27
10-12-82
jpk

(1)

Dr. 896

I-5834

PNL-4299

UC-70

DO NOT MICROFILM
COVER

MASTER

Deposition of Volatile Fission Products During Commercial High-Level Waste Vitrification

M. S. Hanson

J. G. Carter

September 1982

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

PNL-4299

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
201-225	A010
226-250	A011
251-275	A012
276-300	A013

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

PNL--4299

DE83 000661

PNL-4299
UC-70

MASTER

DEPOSITION OF VOLATILE FISSION
PRODUCTS DURING COMMERCIAL
HIGH-LEVEL WASTE VITRIFICATION

M.S. Hanson
J.G. Carter

September 1982

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Pacific Northwest Laboratory
Richland, Washington 99352

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

.

.

SUMMARY

High-level waste from spent commercial PWR fuel was vitrified during the Nuclear Waste Vitrification Project (NWVP), conducted at Pacific Northwest Laboratory in 1978 and 1979. The solidification equipment employed sintered metal filters and a conventional wet off-gas cleanup system to decontaminate the gases generated during waste processing. This report is a summary of a study completed under contract with the U.S. Department of Energy (DOE) to determine the fate of volatile fission products in the filters and off-gas system. The study objectives were to determine 1) the extent of volatile fission product deposition within the sintered metal filters, 2) the distribution of fission products in the off-gas system, and 3) the factors that control the distribution. Such information is needed for the design and operation of future waste immobilization systems.

The scope of the study included identification, preparation, and micro-probe analyses of suitable filter samples and radiochemical analyses of off-gas system samples. The report describes the methods of sample selection and gathering, the analytical methods and results, and the interpretations of the results. Relationships to vitrification system operations are defined and operating conditions to minimize problems recommended.

CONTENTS

SUMMARY	iii
INTRODUCTION	1
CONCLUSIONS AND RECOMMENDATIONS	3
PROCESS DESCRIPTION	5
SPRAY CALCINER	5
SINTERED METAL FILTERS	5
IN-CAN MELTER	11
EFFLUENT CONTROL SYSTEM	11
Quench Scrubber	13
Evaporator	13
Acid Fractionator	14
Scrubber	14
NWVP HISTORY	15
HLW CHARACTERISTICS	15
SC/ICM SOLIDIFICATION PROCESS DATA	17
FILTER GAMMA ENERGY ANALYSIS	21
GROSS GAMMA DISTRIBUTIONS	24
MICROPROBE ANALYSIS OF OFF-GAS FILTERS	29
ANALYTICAL TECHNIQUE	29
SAMPLE PREPARATION	33
ELECTRON MICROPROBE ANALYSIS	33
INTERPRETATION OF RESULTS AND RELATIONSHIP TO OPERATION	59
PROCESS OFF-GAS SYSTEM ANALYSIS	63
SAMPLE DESCRIPTION	63

FISSION PRODUCT DISTRIBUTIONS	64
SOLIDIFICATION SYSTEM DECONTAMINATION FACTORS	65
PROCESS OFF-GAS SYSTEM ACTIVITY	67
PROCESS DECONTAMINATION FACTORS	79
PROCESS OFF-GAS SYSTEM EVALUATION	70
REFERENCES	73
ACKNOWLEDGMENTS	75

FIGURES

1	Spray Calciner/In-Can Melter Operating Temperatures	6
2	Spray Calciner Filter Assembly	7
3	Filter System Configuration	9
4	Assembled Filter System	10
5	In-Can Melter Furnace	11
6	Effluent Control System	12
7a	Spray Calciner Filter Housing with Filters in Place	22
7b	Spray Calciner Sintered Metal Filter Assembly Partially Removed	22
8	Gamma Energy Analysis System Setup for Through-the-Wall Analysis	23
9	Relative Axial Gamma Activities	25
10	Sintered Metal Filter Sample Location and Identification	27
11	Sample Transfer Mechanics	30
12	Shielded Electron Microprobe Assembly	31
13	Electron Microprobe Assembly and Data Analysis System	32
14	Microprobe Scan Through Filter Cross Section	34
15	Filter Sample Mount and Microprobe Path Angles	35
16	Filter Cross Section Showing Calcine Penetration	36
17	X-Ray Spectra, Front Filter Surface	38
18	Spectra Sources, Filter Sample C4-5	39
19	X-Ray Spectra, Rear Filter Surface	41
20	High Ru Activity Site	42
21	Microprobe Scans, Filter Sample C4-1	43
22	Activity Site, Filter Sample C4-1-A	44
23	Activity Site, Filter Sample C4-1-B	45

24	Photomontage of Filter Sample C4-1	47
25	Microprobe Scan, Filter Sample C4-7	48
26	Peak Ru Concentration Area as Indicated on the Filter Cross- Section Scan	49
27	X-Ray Spectra, Filter Sample C4-7 Cross-Section (internal)	50
28	Microprobe Scan, Filter Sample C4-9	51
29	Peak Ru Concentration Area as Indicated on the Filter Cross- Section Scans, A Axis Transverse	52
30	Peak Ru Concentration Area as Indicated on the Filter Cross- Section Scan, B Axis Transverse	53
31	Photomontage of Filter Sample Cross Section C4-9	54
32	X-Ray Spectra, Filter Sample C1-9	55
33	Microprobe Scan, Filter Sample C1-9	56
34	Peak Ru Concentration Area As Indicated on the Filter Cross- Section Scan	57
35	Photomontage of Filter Sample C1-9	58
36	Filter Permeability During Pilot-Scale Spray Calciner Operation	60
37	Specific Activity Levels for the Process Off-Gas System	68

TABLES

1	Spent-Fuel Average Data	15
2	Waste Constituents for NWVP	16
3	Gamma-Energy Analysis	17
4	Nominal Operating Parameters for the Effluent System	18
5	Material Balance	19
6	Fission Product Loadings: NWVP Sintered Metal Filter Sample	26
7	Relative Element Sensitivities to Microprobe Electron Beam	37
8	Typical Elemental Concentrations in Process Tanks	64
9	Process Off-Gas Isotope Concentration	65
10	Particulate Size Distribution Analysis	66
11	Solidification System Decontamination Factors	66
12	Average Decontamination Factors for the Process Off-Gas System	69
13	Gross Activity Released to Stack	71
14	Feed-to-Stack Effluent Decontamination Factors	72

INTRODUCTION

The Nuclear Waste Vitrification Project, conducted at Pacific Northwest Laboratory (PNL) during 1978 and 1979, converted the high-level waste from 1.5 tonnes of spent PWR fuel to a vitreous product in a spray calciner/in-can melter (SC/ICM) (Wheelwright 1979; Bjorklund 1979; Hanson 1980).

Primary calciner-melter off-gas filtration was accomplished with sintered metal filters. Made of a uniformly porous material, the filters have a high specific internal surface area which potentially allows vapor-phase deposition of volatile metals within the cross section of the filter media. In this study PNL examined the sintered stainless steel filters used in the NWVP to determine the extent of plate-out. The sintered metal filter assembly was removed by remote means from the SC/ICM and examined by gamma-energy and wave-length dispersive spectrometry.

An effluent control and cleanup system utilizing condensation, scrubbing, and filtration steps cleaned the process off gas after filtration by the sintered metal filters and prior to release to the atmosphere. Samples from the off-gas system, collected and archived during NWVP, have been radiochemically analyzed.

This report discusses the function of the sintered filters in the NWVP operation, their relationship to the radioactive vitrification process, and the results of the analyses. The effects of the distribution of radiochemicals in the off-gas system in terms of generic off-gas cleanup system design are examined.

This work was conducted for the U.S. Department of Energy as part of the airborne waste management R&D activities directed by the ENICO Airborne Waste Management Program Office at Idaho National Laboratory (INEL).

