuO_2 particulates. Giraud and LeBlaye³² report on such an off-gas system which handles 15% RuO_4 volatilized in operating a pilot plant that calcines high-level waste and produces glass. High DFs for ^{106}Ru on the order of 10^9 to 10^{10} were obtained. More than 99% of the initial ^{106}Ru in the waste appeared in the glass in spite of the high RuO_4 volatilization (15%) because of the efficient liquid off-gas scrubbers and the ease of recycle.

Calculations by the ORNL ORIGEN code shows that after 3 years cooling there is still 70,000 curies of ^{106}Ru left in 1 ton of uranium irradiated at 30,000 Mwd. Because of its long half-life (1.0 y) the deposition of particulate RuO_2 in off-gas systems can be a potential hazard for years. It is imperative that better methods of reducing RuO_4 volatility be found.

Technetium-99 has a long half-life (2.1×10^5 y) and a high fission yield (6.1%). At an irradiation of 30,000 Mwd per metric ton of uranium, 900 g of ^{99}Tc is produced, 80% (~ 720 g) of which remains in the aqueous fission product waste. It has been reported^{33,34} that ^{99}Tc distills as a higher oxide by dehydration of pertechnic acid (HTcO_4) on evaporating an acid solution. Smith, Cobble, and Boyd³⁵ report such high vapor pressures for technetium heptoxide (Tc_2O_7), HTcO_4 , and aqueous solutions of HTcO_4 that these data would seem to indicate the almost complete volatility of ^{99}Tc 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 way of contrast, a detailed look at the properties of the alkaline earth pertechnetate compounds show that these compounds have thermal stability limits at high temperatures³⁶ that increase in the presence of excess alkaline earth oxide. After calcination the fission product nitrates are converted to oxides, which tend to form

stable nonvolatile double salts with metal pertechnetates (Table 1). Since ^{99}Tc volatility from acid solutions volatilizes as Tc_2O_7 or HTcO_4 , wet scrubbing should be effective in removing these compounds from an off-gas stream.

Table 1. High Melting Technetium Oxide Compounds

Compounds	Thermal stability limit ($^{\circ}\text{C}$)	Comment
$\text{Ba}(\text{TcO}_4)_2$	700	
$\text{Ba}_3(\text{TcO}_5)_2$	850	
$\text{Ba}_5(\text{TcO}_6)_2$	850	Mixed oxide with BaO
$\text{Sr}(\text{TcO}_4)_2$	680	
$\text{Sr}_5(\text{TcO}_6)_2$	850	Mixed oxide with SrO
$\text{Ca}(\text{TcO}_4)_2$	650	
$\text{Ca}_5(\text{TcO}_6)_2$	800	Mixed oxide with CaO
$\text{Sr}_2\text{LiTcO}_6$	900	
BaTcO_3	800	
SrTcO_3	1200	

Source: KFK-341 (July 1965).

Iodine-129 has a long half-life (1.7×10^7 y) and a moderate fission yield (1.7%) with the production of 0.1 Ci of ^{129}I per ton of uranium irradiated at 30,000 Mwd. The main fission product liquid waste will contain only approximately 0.5% of the ^{129}I , since 99.5% is evolved during dissolution of the fuel in HNO_3 .²⁶ Iodine is evolved (usually as I_2 or HI) as a result of thermal decomposition during the high temperatures required for calcination. These compounds are trapped by wet scrubbing with an iodine DF of 10 to 100 across a wet scrubber.³⁷ Any iodine passing through the wet scrubber is generally caught on a silver adsorber with an iodine DF greater than 1000.³⁷ Wet scrubbing was found to be adequate in tracing the fate of iodine during calcination.

DESCRIPTION OF EQUIPMENT AND EXPERIMENTAL PROCEDURE

A small quartz pot calciner and a small electrically heated spray calciner were used to investigate the volatility of components from high-level waste. The quartz calciner experimental system is shown in Fig. 2. A two-piece quartz calciner is used. The bottom piece (1) is a 54-mm quartz tube 14 cm long with a 65/40 female quartz joint on top for ease of disassembly. A 15-mm quartz tube sidearm 13 cm long ending in a 28/15 male quartz joint is attached to the bottom piece about 1 cm below the joint. This bottom assembly is designed to be placed inside a small electrically heated laboratory furnace with a 10 × 10 × 10 cm cavity. Asbestos cloth is wrapped around the joint and the sidearm to minimize heat losses and a heat lamp keeps the upper part of the assembly warm.

The upper part of the quartz calciner (2) contains a thermowell, a gas-sweep line, and a solution-addition line (4), which are spaced on centers 120° apart and built into the male quartz joint. The thermowell contains two thermocouples that measure temperatures near the bottom of the quartz calciner and at the level of the sidearm through which the off-gas passes. The solution-addition line (4) contains a 4-mm stopcock that allows the addition of slurries to the quartz calciner. The gas-sweep line incorporates a rotometer (3) with a range from zero to 2500 ml/min and is usually set at a gas flow of 1000 ml/min. When waste is added to the quartz calciner, the pressure builds up because the liquid is converted to vapor, and the gas flow through the rotometer can momentarily fall to zero. Addition of liquid waste to the calciner is resumed when the gas flow through the rotometer builds back up to its set value.

A 9-cm-diam fritted glass disk (5), which is of medium porosity (pore size of 10 to 15 μ) and protected by a glass wool plug, is placed in line to trap particulate matter. The disk is encased in a heating mantle to avoid premature condensation of vapor in the gas stream. Hence the temperature of the heating mantle is maintained at a point higher than the condensation temperature ($\sim 200^\circ\text{C}$) to minimize the loss of RuO_4 in the filter.

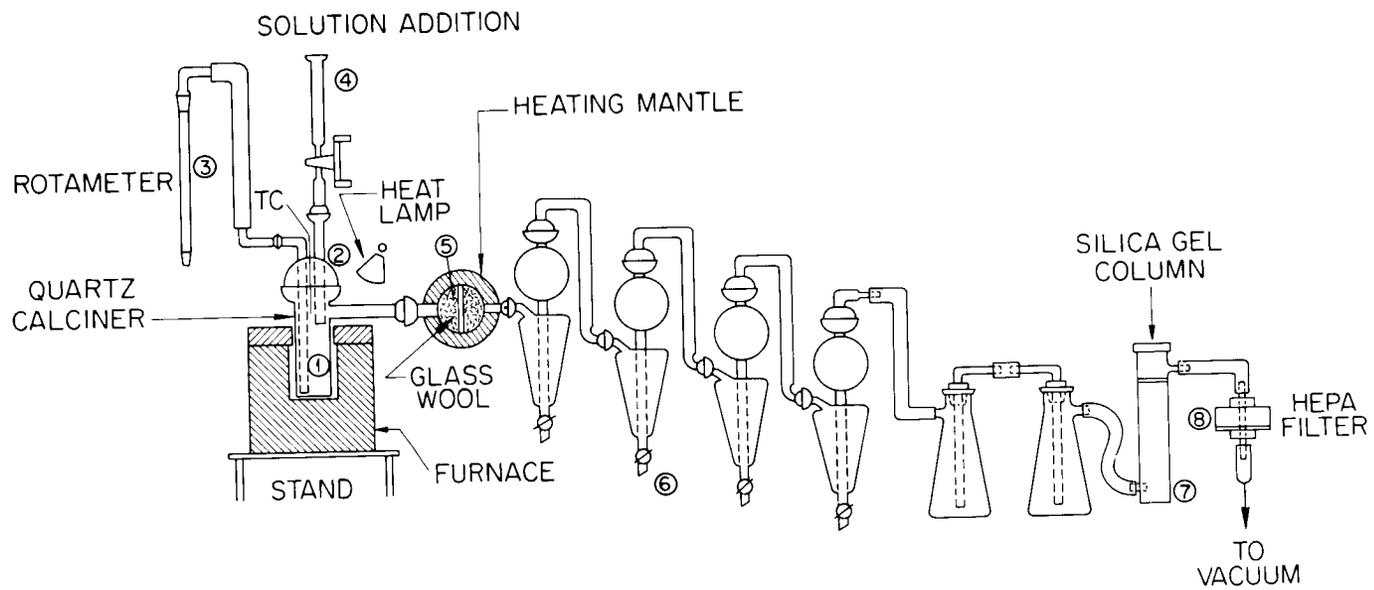


Fig. 2. Quartz pot calciner and off-gas scrubber train.