X

CONCLUSIONS AND RECOMMENDATIONS

Ruthenium was the only volatile fission product found deposited at greater than trace levels in the sintered metal filters. Although significant from a radiochemical standpoint, the mass of Ru found within the filter media was not great enough to inhibit operation. In the 87 h of NWVP operation, 3.18 mg of ^{106}Ru was trapped in the filters. At this rate, the filters would not load sufficiently to affect an operating plant in a 30-yr lifetime. It cannot, however, be predicted whether this rate of deposition would continue or whether it would level out as the process reached equilibrium.

Although the deposition rate is acceptable, care should be taken to minimize the rate. This can be accomplished by maintaining as deep a filter cake on the filters as possible, operating the filters in the temperature range of 250 to 350°C, and avoiding decreasing temperature gradients in the filters. System design must provide adequate pressure-drop allowances for the filters to allow a deep cake.

Decontamination factors in the spray calciner/in-can melter system used for waste vitrification were high, with Ru losses averaging 2.5×10^{-3} . Off-gas cleanup in the off-gas processing equipment was adequate. However, determination of precise decontamination factors for specific equipment pieces during waste vitrification was not possible because portions of the system had been used for waste concentration. Ruthenium found at the end of the off-gas train was primarily in particulate form as evidenced by the high decontamination factors obtained across the high-efficiency particulate air (HEPA) filters. Overall system decontamination factors from feed to stack were 7×10^{10} for alpha activity and 2×10^8 for beta-gamma activity.

Losses to the off-gas system can also be minimized by maintenance of a maximum-allowable-depth filter cake. Enrichment factors in the filter cake of greater than 7.5 for Ru, 1.9 for Cs and 6.1 for Tc demonstrate that the cake acts as a very good volatile fission product adsorber and can keep significant quantities of fission products out of the off-gas system. Sufficient gas-liquid contact time, as was available in the NWVP system, is necessary to

allow the gas-phase Ru to come to equilibrium with the liquid phase. Control following equilibrium should focus on particulate matter and care should be taken to avoid reentrainment.

PROCESS DESCRIPTION

Background information on the processes used during NWVP is discussed in this section. The SC/ICM vitrification process consists of three interconnected systems: 1) the spray calciner (SC), 2) the in-can melter (ICM), and 3) the effluent control system. The majority of the equipment for each of these systems is located in a shielded radiochemical processing cell. Operations are remotely controlled using master-slave manipulators and cranes. Each system and its individual components and functions are described below.

SPRAY CALCINER

The SC, shown in Figure 1, is a vertically-mounted right cylinder 35.6 cm (14 in.) in dia by 197.5 cm (77.9 in.) high with 0.95 cm (3/8 in.) thick walls. During operation, the spray chamber walls are heated to about 750°C by an external, three-zone, resistance-heated furnace that surrounds the cylinder. High-level waste is pneumatically atomized into the top of the spray chamber with a commercially available, internal-mix spray nozzle.

As the atomized waste falls through the calciner spray chamber, the waste is concentrated, dried and oxidized to form a fine calcine product of typically less than 0.5% moisture and 1% nitrate. A side-mounted, air-operated vibrator is periodically operated to prevent a buildup of solids on the chamber walls. Gas-forming material (frit) is metered into the SC cone at a rate proportional to the calcine production rate.

About 15 to 50% of the calcine is nominally entrained by the water vapor and the atomizing air passing through the spray chamber. Sixteen porous, sintered stainless steel filters separate the calcine from the gases that pass to the process off-gas system.

SINTERED METAL FILTERS

Due to the small (typically 1 to 10 μm) particle size of the spray-dried calcine (Hanson 1980), 15 to 50% of the solids are entrained in the vapor and

* AS RECORDED FROM PREVIOUS RUNS

FIGURE 1. Spray Calciner/In-Can Melter Operating Temperatures

the air flowing up through the calciner. Early experiments with various types of dust removal equipment led to the adoption of sintered stainless steel filters. The design of the filters used in NWVP is shown in Figure 2. The filters used were 5.08 cm (2 in.) x 60.96 cm (24 in.) right circular cylinders with a nominal wall thickness of 0.159 cm (1/16 in.) and a nominal mean pore size of 65 μm . The material of construction was 316 extra-low-carbon stainless

FIGURE 2. Spray Calclner Filter Assembly

steel. The filters exhaust into a common plenum area as shown in Figure 3. The assembled filter system prior to installation in the calciner is shown in Figure 4.

An excessive filter differential pressure caused by the buildup of calcine on the filter surface is prevented by using a blowback system to dislodge the filter cake. A venturi increases the entrainment of filtered gas by the blowback gas jet, thus decreasing the amount of external air required to clean the filters. Little information has been reported on venturi design; however, some work was done on the effects of venturi shape on blowback performance (Kaser and Moore 1966; Bjorklund 1976). It is desirable to minimize calciner pressure surges caused by the pulses of blowback air. The variables that affect the magnitude of these surges are blowback pulse duration, blowback pressure, off-gas line flow resistance, and the fraction of filters pulsed simultaneously. Experience at PNL has shown that a short 1/4 s pulse of heated air is effective. With this short pulse, blowback pressures of up to 530 cm Hg could be used to clean one-fifth of the filters without pressurizing the calciner. Clean filters do, however, have a higher permeability (Hanson 1980) and allow calcine to penetrate into the off-gas system.

When used continuously, the lifetime of sintered stainless steel filters may be shortened by gradual blockage of the filter pores. Since some of the calcine is smaller than the pore size of the filter, some particles penetrate the filter media and become lodged there (Pall 1953). Calcine penetration is greatest at the filter surface, but is rapidly reduced when large particles bridge over the pores; this decreases the effective pore opening and acts as a filter precoat. During filter blowback the precoat is partially removed and some particles are again free to enter the filter media. Unfortunately, some of the particles inside the filter media are not removed during blowback, and a slow accumulation occurs. The rate of accumulation is dependent upon operating conditions and is eventually observed as an increase in minimum baseline differential pressure. Bonner (1976) found that a filter cake of stable permeability 1/2 to 1-1/2 mm thick builds up after about 150 to 200 h of operation.

FIGURE 3. Filter System Configuration

FIGURE 4. Assembled Filter System

IN-CAN MELTER

In the ICM process, the final storage canister is used as the melting crucible to vitrify the mixture of calcine and glass-forming frit (Blair 1976). The ICM furnace, shown in Figures 1 and 5, is a six-zone, resistance-heated furnace. Each of the six zones is 35.6 cm (14 in.) high and supplies 15 kW of power. The design operating temperature for the furnace is 1050°C.

EFFLUENT CONTROL SYSTEM

Successful operation of the effluent control system was a major goal of the NWVP demonstration. The system flowsheet can be seen in Figure 6.

FIGURE 5. In-Can Melter Furnace

FIGURE 6. Effluent Control System

The effluent system has two major purposes: 1) decontamination of process off gases and 2) concentration of aqueous HLW feed for the calciner. The system is generally the same as that used in the Waste Solidification Engineering Prototypes (WSEP) program (McElroy et al. 1972), except that the WSEP solidifier condenser was replaced with a quench-scrubber column to enhance gas/liquid contact time.

Quench Scrubber

The quench-scrubber (TK-111) is a 25.4 cm (10 in.) ID, 304L stainless steel column packed with 2.54 cm (1 in.), 304L stainless steel pall rings. Two liquid-distribution weirs, one near the top of the column and one at the column midsection, collect and distribute scrub solution and condensed liquids to the pall-ring packing. A tank at the bottom of the column contains scrub solution. An overflow line that drains to the evaporator maintains a constant liquid level in this tank. The scrub solution from the tank is fed to the recycling pump, cooled by a water-cooled heat exchanger, and then is fed to both the lower and upper weirs. A weak acid stream consisting of fractionator distillate is also fed to the upper weir to scrub the incoming off gas.

A steam jet assembly installed on the downstream side of the scrubber provides vacuum control in the SC. A condenser cools the steam and off gas as they are ejected from the steam jet.

Evaporator

The evaporator (TK-113) has two functions: 1) to concentrate HLW before it is spray-calcined and 2) to concentrate condensate during SC/ICM operation. The evaporator is a tube-thermosiphon type which operates continuously during the vitrification process.

Condensates are recycled to control the acidity of the evaporator overheads at less than about 0.5 M, which improves retention of Ru in the waste.

The evaporator tower has multiple stages of aerosol deentrainment: 1) chevron baffles, 2) two stages of dry impingement caps, and 3) a mist eliminator. At the maximum boil-up rate, the impingement velocities of

Stages 1, 2, and 3 are 11, 15.5 and 25.9 m/s, respectively, which allows theoretical removal of nearly 100% of the aerosols 25, 7 and 4 μm dia, respectively. The nominal evaporator tower pressure drop at maximum capacity is 30.5 cm H_2O .

Acid Fractionator

The all-titanium acid fractionator (TK-115) consists of a packed distillation column on the top of a standard reboil tank. Special features include a tube bundle in the reboiler, a de-entraining sieve plate with bypass provisions in the column, and an integral reflux condenser. The fractionator was designed to accommodate liquid feed with 0.8 M HNO_3 and an overhead fraction of 0.01 M HNO_3 .

The rectifying section of the fractionator column is packed with 2.54 cm dia titanium raschig rings. The exhaust section has a similarly packed section, which is surmounted by a deentraining sieve plate and an integral reflux condenser. The impingement velocity of the vapors through the 3/16 in. dia holes of the sieve plate is 45.7 m/s at maximum capacity. Minimum velocity to restrict weeping to reasonable amounts is 0.6 to 7.6 m/s. The sieve plate has an alternate external drain and chemical-addition piping. The reflux rate is controlled manually.

Scrubber

The process off-gas scrubber (TK-118) is a 1300 L tank surmounted by a 2.54 cm raschig-ring-packed scrubbing column. A recirculation pump recycles the scrub solution at rates up to 40 L/min. Gas flows up to 6000 L/min are acceptable. The scrubber was also used to simultaneously decontaminate off gas from the NWVP fuel dissolver, so sample analyses were not completed on samples from this vessel.

NWVP HISTORY

Discussed in this section are high-level waste characteristics and process system operating data.

HLW CHARACTERISTICS

The spent fuel from which the HLW was generated was exposed in the Point Beach reactor. General data on the spent fuel are given in Table 1. Note that two different wastes were used for the two radioactive runs. Waste from the low-burnup fuel was used for the first run, and waste from both fuels was used for the second run. The constituents of the HLW used in the two radioactive runs are given in Table 2. Nonradioactive chemicals were added to the HLW to simulate the presence of intermediate-level wastes, corrosion products, degraded solvent, etc. The additives were the same for the two runs.

Filter samples were taken following the second run. The filters were not washed between runs, but the blowback systems were activated extensively to remove as much of the filter cake as possible. The majority of the calcine on the filter samples is therefore assumed to be from the second run.

TABLE 1. Spent-Fuel Average Data

<u>Parameter</u>	<u>Low-Burnup Fuel</u>	<u>High-Burnup Fuel</u>
Reactor	Point Beach	Point Beach
Fuel Type	Pressurized Water Reactor	Pressurized Water Reactor
Configuration	14 x 14 (179 rods)	14 x 14 (179 rods)
Initial Enrichment	2.27 wt% ^{235}U	3.04 wt% ^{235}U
Final Enrichment	0.85 wt% ^{235}U	0.94 wt% ^{235}U
Discharge Date	October 1972	April 1974
Burnup	20,500 MWd/MTU	29,282 MWd/MTU
Average Power	29 MW	30 MW
Separation	Dec. 1978-Jan. 1979	Feb.-Mar. 1979

TABLE 2. Waste Constituents for NWVP(a)

Element Fission Products	Waste Constituents, g/MTU	
	Run No. 1	Run No. 2
Ge	0.22	0.003
As	0.05	0.0003
Se	31.7	0.40
Rb	203.0	1.19
Sr	503.0	5.74
Y	284.0	1.60
Zr	2280.0	24.99
Mo	2130.0	22.20
Tc	530.0	2.68
Ru	1350.0	13.36
Rh	288.0	1.40
Pd	838.0	7.88
Ag	41.7	0.19
Cd	45.3	0.40
In	1.0	0.009
Sn	31.5	0.27
Sb	7.7	0.03
Te	348.0	2.73
Cs	1530.0	5.76
Ba	975.0	7.10
La	782.0	2.81
Ce	1520.0	10.85
Pr	738.0	0.87
Nd	2520.0	8.74
Pm	22.1	0.08
Sm	571.0	1.90
Eu	95.3	0.31
Gd	54.3	0.17
Tb	1.2	0.002
Dy	0.8	0.092
SUBTOTAL	17.7×10^3	25.7×10^3
<u>Actinides</u>		
U(b)	4850.0	6.79
Np	252.0	1.06
Pu	38.4	0.16
Am	84.3	0.35
Cm	4.6	11.4
SUBTOTAL	5.23×10^3	6.15×10^3
TOTAL	22.95×10^3	28.35×10^3

(a) Based on 1 MTU.

(b) Addition of depleted U required to achieve this value.

The activity and content of various elements analyzed for in the prepared HLW feed are shown in Table 3.

TABLE 3. Gamma-Energy Analysis

Isotope	Activity, Ci/L	
	Run-1 HLW	Run-2 HLW
⁹⁵ Nb	1.24×10^{-3}	1.97×10^{-3}
¹⁰³ Ru	4.41×10^{-4}	0.20
¹⁰⁶ Ru	4.26	9.14
¹²⁵ Sb	0.30	0.26
¹³⁴ Cs	9.39	20.41
¹³⁷ Cs	59.33	76.13
¹⁴¹ Ce	2.13×10^{-4}	5.68×10^{-4}
¹⁴⁴ Ce	2.85	7.43
¹⁵⁴ Eu	1.94	2.83

SC/ICM SOLIDIFICATION PROCESS DATA

Nominal operating temperatures for the SC/ICM system are shown in Figure 1. The sintered filters operated at an average pressure drop of approximately 6.6 cm H₂O, although during filter blowback the pressure drop increased by 19.0 cm H₂O. Nominal operating temperatures for the process off-gas system liquid and gas phases are shown in Figure 6. Values for off-gas system operating parameters are given in Table 4. The overall material balance for the NWVP operation is given in Table 5. Further details on all system operating parameters are provided by Hanson (1980).

TABLE 4. Nominal Operating Parameters for the Effluent System

Parameter	Run No. 1	Run No. 2
Noncondensable Gas Flow Rate	0.53 m ³ /min	0.65 m ³ /min
Spray Calciner Pressure	-43.7 cm H ₂ O	-26.4 cm H ₂ O
Quench Scrubber		
Vessel Volume	9.3 L	9.3 L
Column Outlet Pressure	-50.8 cm H ₂ O	-36.6 cm H ₂ O
Condensate Tank Pressure	-2.54 cm H ₂ O	-13.2 cm H ₂ O
Evaporator		
Specific Gravity	1.06	1.08
Volume	565 L	522 L
Pressure	-27.9 cm H ₂ O	-19.3 cm H ₂ O
Liquid Temperature	103.5°C	102°C
Vapor Temperature	102°C	100.5°C
Evaporator Condenser Pressure	-30.5 cm H ₂ O	-39.6 cm H ₂ O
Evaporator Condenser to Fractionator Flow	57.7 L/h	62.5 L/h
Evaporator to Fractionator Conductivity	0.43 M H ⁺	NA
Fractionator		
Temperature	97.5°C	99°C
Pressure	-28.5 cm H ₂ O	-35.6 cm H ₂ O
Specific Gravity	1.25	1.23
Volume	1008 L	882 L
Fractionator Condenser to Evaporator Flow	0 L/h	28 L/h
Fractionator Coil Temperature	96°C	97.5°C
Fractionator Distillate Receiver		
Volume	100 to 885 L	184 to 925 L
Pressure	-12.2 cm H ₂ O	-7.1 cm H ₂ O
Preheater Pressure	-66 cm H ₂ O	-71 cm H ₂ O
Scrubber		
Volume	499 L	775 L
Pressure	-31.5 cm H ₂ O	-23.4 cm H ₂ O