The gas scrubber train (6) consists of four inverted 250-ml Erlenmeyer flasks provided with 250-ml round bulbs filled with glass Rashig rings. During operation, the liquid solution is drawn up into the round bulb, where RuO_4 is scrubbed from the gas stream. A fifth scrubber consists of two 250-ml Erlenmeyer flasks arranged as a two-way vacuum break in the scrubbing train. These flasks are dip-leg bubble scrubbers.

A silica gel column and a small high-efficiency particulate air (HEPA) filter complete the gas scrubber train. A vacuum pump pulls the off-gas from the calciner through the gas scrubber train.

An electrically heated spray calciner, 51-cm-long and 10-cm-diam, was used for the spray calciner experiments (Fig. 3). The liquid waste is sprayed through an internal mixing spray-nozzle and falls down the heated cylinder. Calcined solids are collected at the bottom of the de-entrainment unit. The calciner gases exit through a sintered stainless steel filter that is designed to remove particulate matter $>5 \mu$ in diameter. An additional 9-cm-diam fritted glass disk with medium porosity serves as a backup to the stainless steel filter in order to obtain efficient removal of particulate matter. The filtered off-gas then passes through a water-cooled condenser and two filled scrubber columns, each 5 cm in diameter and packed with 0.3-cm ceramic Berl saddles to a height of 30.5 cm. The bubble contactor, silica gel column, HEPA filter, and small vacuum pump complete the gas scrubbing train. The essential elements of the spray calciner and gas scrubbing train are shown schematically in Figs. 3 and 4, respectively.

Waste Preparation and Analyses

A total of ~ 900 g of highly-irradiated UO_2 from the H. B. Robinson-2 reactor was dissolved in 3 *N* HNO_3 at 90°C with periodic additions of 7.5 *N* HNO_3 to maintain the 3.0 *N* HNO_3 concentration. Final concentrations were adjusted to 1.25 *M* uranium (298 g/liter) and 2.5 *N* HNO_3 ; 9 g of gadolinium per kilogram of uranium was added as a poison to simulate the criticality control in the dissolver. (More than 99% of the ^{129}I is evolved as iodine during the dissolution.) A series of four batch

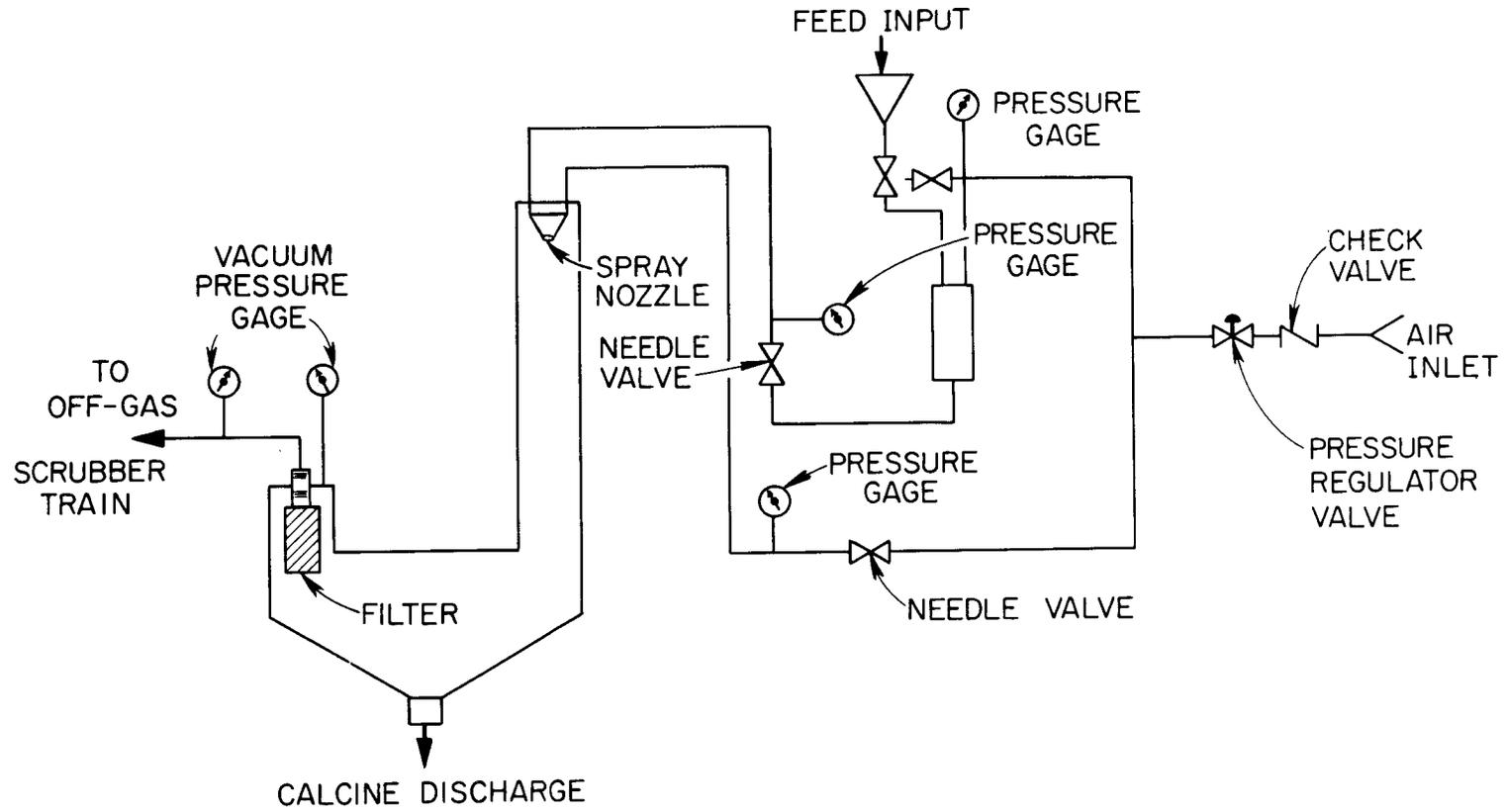


Fig. 3. Spray calciner.

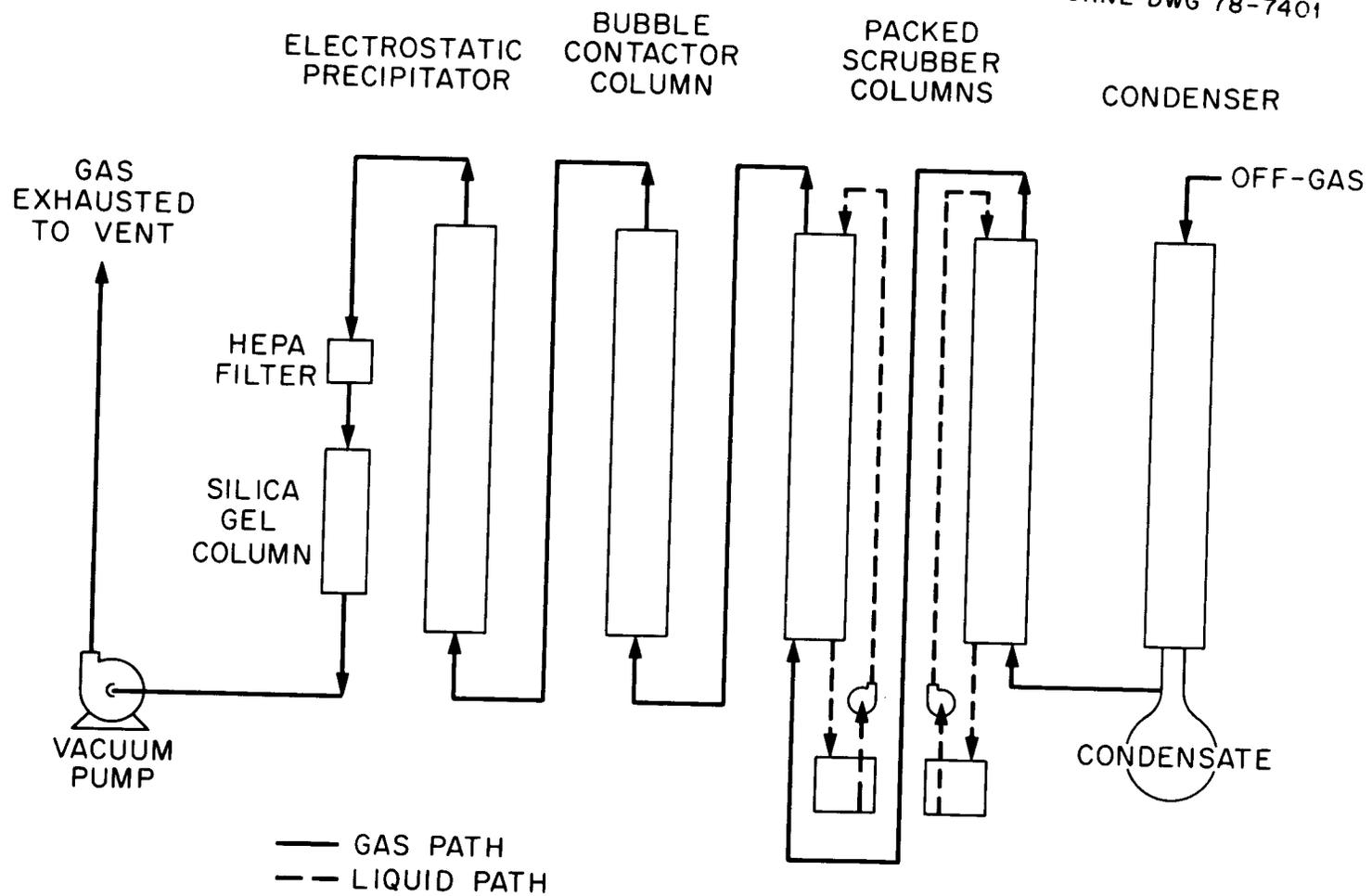


Fig. 4. Spray calciner off-gas train.

solvent extractions with 30% tributylphosphate (TBP) in Amsco (kerosine) diluent at organic-to-aqueous ratios of 1, 1, 1, and 0.4 was carried out to remove more than 99.5% of the uranium from the aqueous phase. The acid waste was evaporated down and adjusted to a final volume of 340 ml after additions of uranium, sodium, gadolinium, and corrosion products (iron, nickel, and chromium). This waste volume corresponds to a volume of 100 gallons of waste per ton of uranium metal processed. The concentrations of the principal constituents are given in Table 2, and the radioactivity concentrations are given in Table 3.

Table 2. Composition of Actual and Simulated Purex Waste
(100 gallons waste per ton of U)

Constituent	Formula	Concentration (molar)	
Nitric acid	HNO_3	4.0	
Uranium nitrate	$\text{UO}_2(\text{NO}_3)_2$	0.123	(1% of original U)
Ruthenium nitrate	$\text{Ru}(\text{NO}_3)_3$	0.061	
Cesium nitrate	$\text{Cs}(\text{NO}_3)$	0.062	
Rare earth nitrates	$\text{M}(\text{NO}_3)_3$	0.1608	
Gadolinium nitrate	$\text{Gd}(\text{NO}_3)_3$	0.1512	(added to simulate neutron poison)
Strontium nitrate	$\text{Sr}(\text{NO}_3)_2$	0.0246	
Barium nitrate	$\text{Ba}(\text{NO}_3)_2$	0.0336	
Cerium nitrate	$\text{Ce}(\text{NO}_3)_3$	0.0477	
Sodium nitrate	NaNO_3	0.0114	
Iron nitrate	$\text{Fe}(\text{NO}_3)_3$	0.0945	
Nickel nitrate	$\text{Ni}(\text{NO}_3)_2$	0.0036	
Chromium nitrate	$\text{Cr}(\text{NO}_3)_3$	0.0102	
Zirconium nitrate	$\text{Zr}(\text{NO}_3)_4$	0.1074	
Molybdenum oxide	MoO_3	0.0981	

Table 3. Radioactivity Concentrations in Authentic Purex Waste

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)

Mixtures of gamma emitters were routinely determined by a process called gamma scanning. In this case a Ge(Li) crystal with coaxial drifting of lithium and a volume of 100 ml responds to gamma ray excitations over a broad spectrum of energies. These responses are converted to gamma ray counts per unit of time and stored in 4000 data channels at 0.5 keV per channel. The Nuclear Data 6600 system includes two microcomputers with two interacting central processing units (CPU), two hard discs for stored software programs and data, and input-output facilities. The raw data are first subjected to a peak search program. Corrections are applied for Compton scattering, counting efficiency and geometry. Counting efficiency generally increases with decreasing gamma ray energy, and is determined by counting standard samples from the National Bureau of Standards at a number of different geometries. A quantitative estimate of the amount of activity in the sample is obtained by summing the gamma ray counts under a specific prominent gamma ray peak and by applying a factor which takes into account the percentage of observed gamma transitions in the overall disintegration of the radioactive nuclide (gamma-ray, branching ratio). Prominent gamma ray peaks are found at 621 keV for ^{106}Ru , 662 keV for ^{137}Cs , 604 and 795 keV for ^{134}Cs , 133 keV for ^{144}Ce , and 1275 keV for ^{152}Eu . The resolution of the Ge(Li) crystal for the 1332 keV peak in ^{60}Co is 2.0 to 3.3 keV. Thus, by gamma scanning it is possible to obtain quantitative estimates on the amounts

of ruthenium, technetium, and iodine activities in the presence of other radioactive elements.

Radioactive tracers of ^{106}Ru , $^{95\text{m}}\text{Tc}$, and ^{131}I were also used to obtain volatility data by gamma scanning. Technetium-99 was also determined radiochemically by adding rhenium carrier, precipitating the tetraphenylarsonium pertechnetate compound, and counting the betas from long-lived ^{99}Tc (half-life = 2.1×10^5 y).

Nitrate analyses were performed by adding Devarda's alloy to a liquid aliquot or to a weighed amount of sample dissolved in phosphoric acid. Nitrate was reduced to ammonia, which was distilled off and titrated with HCl or determined colorimetrically. Extraneous cations in filtered condensates were determined by emission spectroscopy on a 2.25-m, Jarrell-Ash spectrograph mounted in a hot cell. Solution aliquots (0.5 to 1.0 ml) were absorbed in a hollow, porous, graphite cup 3-in.-long. An anode spark was struck, and emission lines from vaporized elements were recorded on 35-mm spectrographic film. The line density was read on a densitometer. A cobalt solution containing 75 μg cobalt per ml was used as an internal standard in obtaining quantitative estimates of element concentration. Accuracies within 5% are possible with an internal standard for the various elements given in Table 4. These concentrations represent conservative lower limits of element detection.

Emission spectroscopy was used to detect elements that could not be determined by gamma scanning. The alkali elements and strontium are determined by flame photometry.

Table 4. Lower Limits of Element Detection by Emission Spectroscopy

Element	Concentration ($\mu\text{g}/\text{ml}$)	Element	Concentration ($\mu\text{g}/\text{ml}$)
Ag	0.5	Mo	5
Al	2	Na	0.5 ^a
Au	25	Nb	50
B	20	Nd	50
Be	0.005	Ni	2
Bi	10	Pb	10
Ca	10	Pd	2
Cd	75	Pt	25
Ce	25	Rb	5 ^a
Co	20	Rh	5
Cr	1	Ru	20
Cs	5 ^a	Sb	10
Cu	0.5	Si	10
Fe	10	Sn	25
Ga	10	Sr	1 ^a
Hf	10	Ta	50
In	20	Tc	25
Ir	50	Te	75
K	5 ^a	Ti	0.5
Li	1 ^a	V	5
Mg	1	W	50
Mn	1	Zn	50
		Zr	2

^aDetermined by flame photometry.