TABLE 5. Material Balance

Parameter	Feed	
	Run No. 1	Run No. 2
Concentration	833 MTU	760 MTU
Acid Concentration	4.4 M H^+	6.6 M H^+
Solids Content	66 g oxide/L	86.15 g oxide/L
Feed Processed	806 L	429 L
Average Feed Rate	15.7 L/h	12.7 L/h
Heat Content	1.12 W/L	2.05 W/L
Activity	313 Ci/L	526 Ci/L

Parameter	Canister	
	Run No. 1	Run No. 2
Net Glass Weight	116 kg	145 kg
Net Calcine Added	22.3 kg	36.96 ^(a)
Net Frit Added	93.7 kg	83.7 ^(a)
Estimated Density	2.8 g/cm ³	2.7 g/cm ²
Fill Level	1.37 m	1.75 m
Glass Volume	41.3 L	52.9 L
Decay Heat	380 W	1012 W
Activity	1.05 x 10 ⁵ Ci	2.64 x 10 ⁵ Ci

(a) 8.16 kg calcine and 16.33 kg of frit were in the canister before Run No. 2 from cleaning out the SC following Run No. 1.

FILTER GAMMA ENERGY ANALYSIS

The first step completed in the evaluation of fission product deposition was gamma energy analysis (GEA) of the sintered metal filters. The objectives were to determine: 1) which filters to sample for electron microprobe analysis and 2) quantitative fission product loadings in the filters.

The filters were removed from the spray calciner still holding the portion of the filter cake formed during NWVP that could not be removed with the blow-back system (see Figure 7). Visual examination of the filter candles showed the calcine coating on the filters to be very uniform, with no obvious anomalies. The calcine layer on the filters was approximately 1 to 2 mm thick. Visual examination alone did not reveal enough significant differences to rank their sampling suitability. Samples of the filter cake were taken for analysis.

Gamma-energy analysis was completed using a Ge(Li) detector (shown in Figure 8) which could view through either a collimated 10 cm processing cell wall penetration or a collimated discrete sample analysis cell wall penetration. Since quantitative results were required from the discrete sample analysis, tests were conducted to assure constant source geometry. Efficiency corrections for source geometry changes were unnecessary.

FIGURE 7a. Spray Calciner Filter Housing with Filters in Place

FIGURE 7b. Spray Calciner Sintered Metal Filter Assembly Partially Removed

FIGURE 8. Gamma Energy Analysis System Setup for Through-the-Wall Analysis

GROSS GAMMA DISTRIBUTIONS

The filter assembly was suspended in front of the GEA penetration at the vertical midpoint of the filter candles and relative Ru and Cs activities determined. Ruthenium and Cs high/low activity rates found for the different filters are 1.96 and 1.93, respectively. The closeness of the ratios indicates that, at least at the filter candle midpoint, the variations between candles are probably due to calcine variations.

Flow regimes and temperature profiles during operation are unknown, but are probably responsible for activity variations. The filter chamber itself is not heated and the temperature is not controlled. Heat input to the filters is from the gases being filtered. Flow profiles would be straight down the length of the filters due to the buildup of calcine were it not for the blow-back system (Bjorklund 1976). During blowback, a shock wave travels down the filter, removing the cake. The shock wave bounces off the solid bottom of the filter, returning upward. The sum of the initial as well as the reflected waves may not remove the cake linearly from the length of the filters. Although cake removal was not studied, it is postulated that the resulting flow regimes are partially responsible for deposition location.

Analysis of the axial filter activity indicated a profile as shown in Figure 9. Activity varied from 0.75 to 1.37 times the mean. Again, flow regimes and temperature profiles are probably the causes of the variations. Removal of the filter cake at various locations allows the volatile materials to deposit in the filter media rather than in the cake.

Based on GEA, two filter candles (the most active and a typical candle) were chosen for detailed analysis. These were removed from the filter assembly and each was sectioned into 10 samples. Five samples from each filter candle were mounted in preparation for microprobe analysis.

The remaining five samples from each filter candle were transferred for gamma analysis to determine quantitative loadings. Fission product loadings found on the samples are given in Table 6, with the locations of the samples shown in Figure 10.

FIGURE 9. Relative Axial Gamma Activities

Using a mean value of $0.2 \mu\text{g}/\text{cm}^2$ for ^{106}Ru , the fission product of concern, and integrating the value across the total surface area ($15,567 \text{ cm}^2$) gives an estimated total filter loading of $3.18 \text{ mg } ^{106}\text{Ru}$. Based on the Ru fed to the calciner during the 87 h of operating time, 0.27% of the Ru was trapped in the filters. If Eu is assumed to be nonvolatile, then by comparing Eu and Ru in the filters to Eu and Ru in the feed, it can be determined that 97% of the Ru in the filters was emplaced via volatilization.

Analyses of calcine samples taken from the filter cake found on the sintered metal filters showed that the filter cake acted as a trap for volatile fission products. Enrichments of 7.6, 1.9 and 6.1 times that of bulk calcine were found for Ru, Cs and Tc, respectively.

TABLE 6. Fission Product Loadings: NWVP
Sintered Metal Filter Samples

<u>Filter Sample</u>	<u>Element Loading, $\mu\text{g}/\text{cm}^2$</u>		
	<u>^{106}Ru</u>	<u>^{154}Eu</u>	<u>^{137}Cs</u>
C-4-2	0.13	0.06	15.0
C-4-4	0.32	--	--
C-4-6	0.29	0.09	28.0
C-4-8	0.31	0.17	28.0
C-4-10	0.24	0.02	15.0
C-1-2	0.08	0.08	32.0
C-1-6	0.12	0.09	32.0
C-1-8	0.17	0.08	35.0
C-1-10	0.18	0.05	31.0

The relationship of these results to system operation is discussed in the following section.

PLAN VIEW

FIGURE 10. Sintered Metal Filter Sample Location and Identification

MICROPROBE ANALYSIS OF OFF-GAS FILTERS

Microprobe analysis of the sintered metal filters was completed to determine the types, amounts, and distribution of fission products deposited within the filters. The method chosen for investigation of deposition was shielded electron microprobe spectrometry.

The off-gas filters are formed from powdered 316L stainless steel and have a high specific internal surface area. Since Ru tends to deposit on stainless steel surfaces, the filters have a high potential for internally trapping Ru and other potentially volatile fission products. The operating temperatures (see Figure 1) of the filters varied, generally in the range from 330 to 360°C, which is at the high end of the 250 to 350°C range recommended for minimizing Ru deposition (Christian 1976). The carrier was typically composed of 18 wt% O₂ and 61 wt% N₂ with 0.09% NO and 1.4% NO₂. The conditions, although not optimal for deposition, are in the ranges sufficient for deposition.

ANALYTICAL TECHNIQUE

The electron microprobe used for the analyses generates a fine beam of electrons by means of an electron gun, focuses with electromagnetic lenses, and impinges the beam onto the sample surface. The beam diameter can be controlled down to approximately 1 μm and the energy up to 50 KeV. A crystal dispersive spectrometer quantitatively discriminates the resulting rays. To provide details of larger surfaces, the beam is moved over a raster on the sample surface.

The microprobe is tungsten-shielded, allowing the analysis of samples with activities of up to 100 R/h at a 30 cm distance. Transfer of the samples is accomplished by a cask which is fitted to the microprobe assembly (see Figure 11). Once the sample is in the microprobe, analysis can be completed using the adjacent spectrometers (see Figure 12). Figure 13 shows the entire assembly, including the data analysis system.