Ruthenium Behavior During Calcination

RuO₄ Volatility as a Function of Initial HNO₃ or Nitrate Concentration in the Waste

A series of calcinations with the use of the quartz pot calciner in the flash evaporation mode were made, in which only the initial HNO₃ concentration was varied. The 4.0 N HNO₃ feed was added to a hot formic acid solution to obtain lower initial HNO₃ concentrations. The calcination temperature was held constant at 350°C, which previous experiments had indicated was the optimum temperature for RuO₄ volatilization. An optimum temperature for volatilizing RuO₄ is used to facilitate detection of any increase in RuO₄ volatility with increasing initial nitrate concentration. Tests were run on simulated waste with tracer ¹⁰³Ru and on authentic waste. Since hydrogen peroxide accumulates to the extent of

0.05 to 0.10 *M* in high-level radioactive solution, hydrogen peroxide to a molarity of 0.10 was added to the 4.0 *N* HNO₃ solution of fission products in order to simulate high-level radiation effects. The results of these tests are presented in Fig. 5 and Table 5. Additional data on tracer runs are presented in the Appendix.

Table 5. RuO₄ Volatility as a Function of Initial HNO₃ Acid Concentration on Calcining an Acidic Purex Waste at 350°C

Initial HNO ₃ molarity	RuO ₄ volatility (%)	
	High-level waste	Tracer
8.0		14.7
4.0	34.8	14.0
4.0 ^α		20.4
2.0	15.7	20.1
Zero	0.4	1.0

^αPeroxide added.

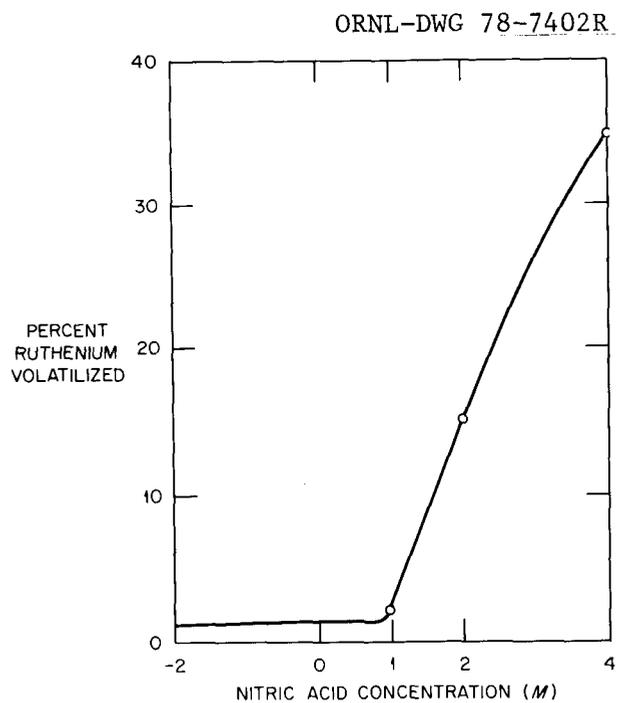


Fig. 5. Ruthenium volatility vs nitric acid concentration from high-level waste (pot calcined at 350°C).

The RuO_4 volatility increases with increasing concentration of initial HNO_3 and decreases abruptly to approximately 1.0% on decreasing the initial nitrate concentration to approximately 0.5 *N*. The addition of 0.1 *M* H_2O_2 increases the RuO_4 volatility from 14 to ~20%. Volatility of RuO_4 from authentic waste was 34.8% compared to 14% from a simulated waste of the same composition (4.0 *N* HNO_3) and the same calcination temperature (350°C) with tracer ^{103}Ru . Increasing the initial HNO_3 concentration from 4.0 *N* to 8.0 *N* in the simulated waste does not significantly increase the RuO_4 volatility (14 and 14.7% respectively). The results of analyses by emission spectroscopy showed only the presence of ruthenium in the acid scrub solution. Although a low RuO_4 volatility of approximately 1% was attained by decreasing the initial HNO_3 concentration, much lower values are desirable for the cleanup of an off-gas stream containing radioactive ^{106}Ru in a volatile form. Mendel et al.²² report a 30% ^{106}Ru volatility loss on calcining a high-level Purex waste prior to the preparation of a fully radioactive glass. This value is in agreement with our high ^{106}Ru volatility value reported above for an untreated high-level waste.

Ruthenium Volatility and Nitrate Elimination as a Function of Temperature and Formic Acid Pretreatment

Thermal denitration of a salt results in the evolution of an acid vapor (NO_x) with formation of an alkaline residual calcine (the metal oxide). The alkaline oxide matrix fixes ruthenium as the ruthenate and suppresses the formation of volatile RuO_4 that usually forms on concentrating an HNO_3 solution. It is assumed that the incoming HNO_3 waste reacts rapidly with the alkaline oxide matrix. Then, if the temperature is high enough, the nitrate salt is thermally denitrated with formation of the metal oxide. According to this view, the metal oxide acts as a medium to hold the ruthenium in a nonvolatile ruthenate form during denitration of the metal nitrate. If the thermal denitration is slow, the addition of acid feed results in the creation of high local acidity with the evolution of the volatile RuO_4 that forms under acid conditions. The treatment of an HNO_3 waste with formic acid (2 moles formic acid/mole nitrate) results in chemical denitration at lower temperatures and the

suppression of RuO_4 volatility under conditions where the untreated waste would give a high RuO_4 volatility.

To test the above hypothesis, two series of calcinations at 250, 350, 450, and 600°C were run with untreated HNO_3 waste and with waste pretreated with formic acid (2 moles formic acid/mole nitrate). The nitrate content in the residual salt was determined as a measure of the alkalinity of the residual salt. The higher the nitrate content of the calcined material, the lower the basicity or alkalinity of the residual salt and the more probable it would be to find a high RuO_4 volatility. The results of these calcinations are presented in Fig. 6 and Table 6.

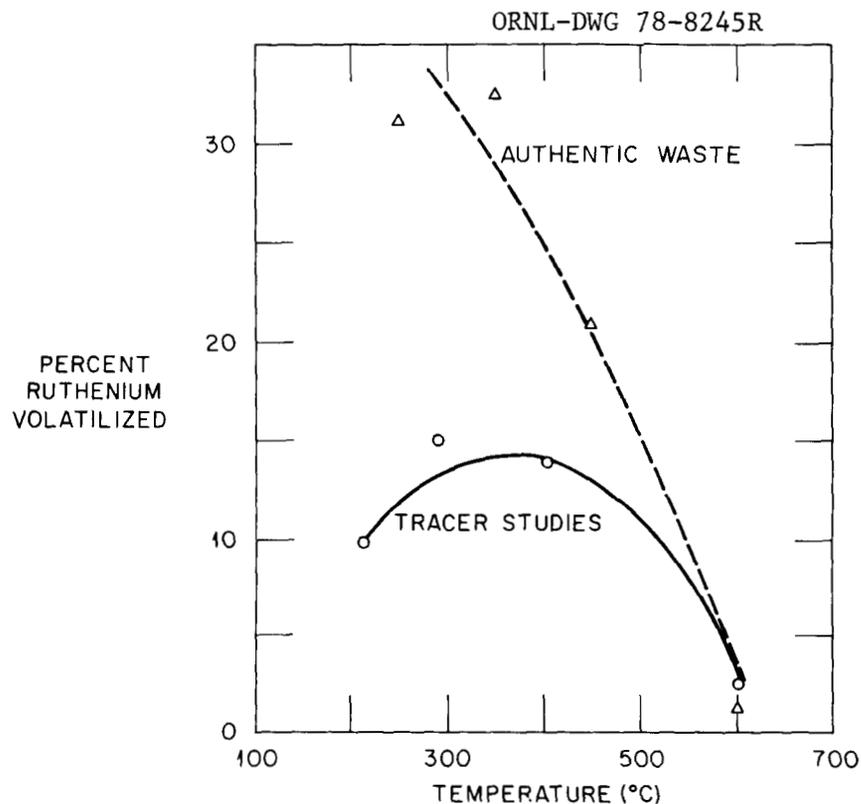


Fig. 6. Ruthenium volatility vs temperature.

In the case of the untreated waste (initial HNO_3 acid of 4.0 *N*), the RuO_4 volatilities at 250 and 350°C are relatively high (32.3 and 34.8%, respectively) while the nitrate content in the calcined salt is also high (36.8 and 21.2%, respectively). At the same temperatures (250 and 350°C), the waste pretreated with formic acid shows low RuO_4 volatilities and low nitrate content in the calcined salt.

Table 6. Ruthenium Volatility and Nitrate Elimination from Untreated and Formic-Acid-Treated Authentic HNO_3 Wastes at Various Temperatures

Temperature (°C)	^{106}Ru volatility (%)		Nitrate in residual salt (%)	
	Untreated	Treated with formic acid ^a	Untreated	Treated with formic acid ^a
250	32.3	0.15	36.8	3.3
350	34.8	0.2	21.2	5.3
450	21.6	0.13	1.03	3.3
600	2.4	0.2	0.39	0.22

^aTreated with 2 moles of formic acid per mole of nitrate.

After calcination at 450°C the untreated HNO_3 waste shows a rather high RuO_4 volatility (21.6%) along with a low nitrate content (1%) in the residual salt. In this case the thermal denitration is so slow that the addition of acid feed creates a high local acidity that favors the evolution of volatile RuO_4 . At a calcination temperature of 600°C, both the untreated and the formic-acid-treated wastes show low RuO_4 volatilities of 2.5 and 0.2%, respectively, with low nitrate contents in the calcined residues. No significant amounts of other elements could be detected by emission spectroscopy or by gamma scanning.

RuO_4 Volatility From the Stainless Steel Spray Calciner

The electrically heated spray calciner was operated at wall temperatures of 400, 500, and 725°C in these experiments. A 10- to 40-ml waste volume containing ^{103}Ru tracer was fed to the spray nozzle at a rate of 1.5 ml/min. The off-gas stream passing through the stainless steel filter and a medium-porosity, fritted-glass filter was scrubbed with water to remove the RuO_4 , and the amount of radioactive tracer in the scrub solution was determined by gamma counting. The percentage of RuO_4 released was determined for a spray-dried, untreated waste that had an initial HNO_3 concentration of 4.0 N and also for a spray-dried, fission product, nitrate waste that had been pretreated with 2 moles of formic acid per mole of nitrate. The results are presented in Table 7.

Table 7. RuO₄ Volatility of a 4 N HNO₃ Simulated Waste in a Spray Calciner at Various Wall Temperatures with and without Waste Pretreatment

Wall temperature of spray calciner (°C)	RuO ₄ volatility (%)	
	Untreated waste (4.0 N HNO ₃)	Pretreated waste (2 moles formic acid/mole nitrate)
725	0.120	0.013
500	0.240	0.197
400	0.510	0.045

The percentages of RuO₄ volatilized are all very low, and RuO₄ volatility appears to decrease with increasing temperature. With the exception of the result at 500°C, the volatilities from the pretreated waste are an order of magnitude lower than the RuO₄ volatilities from the untreated waste. The RuO₄ appears to have reacted with the heated stainless steel walls of the spray dryer. The review of this interaction by Christian²⁰ can explain the anomalously low results obtained with the untreated waste.

Pretreatment of Waste to React With the Nitrate and Nitro Complexes of Ruthenium

As indicated in the literature review, a number of researchers¹⁻¹⁰ have made observations that are useful in deducing the mechanism for the formation of RuO₄ from the decomposition of various ruthenium complexes. At this point we present a summary of the range of RuO₄ volatilities as a function of pretreatment conditions on calcining a 4.0 N HNO₃ authentic fission product waste at 350°C. These results are shown in Table 8; with no pretreatment the RuO₄ volatility is high at 34.8%.

Table 8. RuO₄ Volatility as a Function of Pretreatment Conditions on Calcining a 4.0 *N* HNO₃, Authentic Fission Product Waste at 350°C

RuO ₄ volatility (%)	Pretreatment conditions
34.8	None (4.0 <i>N</i> HNO ₃)
1	Nitrate reduced to 0.5 <i>N</i> or lower
0.1	Two moles of formic acid per mole of nitrate
0.007	15% excess of formic acid above 2 moles of formic acid per mole of nitrate

Brown⁵ notes that oxidizing conditions lead to the formation of Ru(IV) solutions with the production of a (RuORu)VI nitrate polymer, which is rapidly oxidized to RuO₄. Fletcher^{1,2} argues for the formation of a fully nitrated anion complex or compound, which is oxidized to ruthenium tetroxide at higher temperatures. Thus, it is possible to explain the high volatility of RuO₄ from HNO₃ solution by the existence of a highly nitrated ruthenium complex that decomposes with evolution of RuO₄.

It is more difficult to explain the low RuO₄ volatility of 1%, which is obtained on calcining a solution of low or moderate nitrate concentration (0.5–1.0 *M*), and the even lower RuO₄ volatility of 0.1%, which is obtained on calcining a solution pretreated with 2 moles of formic acid per mole of nitrate. It should be emphasized that researchers in the field^{4,6-10} have frequently noted the existence of mixed, multiple chemical forms of ruthenium and the slowness of interconversion reactions. Furthermore, it should be stressed that these low RuO₄ volatilities (1 and 0.1%) can be obtained reproducibly in our equipment with high decontamination from cesium and cerium activities on calcining authentic high-level Purex waste. Thus, it is tempting to assume that at low or moderate nitrate concentrations, the low RuO₄ volatility of ~1% occurs as a result of the presence of polymeric ruthenium, a small amount of which can exist in solution for a considerable length of time.

However, the question remains as to how to explain a decrease in RuO_4 volatility by another order of magnitude to 0.1% with the use of 2 moles of formic acid per mole of nitrate. Since nitrate complexing in ruthenium compounds is relatively weak, and since formic acid is a reducing agent that can react with the labile nitrate ion, it is reasonable to assume that the reduced ruthenium formate complex, which forms on interaction of the ruthenium nitrate complex with formic acid, decomposes on calcination to nonvolatile forms of ruthenium (RuO_2). Furthermore, in the presence of nitrous acid it is possible to form relatively stable nitro ruthenium complexes,^{4,5} which are slowly oxidized to RuO_4 under oxidizing conditions. These nitro compounds can be decomposed at atmospheric pressure at a temperature of 170°C or higher.³ Thus, at calcination temperatures of 350°C and higher, it is entirely plausible that small amounts of RuO_4 (~0.1%) would be formed from the decomposition of nitro ruthenium complexes under calcination conditions.

Although the ruthenium nitro complex is very stable, the nitro group can be attacked by reducing agents such as ferrous sulfate or ferrous sulfamate⁸ and also by formic acid, which is a rather strong reducing agent. To promote the removal of nitrate and nitro groups prior to the calcination step, it is necessary to allow sufficient time for the reaction to occur. It should be remembered that the behavior of fission ruthenium in solution can vary because of slow changes among a wide variety of compounds similar to the changes occurring with the element carbon in organic chemistry. Preliminary evidence of the importance of the time factor was obtained on calcining a simulated acid waste containing ^{103}Ru tracer that had been treated with 2 moles of formic acid per mole of nitrate and set aside for two to three months. Waste calcinations on this batch of waste at 250 and 450°C showed RuO_4 volatilities of 0.0110 and 0.0108%, which are an order of magnitude lower than the RuO_4 volatilities (~0.10%) usually observed under these calcination conditions. This experiment was repeated to verify the results obtained. The simulated acid waste with the ^{103}Ru tracer was pretreated by digesting 1 h at 90°C with 2 moles of formic acid per mole of nitrate. Half of this pretreated waste was calcined immediately at

350°C and the RuO_4 volatility was found to be 0.13%. Three days later the other half of the same batch of waste was calcined at 350°C, and the RuO_4 volatility was found to be a factor of 8 lower, or 0.016%. An additional confirmatory series of two runs showed a RuO_4 volatility of 0.022% on immediate calcination at 350°C and a lower RuO_4 volatility of 0.00082% on the same waste when the calcination was performed the next day. These results indicate that batch denitration of waste would be favored over continuous denitration achieved by mixing formic acid with high-level waste in the spray nozzle of a spray calciner, except if excess formic acid is used (see below).¹² More time would be available to denitrate the nitro ruthenium complexes with batch denitration.

The concentration of the reactants is an important factor in promoting the reaction rate. Consequently, the simulated acid waste containing ^{103}Ru tracer was treated with a 15% mole excess above a ratio of 2 or 2.3 moles of formic acid per mole of nitrate. The first batch was calcined immediately after the formic acid pretreatment. Successive calcinations at 350°C were performed from this same batch of pretreated waste with at least 24 h between calcinations. The RuO_4 volatilities were 0.0017, 0.0038, 0.0038, and 0.0032%, respectively, on four successive batches. In this case the RuO_4 volatilities are all low because the reaction kinetics had been completed before the first calcination. The time factor is less important with a 15% excess of formic acid. Apparently, a 15% mole excess of formic acid leads to rapid formation of a reduced ruthenium formate complex, which on calcination decomposes mainly with the formation of nonvolatile RuO_2 .