Microprobe analysis was completed in two modes: discrete and swath areas. Swath views were used to determine distributions through the filter

FIGURE 11. Sample Transfer Mechanics

FIGURE 12. Shielded Electron Microprobe Assembly

FIGURE 13. Electron Microprobe Assembly and Data Analysis System

cross section and locate discrete hot spots, which could then be individually investigated. Swaths of width 200 μm and smaller were made across the filter cross sections at angles 30° from perpendicular to the filter surface (see Figure 14). Iron was used as the reference element to indicate filter pores.

SAMPLE PREPARATION

The samples were remotely mounted in pairs in a radiochemical hot cell. The filter samples, typically 0.6×1.3 cm, were mounted in boat resin, ground and polished through a 0.5 μm diamond finish to present a flat surface (see Figure 15). Kerosene was used as the wetting agent during polishing, and particular care was taken to assure that no filter pores were smeared shut. The sample was finally coated with several hundred angstroms of carbon and stored in an inert atmosphere prior to microprobe analysis.

ELECTRON MICROPROBE ANALYSIS

Photomicrographs were taken of calcine-coated filter sections to determine depth of normal calcine penetration into the filters. It is known (Hanson 1980) that some calcine particles completely penetrate the filters during normal operation, but as shown in Figure 16 and found in the microprobe analyses, gross calcine buildup and filtration typically take place on the first 10 to 20% of the filter cross section.

Three different sample currents (0.1, 0.9 and 1.5 μamp) were used in the microprobe analysis, the choice indicated by elemental concentration at the point of interest. Different elements of interest respond at different levels; Table 7 gives the relative element sensitivities, with Ru used as the reference. It was chosen as the reference and as the isotope of interest because of its volatile behavior and because decontamination factors required to meet allowable off-gas release limits are generally harder to accomplish for Ru than for other potentially volatile fission products.

Ruthenium is not merely a volatile metal, but also forms many volatile species. At temperatures about 800°C or above, gaseous RuO_4 is formed. At higher temperatures, the RuO_3 vapor species is formed by the reaction of O_2 or

FIGURE 14. Microprobe Scan Through Filter Cross Section

NO_2 with RuO_2 . The formation reactions become more thermodynamically favorable as the temperature increases. A stable, gaseous complex, nitrosyl-nitrate form of Ru is formed at temperatures about 800°C or below in the presence of nitric acid. The volatility of the complex form of Ru increases as the solidifier temperature decreases. Deposition of the material, generally

FIGURE 15. Filter Sample Mount and Microprobe Path Angles

FIGURE 16. Filter Cross Section Showing Calcine Penetration

TABLE 7. Relative Element Sensitivities
to Microprobe Electron Beam

<u>Element</u>	<u>Relative Sensitivity (a)</u>
Ba	0.8
Ca	1.1
Cs	0.8
La	1.0
Ce	
Pr	
Nd	
Sm	
P	1.8
Ru	1.0
Si	1.7
U	0.6
Zr	0.6

(a) Ruthenium referenced.

as RuO_2 , is a complex phenomena, controlled by temperatures, flow rates, gaseous environment, surface geometry, and turbulence (Christian 1976). Although the effect of many of these factors in NWVP cannot be determined, the sintered stainless steel filters provide a potential location for deposition.

The initial step in the analyses was to look at large areas on the sample cross section (about $250 \times 250 \mu\text{m}$) and determine which fission products were present. Analyses were started at low current to prevent damage to the sample surface. Current was increased as necessary to determine results. Figure 17 shows a typical spectra generated from a large area of a filter. The spectra were taken at the front surface of the filter and show calcine, as can be seen in the microphotograph of the area shown in Figure 18. The spectra at $0.1 \mu\text{amp}$ showed only the presence of fission product Ru. Since this was a view of a calcine-coated surface, other fission products are present; the spectra generated at a specimen current of $0.8 \mu\text{amp}$ shows some of these and confirms the

FIGURE 17. X-Ray Spectra, Front Filter Surface (C4-5)

FIGURE 18. Spectra Sources, Filter Sample C4-5

analytical methodology. Higher currents which would have shown all of the fission products present were not used because they would have damaged the surface. Enrichment in Ru content is seen at the filter surface, confirming the fact that the filter cake works as a partial trap for volatile materials.

The probe was moved to the inner surface of the filter media cross section and another 250 x 250 μm area surveyed. No fission products were found here, which was typical of the inner surface samples analyzed.

Microprobe scans were made through the cross section of the filter media to determine the distribution of fission products within the interior of the media. The 200 μm wide initial beam width was narrowed to increase discrimination and to pinpoint specific activity locations. The distribution of Ru across the filter cross section was determined by simultaneously monitoring the Ru and Fe x-ray lines during a scan across the filter. Monitoring the Fe x-ray lines indicated the position of pores in the filter, allowing the determination of Ru activity sites. Figure 19 shows a cross section of Ru distribution made with a 2 μm dia beam crossing. In the probe crossing from filter rear or inside to filter front side, the recording pen for the Ru led the pen for the Fe, so in order to compare the site activities on Figure 19, the Ru curve must be shifted left about 2 mm. Figure 19 shows Ru activity in the front 25% of the filter, which is attributable to calcine penetration. It also shows a site within the interior, near the midpoint. Ruthenium found within the interior of the filter media was in localized areas and not generally distributed.

Following location of a site in the media interior, the probe was moved to the site and a large raster completed to determine the sites and manner in which the Ru was located. Figure 20 shows a 400 x 400 μm raster of the high activity site located from the scan shown in Figure 19. The specimen current is similar to a photograph, showing the physical characteristics of the location. The elemental concentrations and distributions for Fe, Ru, Mo and Co are shown with the intensity of the dot matrix indicating the concentrations. When scanning a large surface area such as that pictured in Figure 20, the microprobe beam does not penetrate the sample surface deeply, so what is seen is essentially a projected surface image. The pores in the filter media, exposed

FIGURE 19. X-Ray Spectra, Rear Filter Surface (C4-5)

when the material was cut and polished, show up as dark areas on the Fe distribution. The Mo and Co are uniformly distributed with the Fe and represent components of the stainless steel. The amount of Ru is deposited on the pore surfaces is significant. That the Ru was emplaced via a volatilization mechanism is confirmed by the following: 1) Ru is the only fission product found at the site in any significant quantity, and 2) the Ru present is formed as a surface coat. What initiated the deposition at this specific site is not known, but it is obvious from Figure 20 that a group of surrounding pores are coated, so the deposition may be self-catalyzing.

Microprobe scans made across filter sample C4-1, which came from the top of the filter candle, are shown in Figure 21. Most of the Ru is concentrated in the front 25% of the filter. The absence of internal Ru depositions is probably due to gas flow patterns and temperature profiles. The activities at the tops of the filter candles were uniformly low with the major activities near the bottom. The three scans in Figure 21 were taken at three locations

FIGURE 20. High Ru Activity Site (C4-5)

FIGURE 21. Microprobe Scans, Filter Sample C4-1

in the sample. A couple of minor activity sites which were located by the scans were investigated (Figures 22 and 23), again showing that the deposition here is also a surface phenomena.

A photomontage made from filter sample C4-1 (Figure 24) shows the distribution of Ru across the filter. The area covered by the montage is approximately $300 \times 1700 \mu\text{m}$, which is about two-thirds of the filter cross section. The specimen current images detail the physical characteristics, showing depth of pores. The Fe images indicate the depth of penetration of the beam. The Ru shows up on the front cross-section surfaces as expected and drops off rapidly to background levels. The amount of Ru in sample C4-1 is fairly small.

A microprobe scan of filter sample C4-7 at low specimen current ($0.1 \mu\text{amp}$) showed a relatively large Ru response (see Figure 25). Since the specimen current was low, the response showed a large activity site within the filter. The probe was focused on the source and the images in Figure 26 obtained. It could not be determined whether the material was surface plated, so x-ray spectra of the site were taken. Figure 27 shows the results and indicates that even at a high specimen current, the only fission product detected was Ru.