It is possible that some artifact associated with radiation could influence the results. Hence, the previous experiment was repeated with an authentic high-level acid waste containing a fission product mixture. This waste was pretreated with a 15% mole excess of formic acid above a ratio of 2 moles of formic acid per mole of nitrate. Successive calcinations were performed at 350°C from this same batch of waste with a period of seven days between calcinations. The first calcination run showed a ^{106}Ru carry-over of 0.024% with a ^{137}Cs carry-over of 0.034%. In this case, because of the high accompanying ^{137}Cs carry-over, it was

inferred that radioactive particulate had carried over as a result of cracks in the 10-cm fritted glass disk, which was replaced with a new one. The second calcination run from the same batch of waste showed a ^{106}Ru volatility of 0.0076% with a low ^{137}Cs carry-over (0.00026%). Thus, pretreatment of the waste with 15% excess formic acid led to a factor of 15 decrease in RuO_4 volatility over the lowest previous volatility for a Purex waste pretreated with formic acid ($\sim 0.10\%$). In this case the RuO_4 volatility was so low that a small amount of ^{137}Cs contamination was detected for the first time by gamma scanning. Previously it was necessary to determine ^{137}Cs and ^{144}Ce contamination by radiochemical procedures.

Wet Scrubbing of RuO_4 With Water or Weak Reducing Acid Solutions

To evaluate the efficacy of liquid scrubbing, the distribution of ^{106}Ru in the five liquid traps was determined during six different runs with the RuO_4 volatility varying from 0.4 to 39.7%. The data are presented in Table 9. Small amounts of oxalic acid were added to traps 1 and 2 as a reducing agent for efficient trapping of the strongly oxidizing ruthenium tetroxide, and formic acid was used in traps 3 and 4. Sodium hydroxide was used as a scrubbing agent in trap 5 but is not recommended for process use because of the unnecessary introduction of sodium ions into the waste stream. Water alone is satisfactory as a scrubbing agent and has been used in subsequent experiments. It is anticipated that the liquid condensate from the off-gas stream can be utilized as the scrubbing medium.

The percentage of ^{106}Ru in each trap is calculated by ignoring the ^{106}Ru activity in previous traps and by taking into account the ^{106}Ru present in the trap under consideration. For example, for run 1 the ^{106}Ru in trap 1 is $332,500 \times 100/339,009$, or 98.1%, where 339,009 is the total microcuries of ^{106}Ru activity in all five traps. Similarly, the ^{106}Ru in trap 2 is $6,479 \times 100/6,509$ (total in four traps), or 99.5%. The DF across a single trap is calculated from the percent ^{106}Ru in each trap by dividing the percent of untrapped ^{106}Ru into 100. Thus, the DF for trap 1 in run 1 is $100/1.9$, or 52.6. In this case the untrapped ^{106}Ru is $100 - 98.1$ (the percentage of trapped ^{106}Ru), or 1.9%. The DF for

Table 9. Ruthenium-106 Distribution in Traps 1 to 5

Trap No.	Volume (ml)	Activity, μCi		^{106}Ru per trap (%)	Decontamination factor	
		Per ml	Per trap		Per trap	Overall
Run 1 - 39.7% RuO_4 volatilized from 4 N HNO_3 calcined at 350°C						
1 (oxalic)	190	1750	332,500	98.1	52.6	52.6
2 (oxalic)	190	34.1	6,479	99.5	200	10,500
3 (formic)	185	0.111	26.64	89.4	9.4	98,800
4 (formic)	200	0.00828	1.656	52.5	2.1	208,000
5 (caustic)	450	0.00333	1.50			
Run 2 - 2.42% RuO_4 volatilized from 4 N HNO_3 calcined at 600°C						
1 (oxalic)	180	102	18,360	90	10	10
2 (oxalic)	190	10.7	2,033	99.4	166.7	1,667
3 (formic)	112	0.0521	5.835	44.7	1.81	3,017
4 (formic)	90	0.065	5.85	81.1	5.29	15,960
5 (caustic)	390	0.0035	1.365			
Run 3 - 1.06% RuO_4 volatilized from waste pretreated with formic acid and calcined at 350°C						
1 (oxalic)	195	45.7	8911.5	98.5	66.7	66.7
2 (oxalic)	190	0.671	127.5	94	16.7	1,114
3 (formic)	190	0.0391	7.429	90.8	10.9	12,140
4 (formic)	185	0.00174	0.322	42.9	1.75	21,250
5 (caustic)	390	0.0011	0.429			
Run 4 - 0.41% RuO_4 volatilized from waste pretreated with formic acid and calcined at 350°C						
1 (oxalic)	200	16.7	3,340	94.7	18.9	18.9
2 (oxalic)	190	0.936	177.84	94.4	17.9	338
3 (formic)	190	0.0140	2.66	25.3	1.34	453
4 (formic)	190	0.0360	6.84	87.2	7.8	3,536
5 (caustic)	375	0.00268	1.005			
Run 5 - 15.7% RuO_4 volatilized from 2 N HNO_3 waste calcined at 350°C						
1 (oxalic)	180	646	116,280	86.3	7.3	7.3
2 (oxalic)	185	96.5	17,853	96.5	28.6	208.8
3 (formic)	200	3.13	626	97.3	37	7,725
4 (formic)	200	0.0645	12.9	75	4	30,900
5 (caustic)	390	0.011	4.3			
Run 6 - 1.55% RuO_4 volatilized from waste pretreated with formic acid and calcined at 600°C						
1 (oxalic)	155	48.1	7,456	52.2	2.1	2.1
2 (oxalic)	210	31	6,510	95.3	21.2	44.5
3 (formic)	190	1.65	313.5	98.6	71.4	3,179
4 (formic)	185	0.0186	3.44	79.4	4.85	15,400
5 (caustic)	190	0.0047	0.893			

trap 2 is 100/0.5 or 200. The overall DF is the product of the DFs for the individual traps. Thus, the overall DF through trap 2 is 52.6×200 or 10,500 for run 1.

It should be noted that an overall DF of 10^3 to 10^5 is attained by wet scrubbing with a weak reducing acid or with water across the first three traps. In contrast, the average DF across trap 4 for the six runs is only 4.3 compared to 41.2 for each of the first three traps. The average decontamination values are 22 for trap 1, 75.2 for trap 2, and 26.3 for trap 3. Even if the results of high RuO_4 volatility runs (39.7 and 15.7% in runs 1 and 5, respectively) are considered separately from the results of relatively low volatilities (2.42, 1.06, 0.41, and 1.55% in runs 2, 3, 4, and 6, respectively), similar values are obtained for the DFs across the different traps. Thus the DFs across trap 4 are only 3.1 and 5 for the high and low volatility groups respectively. Trap 1 gives an average DF of 30 for the high RuO_4 volatility group compared to 24.4 for the low volatility group. The average DFs are 110.6 and 55.6 for the high and low RuO_4 volatility groups for trap 2 and 23.2 and 12.8 for trap 3. The average DFs across traps 1, 2, and 3 increase with increasing RuO_4 concentration in the off-gas stream, while those across trap 4 do not change. These DFs are given in Table 10. This behavior indicates the presence of two forms of ruthenium — RuO_4 and an RuO_2 aerosol. The RuO_4 is scrubbed out in the first three traps, while RuO_2 is trapped partially in trap 4.

Table 10. Average Decontamination Factors in Water Scrubbers

Trap No.	Average decontamination factor		
	Six high-level runs	High RuO_4 volatility runs ^a	Low RuO_4 volatility runs ^b
1	22	30	24.4
2	75.2	110.6	55.6
3	26.3	23.2	12.8
4	4.3	3.1	5.0

^aVolatilities = 39.7 and 15.7%.

^bVolatilities = 2.42, 1.06, 0.41, and 1.55%.

An approximate value for the percent ^{106}Ru present as RuO_2 aerosol can be estimated by dividing the amount of ^{106}Ru that is volatilized by the overall DF across trap 3. This estimate assumes that the RuO_4 form is completely scrubbed out in the first three traps. The results of this calculation are presented in Table 11. The amount of ^{106}Ru present as an RuO_2 aerosol is rather small since these experiments were run in all-glass equipment. After the RuO_4 interacts with stainless steel walls and equipment, an increase in the fraction of RuO_2 aerosol would be expected.

Table 11. Percentage of ^{106}Ru Present as RuO_2 Aerosol after Volatilizing RuO_4

Run No.	^{106}Ru volatilized from batch (%)	Decontamination factor through trap 3, DF3	^{106}Ru present as RuO_2 aerosol, % ^{106}Ru volatilized/DF3
1	39.7	98,800	4.02×10^{-4}
2	2.42	3,017	8.02×10^{-4}
3	1.06	12,140	0.87×10^{-4}
4	0.41	453	9.05×10^{-4}
5	15.7	7,725	20.3×10^{-4}
6	1.55	3,179	4.88×10^{-4}

These experiments demonstrate the high efficiency of gas-liquid scrubbing for the removal of RuO_4 from an off-gas stream. High radiation fields promote the formation of dilute hydrogen peroxide ($\sim 0.05\text{ M}$) in aqueous systems, which reacts with RuO_4 in solution to give lower valence states of ruthenium in solution.

Technetium Volatility on Calcining HNO_3 Waste

Since ^{99}Tc is an essential constituent of the fission product HNO_3 waste, radiochemical analyses on ^{99}Tc were carried out in order to determine the ^{99}Tc volatility under the varied calcination conditions outlined above. The ^{99}Tc volatility was found to vary from 0.2 to 1.4% over the temperature range 250 to 600°C. On simulated waste containing the full amount of ^{99}Tc tagged with the gamma emitter $^{95\text{m}}\text{Tc}$, the ^{99}Tc

volatility values varied from 0.06 to 0.48%, which are low. Detailed data are presented in Appendix A. The Tc_2O_7 or $HTcO_4$ can be scrubbed from the off-gas stream along with RuO_4 and, after concentration by evaporation, these volatile technetium compounds can be recycled.

Thus it can be concluded that the high thermal stability limits of alkaline earth pertechnetates and technetates shown in Table 1 (decomposition temperatures taken from ref. 36) are accurate indicators of the unexpectedly low ^{99}Tc volatilities that are observed on calcining HNO_3 wastes at $350^\circ C$. Mendel²² also noted the low volatility of ^{99}Tc during the glass-making stage.

Iodine Volatilization During Calcination

The volatility of ^{131}I was determined as a function of temperature on calcining untreated HNO_3 waste and the same waste pretreated with formic acid at a ratio of 2 moles of formic acid per mole of nitrate. The distribution of iodine across five traps connected in series was determined. The results are presented in Table 12 and Fig. 7.

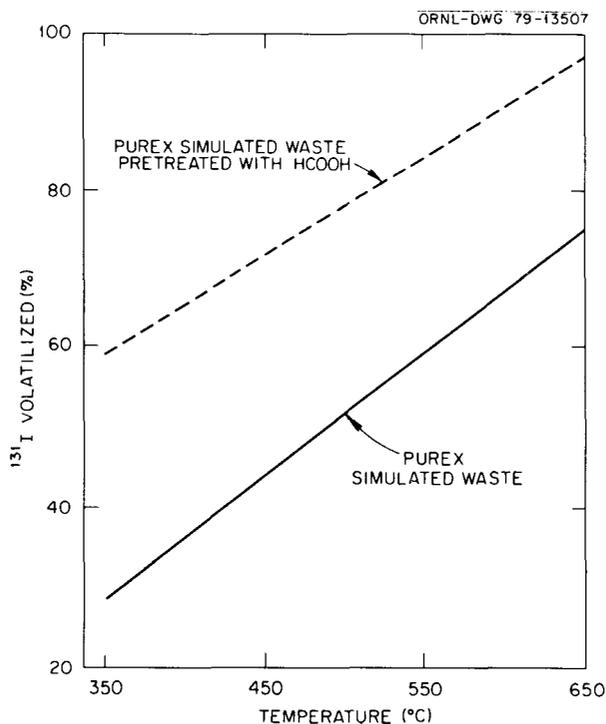


Fig. 7. Iodine-131 volatilization (%) vs temperature ($^\circ C$).

Table 12. 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	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
Volatiles distribution							
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	0.02	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.

The plots in Fig. 7 show that ¹³¹I volatility increases with increasing temperature and that the volatility is so high that ¹³¹I cannot be retained in the solid residue. Hence, it is concluded that wastes containing iodine should be segregated and treated separately.

The iodine distribution study shows that iodine concentrates preferentially in the first two traps. An iodine concentrate could be withdrawn from the first two traps if further iodine processing is considered desirable.

CONCLUSIONS AND RECOMMENDATIONS

Ruthenium-106

High RuO_4 volatilities ($\sim 35\%$) are observed on calcining a fission product, HNO_3 solution 4.0 *N* or higher at 350°C . The RuO_4 volatility decreases to $\sim 1.0\%$ on decreasing the initial nitrate concentration to 1.0 *N* or lower. Decomposition of a ruthenium formate complex leads to very low RuO_4 volatilities (0.001% or lower). The decomposition of HNO_3 by formic acid leads to the formation of noncondensable gases (nitrous oxide and carbon dioxide), which may be eliminated through filters after scrubbing in efficiently designed gas-liquid scrubbers to remove gaseous RuO_4 . The liquid scrubbing medium is easily recycled after evaporating water, and thus more than 99% of the initial ^{106}Ru in the waste can be retained in the solid calcine. High off-gas decontamination factors for ^{106}Ru can be attained at the same time.

Because of the reaction of volatile RuO_4 with stainless steel components in the off-gas system and the subsequent formation of a RuO_2 aerosol, it is necessary to investigate the kinetics of this reaction and to remove or minimize the accumulation of radioactive ^{106}Ru in the form of insoluble RuO_2 on the various metal components of the off-gas system.

Technetium-99

Less than 1% of the ^{99}Tc volatilizes as Tc_2O_7 or HTcO_4 on calcining a fission product, HNO_3 solution over a range of temperatures. This small amount of ^{99}Tc is readily removed from the off-gas stream by wet scrubbing and can be recycled along with the ^{106}Ru activity.

Even though this study points to the formation of a high-melting, nonvolatile, technetium oxide compound, efforts should be directed to identifying the actual compound formed under calcination conditions. The behavior of this technetium compound in silicate systems, especially its leaching behavior, should be investigated.

Iodine-129

A high fraction of iodide compounds are decomposed under calcination conditions. The evolved iodine or hydrogen iodide are easily trapped in the wet scrubbers from which an iodine concentrate can be withdrawn, if necessary, for further processing.

Iodine-containing wastes should be kept segregated and incorporated as an insoluble iodide complex or iodate compound into cement at a low temperature, at which iodine is not evolved. In addition, methods should be developed to withdraw an iodine concentrate from the wet scrubbers in order to prevent the buildup and breakthrough of iodine activity in the off-gas stream.