Microprobe scans across filter sample C4-9, as shown in Figure 28, detected very high levels of Ru near the front surface and significant spots within the interior of the media. Interior sites of high activity as determined by the scans of C4-9A and B were chosen and investigated. Figures 29 and 30 show that the depositions are fairly heavy on the pore surfaces.

A photomontage made of the cross section of sample C4-9 is pictured in Figure 31. The montage area covers approximately $300 \times 1600 \mu\text{m}$, two-thirds of the way through the filter media cross section. Depositions of Ru are heavy in the first third of the filter media cross section, but taper off rapidly to background in the second third.

Filter sample C1-9 is discussed here for comparison. It is the most active sample from the least active filter candle. X-ray spectra generated from a $250 \times 250 \mu\text{m}$ area on the front-filter cross-section surface are shown in Figure 32. Ruthenium was found at very low levels even at a high specimen current. Expected enrichments are not as obvious as with filter candle C-4.

FIGURE 22. Activity Site, Filter Sample C4-1-A

FIGURE 23. Activity Site, Filter Sample C4-1-B

FIGURE 24. Photomontage of Filter Sample C4-1

FIGURE 25. Microprobe Scan, Filter Sample C4-7

Scans taken across the filter cross section (Figure 33) do show some internal peaks; however, closer examination (Figure 34) reveals that the depositions are not as defined as in the other filters. The photomontage of the cross section (Figure 35) covers an area of about 300 x 1900 μ m and indicates very little interior deposition.

FIGURE 26. Peak Ru Concentration Area as Indicated on the Filter Cross-Section Scan (C4-7)

FIGURE 27. X-Ray Spectra, Filter Sample C4-7 Cross Section (internal)

FIGURE 28. Microprobe Scan, Filter Sample C4-9

FIGURE 29. Peak Ru Concentration Area As Indicated on the Filter Cross-Section Scans,
A Axis Transverse

FIGURE 30. Peak Ru Concentration Area As Indicated on the Filter Cross-Section Scans,
B axis transverse

FIGURE 31. Photomontage of Filter Sample Cross Section C4-9

FIGURE 32. X-Ray Spectra Filter Sample C1-9

FIGURE 33. Microprobe Scan, Filter Sample C1-9

FIGURE 34. Peak Ru Concentration Area As Indicated on the Filter Cross-Section Scan

FIGURE 35. Photomontage of Filter Sample C1-9

INTERPRETATIONS OF RESULTS AND RELATIONSHIP TO OPERATION

Significant quantities of Ru were found in the sintered metal filters. The Ru was generally found in the first third of the filter cross section, with local sites of high activity found within the interior of the media. Whether the filters will continue to load at this or a greater rate, or whether this is a steady-state value, cannot be determined from the short operation completed in NWVP. Although deposition rates are not great enough to upset operations, certain operational strategies are warranted to ensure that this potential problem does not encumber an operating facility. The strategies are discussed here.

The primary strategy is to contain the Ru in the calcine and glass. Since it is unlikely that this can be accomplished at a 100% confidence level, the secondary objective is to ensure that any Ru leaving the SC/ICM passes through the filters freely and is caught in the off-gas cleanup system, where it can be recycled.

In the 87 h of NWVP operation, 3.18 mg ^{106}Ru was trapped in the filters. Accounting for all Ru, this rate is not sufficient to plug the sintered metal filters over the life of a plant. Whether this rate of deposition will be maintained is questionable. Bonner (1976) found that filter permeability decreased and reached equilibrium after about 200 h (Figure 36). It is probable that particulate penetration into the filter contributed more to the decrease than deposition of volatile materials. At the rates of deposition found in NWVP, less than 10 mg would have been deposited after 200 h of operation. It would take about 10 kg of RuO_2 to fill the pores in a sintered metal filter used in NWVP. Even conservatively assuming that 10% of total fill would be enough to affect operation, an operating plant would not be affected in a 30 yr lifetime.

It would be prudent, however, to operate in a manner in which potential problems can be avoided. A primary operational control is the maintenance of a filter cake of maximum allowable depth. Maintenance of the filter cake complements off-gas cleanup, since penetration of the filters during and immediately following blowback is a major contributor to contamination in the

FIGURE 36. Filter Permeability During Pilot-Scale Spray Calciner Operation

off-gas system (Hanson 1980). It has been demonstrated that the filter cake is a very effective volatile fission product absorber. Ruthenium enrichments of 7.6 found in the filter cakes in this study indicate that much more Ru would have passed into the filters and off-gas cleanup system without the cake. Filter cake depth maximization was not possible in NWVP due to pressure drop limitations, so it is probable that greater control could have been obtained.

Temperature control is also a primary method of deposition control. Christian (1976) defined the reaction constants for the two primary reactions of concern:

$$\ln K_{\text{rxn}} = \frac{14880}{T} + 11.53 - 1.135 \ln T$$

$$\ln K_{\text{rxn}} (\text{atm}) = \frac{28080}{T} + 17.34 + 2\text{NO}$$

both for $25^\circ \leq T \leq 750^\circ\text{C}$.

Based on his work, he recommends that surfaces such as the sintered metal filters, where depositions are not wanted, should be operated at temperatures of 250 to 350°C. Decreasing temperature gradients should be avoided. External heating or insulation may have to be applied from the solidification process through the filters and off-gas line to the primary off-gas cleanup step. Dilution of the oxygen in the off-gas stream with inert gases may also help prevent deposition, as well as help control volatilization.

62

PROCESS OFF-GAS SYSTEM ANALYSIS

Process off-gas cleanup system samples were drawn from the liquid-phase generating and containing vessels during NWVP and archived at that time for later evaluation. The evaluations have been completed and the results reported here.

The process off-gas cleanup system, as detailed under the Process Description section, is a series of wet scrubbers, reboilers, and condensers. The original philosophy behind the design of the system was to duplicate that which might be found in an integrated fuel reprocessing/waste management facility (Schneider 1969). The reboiler systems were designed for use in acid recovery. The primary reboiler is termed the evaporator because it is used for condensate evaporation. It is also used for concentration of waste prior to solidification. The quench scrubber used in NWVP is a change from the original tube and shell condenser. It was hoped that the extension of the gas/liquid phase contact in the off-gas system would allow volatilized Ru to come to equilibrium with the liquid phases earlier in the off-gas train, minimizing liquid contamination.

The objectives of the evaluation were to determine the distribution of fission products in the off-gas cleanup system and the efficiency with which the gas was cleaned.

SAMPLE DESCRIPTION

The samples analyzed were a variety of liquid samples taken from the liquid-phase holding tanks during NWVP operation. The samples were taken in 15 ml glass bottles by recirculating samplers (Hanson 1980). The quench scrubber and condensers have very small liquid holdups, so that samples from them are indicative of the conditions at the time of sampling as compared to the time-averaged samples from the tanks. The condensers and scrubber drained to the tanks sampled so that the sample locations allowed calculation of various decontamination factors (see Figure 6).

FISSION PRODUCT DISTRIBUTIONS

Results of the analyses indicate the fission product distributions as shown in Table 8. The table also indicates the elemental breakdown of the analyses.

Although the implications of the results are discussed in detail in later sections, some important observations should be noted here. As mentioned earlier, the process off-gas cleanup system is used to concentrate the HLW feed prior to its solidification. Although the system is acid- and water-flushed following feed concentration, residual contamination remains and has to be accounted for in the analysis of the data in Table 8. Decay rates of the isotopes have been used to adjust for the time differences between process off-gas system operation and sample analyses.