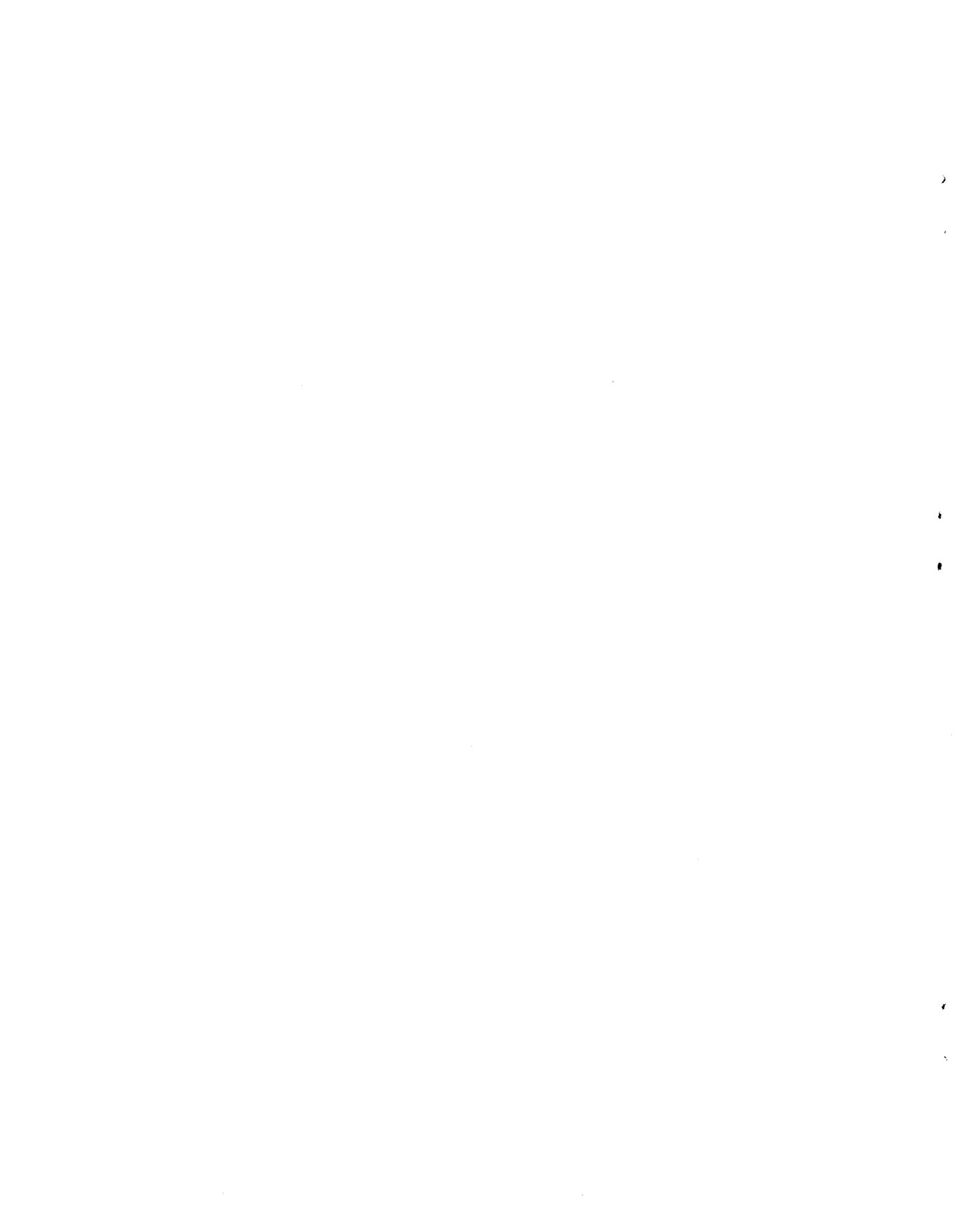


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A P P E N D I X



Table A-1. RuO₄ and Tc₂O₇ Volatilities Under Various Conditions — Authentic High-Level Waste Runs

Run No.	Calcination temperature (°C)	RuO ₄ volatilized (%)	Tc ₂ O ₇ volatilized (%)	Nitrate molarity of starting solution	Remarks
1	250	32.3	1.1	6.2	4.0 <i>N</i> HNO ₃ and 2.2 <i>N</i> metal nitrates in starting solution
2	350	39.7	<4.4	6.2	
2a	350	29.8	4.9	6.2	
3	450	21.6	0.6	6.2	
4	600	2.4	<0.02	6.2	
5	350	15.7	1.04	4.2	2.0 <i>N</i> HNO ₃ + 2.2 <i>N</i> metal nitrates
6	350	0.41	1.4	2.2	2.2 <i>N</i> metal nitrates
7	650	1.6	<0.14	6.2	2 moles formic acid/mole nitrate
8	350	1.06	<0.01	6.2	2 moles formic acid/mole nitrate
9	350	0.024		6.2	2.3 moles formic acid/mole nitrate
10	350	0.008		6.2	2.3 moles formic acid/mole nitrate plus 13 days reaction time

Table A-2. RuO₄ and Tc₂O₇ Volatilities from Purex Waste Under Various Conditions
Tracer ¹⁰³Ru Runs

Run No.	Calcination Temperature (°C)	RuO ₄ Volatilized (%)	Nitrate Molarity of Starting Solution	Remarks
1	200	9.66	6.2	4.0 N HNO ₃ + 2.2 N metal nitrate
2	300	14.8	6.2	4.0 N HNO ₃ + 2.2 N metal nitrate
3	400	13.4	6.2	4.0 N HNO ₃ + 2.2 N metal nitrate
4	350	14.0	6.2	4.0 N HNO ₃ + 2.2 N metal nitrate
5	500	11.6	6.2	4.0 N HNO ₃ + 2.2 N metal nitrate
6	140-600	3.6	6.2	1.6% RuO ₄ volatilized at 140°C and 2.0% RuO ₄ volatilized on heating to 600°C
7	350	20.1	4.2	2.0 N nitric acid + 2.2 N metal nitrate
8	350	1.9	2.2	2.2 N metal nitrate
9	350	0.24		2 moles formic acid/mole nitrate
10	350	23.7	6.2	Argon sweep gas
11	350	0.66	2.6	0.4 N HNO ₃ + 2.2 N metal nitrate
12	350	17.0	6.2	4.0 N HNO ₃ + 2.2 N metal nitrate; loose stainless steel liner 6 × 5 in. was placed inside quartz calciner; on run 12 there was a hole in liner matching off-gas sidearm of calciner vessel
13	350	16.5	6.2	
14	510	10.5	6.2	
15	600	2.4	6.2	4.0 N HNO ₃ + 2.2 N metal nitrate
16	350	15.9	6.2	4.0 N HNO ₃ + 2.2 N metal nitrate; argon sweep gas.
17	350	22.2	6.2	Feed was 0.09 M in hydrogen peroxide
18	350	18.7	6.2	Feed was 0.18 M in hydrogen peroxide
19	350	20.6	6.2	Feed was 0.18 M in hydrogen peroxide
20	350	19.0	6.2	Feed was 0.18 M in hydrogen peroxide (4.0 N HNO ₃ + 2.2 N metal nitrate)
21	675	0.34	6.2	All runs pretreated with 2 moles formic acid/mole nitrate; run 23 was 0.06 M in hydrogen peroxide; argon sweep gas used in run 24; argon sweep gas and 0.06 M in H ₂ O ₂ used in run 25; air sweep used in run 26; air sweep and 0.06 M in H ₂ O ₂ used in run 27
22	640	0.16	6.2	
23	650	0.61	6.2	
24	650	0.24	6.2	
25	650	0.44	6.2	
26	830	0.25	6.2	
27	910	0.28	6.2	

Table A-2. (Continued)

Run No.	Calcination Temperature (°C)	RuO ₄ Volatilized (%)	Nitrate Molarity of Starting Solution	Remarks
28	250	0.011	6.2	2 moles formic acid/mole nitrate used in each run;
29	450	0.011	6.2	reaction time was 47-48 days in each run
30	350	14.7	10.2	8 N HNO ₃ and 2.2 N metal nitrate
31	350	0.13	6.2	2 moles formic acid/mole nitrate used in each run;
32	350	0.016	6.2	reaction time was 1 h in run 31 and 3 days in run 32
33	350	0.0017	6.2	Mole ratio of formic acid to nitrate was 2.3 for each of
34	350	0.0038	6.2	four runs; reaction times were 1 h for run 33, 1 day
35	350	0.0038	6.2	for run 34, 6 days for run 35, and 7 days for run 36
36	350	0.0032	6.2	
37	350	0.022	6.2	Mole ratios of formic acid to nitrate were 2.0 for run 37
38	350	0.00082	6.2	and 2.3 for run 38

Table A-3. RuO₄ and Tc₂O₇ Volatilities Under Various Conditions
Tracer ⁹⁵Tc Runs

Run No.	Calcination temperature (°C)	Tc ₂ O ₇ volatilized (%)	Nitrate molarity of starting solution	Remarks
1	350	0.06	6.2	4.0 N HNO ₃ + 2.2 N metal nitrate
2	350	0.20	10.2	8.0 N HNO ₃ + 2.2 N metal nitrate
3	350	0.48	10.2	8.0 N HNO ₃ + 2.2 N metal nitrate

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