TABLE 8. Typical Elemental Concentrations in Process Tanks

Isotope	Tank (a)			
	Feed	Evaporator	Fractionator	Distillate Receiver
^{90}Sr	9.49×10^{10}	2.19×10^6	9.24×10^7	---
^{99}Tc	2.13×10^6	<572	2.21×10^3	<100
^{106}Ru	7.82×10^9	2.57×10^7	4.52×10^6	2.6×10^4
^{125}Sb	2.20×10^9	5.67×10^5	7.15×10^5	$<4.82 \times 10^2$
^{125}Te	9.07×10^8	<0.01 ppm	0.07 ppm	
^{144}Ce	4.58×10^9	$<8.77 \times 10^5$	1.35×10^6	$<5.38 \times 10^2$
^{154}Eu	6.84×10^9	$<1.06 \times 10^5$	2.55×10^6	$<3.89 \times 10^2$
^{157}Cs	1.36×10^{11}	3.50×10^6	7.05×10^7	1.64×10^3
^{234}Cs	2.95×10^{10}	3.04×10^5	8.76×10^6	2.08×10^2
Co		$<1.24 \times 10^4$	2.59×10^4	$<1.38 \times 10^2$
U	9.2 g/L	2.1 ppm	10 ppm	---

(a) Isotope concentration in disintegrations/minute/milliliter except as noted otherwise.

The gas-phase streams were sampled during NWVP operations, but analyses of these samples were not completed because of lack of confidence in sample quality. Off-gas analyses in terms of volatiles and particulates carried from the process were completed, however, and the results reported by Goles (1979). The concentration of isotopes in the off gas prior to final HEPA filtration and release to the stack is shown in Table 9.

Table 10 details particulate size distribution data for the solids in the final off-gas stream prior to final filtration and stack dilution. The particles are quite small, making significant cleanup difficult.

SOLIDIFICATION SYSTEM DECONTAMINATION FACTORS

The decontamination factors for the SC/ICM system are shown in Table 11. These factors are defined as the ratio of the activity of the given isotope entering the system to the activity exiting.

TABLE 9. Process Off-Gas Isotope Concentration(a)

Isotope	Concentration, nCi/m ³ (D/min/m ³)	
	Volatile	Particulate
⁷⁹ Se	<20 x 10 ⁻⁶ (<4.44 x 10 ⁻²)	
⁹⁹ Tc	1.6 x 10 ⁻³ (3.55)	
¹⁰⁶ Ru	<200 (<4.44 x 10 ⁵)	44 (9.77 x 10 ⁴)
¹²⁵ Sb	<200 (4.44 x 10 ⁵)	0.52 (1.15 x 10 ³)
¹²⁶ Sb	<3 (<6.66 x 10 ³)	
^{125m} Te	<0.1 (<222)	1.7 (3.77 x 10 ³)
¹³⁴ Cs	<6 (<1.33 x 10 ⁴)	7.8 (1.73 x 10 ⁴)
¹³⁷ Cs	<100 (<2.22 x 10 ⁵)	52 (1.15 x 10 ⁵)
¹⁴⁴ Ce		0.82 (1.8 x 10 ³)
¹⁵⁴ Eu		0.28 (622)
¹⁵⁵ Eu		0.18 (400)
²⁴¹ Am		0.19 (422)

(a) Prior to final filtration and stack dilution.

TABLE 10. Particulate Size Distribution Analysis

Parameter ^(a)	Empirical	Log Normal
Geometric Mean Diameter	0.13 μm	0.10 μm
Geometric Standard Deviation	1.51	2.01
Correlation Coefficient	—	—
Mass Mean Diameter	—	0.55 μm
Particle Concentration	168/cm ³	—
Particle Mass Concentration ^(b)	84.7 pg/cm ³	—

(a) All parameters relate to undiluted process off gas before final HEPA filtration.

(b) Assumed calcine density = 3 g/cm³.

TABLE 11. Solidification System Decontamination Factors

Isotope	Decontamination Factor
⁹⁰ Sr/ ⁹⁰ Y	1.56×10^5
⁹⁹ Tc	$>4.38 \times 10^4$
¹⁰⁶ Ru	4.30×10^4
¹²⁵ Sb	1.12×10^5
¹³⁴ Cs	1.19×10^5
¹³⁷ Cs	8.66×10^4
¹⁴⁴ Ce	1.49×10^5
¹⁵⁴ Eu	2.48×10^5

Ruthenium losses from the solidification system were low: only $2.3 \times 10^{-3}\%$ were found in the condensate. The amount of Ru found in the sintered metal filters is even less; accounting for it only drops the decontamination factor for the solidification system from 4.3×10^4 to 4.09×10^4 . The losses rise from 2.3×10^{-3} to $2.45 \times 10^{-3}\%$. The Ru distributions between volatile material and solids penetrating the filters were 80 and 20%, respectively. These losses compare favorably with those reported by Christian (1976) for other processes.

The low volatilities are primarily controlled by three functions: glass formulations, residence time during solidification, and filter cake deposition. The borosilicate glass formulation used in NWVP does not cause high Ru volatilities at the 1050°C melt temperature. This, combined with the continuous dumping of a calcine "cold cap" on top of the molten surface to act as a containment and reflux for volatiles, does not allow much Ru to escape from the ICM. In the SC the transition from nitric acid-based HLW to metal oxide calcine takes place very rapidly; the residence time for the reaction is very short. From a kinetics viewpoint the material may not have time to volatilize. The third controlling mechanism, the filter cake on the sintered metal filters, acts as a final control on volatile material within the solidification system. As discussed earlier, Ru enrichments of greater than 7.5 have been found, demonstrating that the cake efficiently traps volatile material. The temperature in the filter chamber, which operated in the range of 330 to 360°C, gave a sufficient gradient from the 400°C in the calcining chamber to allow deposition on the filter cake. It is recommended that a filter cake as thick as possible while still allowing operation be maintained.

All isotopes investigated showed satisfactory decontamination factors. The decontamination factor for ^{99}Tc is based on the analytical detection limit, which when combined with the relatively small amount of ^{99}Tc in the HLW feed, allows the calculation of only a small decontamination factor. However, the amount of ^{99}Tc in the final process off gas and particulate melter (Tables 9 and 10) was small, showing satisfactory removal from the off gas.

PROCESS OFF-GAS SYSTEM ACTIVITY

The specific activity levels of the isotopes studied in the various process vessels of the off-gas system are shown in Figure 37. The rise in activity in the evaporator is deceptive; the evaporator was used to concentrate HLW prior to its solidification and thus contained residual contamination. Its activity levels and the vessels downstream are a combination of both waste concentration and solidification.

FIGURE 37. Specific Activity Levels for the Process Off-Gas System

Ruthenium volatility from the evaporator appears to be low, as indicated by the relatively low activity in the fractionator. The evaporator condenser and the acid fractionator reflux tower, both downstream of the evaporator, do not remove Ru very effectively. Following a second condensation in the acid fractionator condenser, a larger fraction (relative to the other isotopes present) of the Ru ends up in the distillate receiver.

The acid fractionator was operated at equilibrium with 10 M acid in the bottom and 0.1 M acid in the distillate. The off gas from the evaporator condenser enters the fractionator with the acid condensate, then exits through the rectifying section of the fractionator before entering the fractionator

condenser. From Figure 37, it appears as though the scrub solution (weak acid) in the fractionator rectifying section does not absorb the Ru well, but is good at scrubbing the other isotopes. The flatness of the curve connecting the Ru concentration points shows that the two condensers are obtaining essentially the same gas decontamination for Ru, with none for the fractionator rectifying section. The activity concentration increase in the fractionator for the other isotopes shows that the rectifying section is accomplishing some decontamination.

PROCESS DECONTAMINATION FACTORS

Reporting decontamination factors from feed to the various process tanks would be meaningless due to the fact that the evaporator was used for feed concentration. However, decontamination factors from the feed to the end of the off-gas train prior to final filtration do give an overall indication of the efficiency of the off-gas cleanup equipment. Table 12 details the factors. It is expected that the decontamination factors would be one to two orders of magnitude higher if the system had not been used for feed concentration.

The facility stack was monitored during NWVP processing and system decontamination factors given were obtained in real time. Gross activities

TABLE 12. Average Decontamination Factors for the Process Off-Gas System^(a)

<u>Isotope</u>	<u>Decontamination Factor</u>
¹⁰⁶ Ru	3.28×10^6
¹²⁵ Sb	3.66×10^7
¹³⁴ Cs	1.93×10^7
¹⁴⁴ Ce	1.41×10^8
¹⁵⁴ Eu	1.30×10^8

(a) Prior to final HEPA filtration.

released during NWVP operations via the building stack are presented in Table 13. Greater than 1.03×10^6 Ci of beta-gamma and 4.14×10^3 Ci of alpha materials were concentrated and solidified. Discounting the activity releases from all other sources in the building, the effluent system provided the decontamination factors given in Table 14. The only processing done on the gas to account for the differences between Table 12 and 14 is HEPA filtration. The increase in decontamination factors, particularly for the beta-gamma emitters, shows that the material is in a particulate form at this point and HEPA filtration does effectively lower the quantity of released material.

PROCESS OFF-GAS SYSTEM EVALUATION

The process off-gas system used in NWVP was a complex system which may or may not be the type that system designers use in future plants. In terms of the low volatilities found in this experiment it is probable that the present system is more than adequate if used for solidification alone. The use of the evaporator for feed concentration as well as condensate evaporation would not be recommended for an operating plant. The decontamination factor increases from 3.28×10^6 for Ru to the beta/gamma factor of 2×10^8 over the final HEPA filters in the facility shows that the Ru is primarily entrained particulate matter at this point in the off-gas train. It is also likely that much of it is reentrained material which with careful design could be minimized.

TABLE 13. Gross Activity Released to Stack

Operation	Activity Released, Ci			Activity Concentration, Ci/m ³		
	Alpha	Beta		Alpha	Beta	Gamma
Run 1						
HLW Concentration ^(a)	1.25×10^{-7}	3.48×10^{-7}	(b)	1.56×10^{-15}	4.27×10^{-15}	(b)
SC/ICM ^(a) Operations	4.1×10^{-8}	4.6×10^{-8}	(b)	1.5×10^{-15}	1.6×10^{-15}	(b)
Run 2						
HLW Concentration ^(a)	1.7×10^{-8}	7.8×10^{-8}	(b)	6.4×10^{-16}	2.7×10^{-15}	(b)
SC/ICM Operations	1.8×10^{-8}	7.3×10^{-8}	1.64×10^{-3}	6.5×10^{-16}	2.7×10^{-16}	9.5×10^{-16}

(a) During spray calciner/in-can melter (SC/ICM) operations, the spent fuel dissolution system was in operation, contributing an undetermined amount to the activities shown (Wheelwright 1979).

(b) Data not available.

TABLE 14. Feed-to-Stack Effluent Decontamination Factors

<u>Operation</u>	<u>Decontamination Factor</u>	
	<u>Alpha</u>	<u>Beta-Gamma</u>
Run 1		
HLW Concentration	7×10^7	(a)
SC/ICM Operations	2×10^{10}	(a)
Run 2		
HLW Concentration	7×10^{11}	(a)
SC/ICM Operations	7×10^{10}	2×10^8

(a) Data not available.

REFERENCES

- Bjorklund, W. J. 1976. Development and Use of Sintered-Metal Filters with Fluidized Bed and Spray Calcination of Simulated High-Level Waste. BNWL-2074, Pacific Northwest Laboratory, Richland, Washington.
- Blair, H. T. 1976. Vitrification of Waste Calcines by In-Can Melting. BNWL-2061, Pacific Northwest Laboratory, Richland, Washington.
- Bonner, W. F., H. T. Blair and L. S. Romero. 1976. Spray Solidification of Nuclear Waste. BNWL-2059, Pacific Northwest Laboratory, Richland, Washington.
- Christian, J. D. 1976. "Process Behavior and Control of Ruthenium and Cerium." In Proceedings--Controlling Airborne Effluents from Fuel Cycle Plants. American Nuclear Society, American Institute of Chemical Engineers, Sun Valley, Idaho.
- Goles, R. W., et al. 1979. Characterization of Gaseous and Particulate Effluents from the Nuclear Waste Vitrification Project. PNL-3181, Pacific Northwest Laboratory, Richland, Washington.
- Hanson, M. S. 1980. Spray Calcination/In-Can Melting: Effluent Characterization and Treatment. PNL-3109, Pacific Northwest Laboratory, Richland, Washington.
- Kaser, J. D., and J. E. Moore. 1966. "The Development of Spray Calciner Melter." In Processing of the Symposium on the Solidification and Long-Term Storage of Highly Radioactive Wastes, ed. W. H. Region, pp. 350-351. USDOE CONF-66-2-8, National Technical Information Service, Springfield, Virginia.
- McElroy, J. L., et al. 1972. Waste Solidification Program Summary Report. Vol. II, BNWL-1667, Pacific Northwest Laboratory, Richland, Washington.
- Pall, D. B. 1953. "Filtration of Fluid Catalyst Fines From Effluent Gases." I. and E. Chem. 45:1197-1202.
- Schneider, K. J., and V. P. Kelly. 1969. Waste Solidification Program. Volume II: Design Features of the Waste Solidification Engineering Prototypes. BNWL-968, Pacific Northwest Laboratory, Richland, Washington.
- Wheelright, E. J., et al. 1979. Technical Summary--Nuclear Waste Vitrification Project. PNL-3038, Pacific Northwest Laboratory, Richland, Washington.

ACKNOWLEDGMENTS

The authors would like to acknowledge the assistance provided by the staff of the Chemical Technology Department of PNL: C. O. Harvey for the gamma energy scanning, E. L. Doan and S. D. Halstad for hot cell work, and S. J. Kostorowski for supervision of cell work. We would also like to thank E. D. Jenson and A. C. Leaf, both of Westinghouse-Hanford Engineering Development Laboratory, for the microprobe and radiochemistry analyses.

DISTRIBUTION

No. of
Copies

No. of
Copies

OFFSITE

27	DOE Technical Information Center R. E. Cunningham Office of Nuclear Safety Materials and Safeguards Room 562 Nuclear Regulatory Commission 7915 Eastern Avenue Silver Springs, MD 20910	7	DOE Office of Defense Waste and Byproducts DP-12, GTN Washington, DC 20545 ATTN: A. A. Camacho T. Chee J. E. Dieckhoner D. J. McGoff J. Jicha G. Oertel V. G. Trice
2	Division of Waste Management Nuclear Regulatory Commission Washington, DC 20555 ATTN: J. B. Martin R. Dale Smith W. E. Mott DOE Division of Environmental Control Technology Washington, DC 20545	3	Exxon Nuclear Idaho Corporation Box 2800 Idaho Falls, ID 83401 ATTN: R. A. Brown J. D. Christian T. R. Thomas W. F. Holcomb National Institutes of Health Bldg. 21, Radiation Safety Branch Bethesda, MD 20205
8	DOE Nuclear Waste Management and Fuel Cycle Programs NE 30, GTN Washington, DC 20545 ATTN: W. W. Ballard F. E. Coffman H. Feinroth O. Gormley M. Lawrence W. McVey R. W. Ramsey J. A. Turi		S. A. Mann DOE Chicago Operations and Region Office Argonne, IL 60439 J. Neff Department of Energy Columbus Program Office 505 King Avenue Columbus, OH 43201

No. of
Copies

No. of
Copies

- 2 DOE Idaho Operations Office
550 2nd St.
Idaho Falls, ID 83401
ATTN: J. P. Hamric
M. A. Widmayer
- Office of the Assistant Manager
for Energy Research & Development
DOE Oak Ridge Operations Office
P.O. Box E
Oak Ridge, TN 37830
- 3 Oak Ridge National Laboratory
P.O. Box Y
Oak Ridge, TN 37830
ATTN: J. O. Blomeke
A. L. Lotts
L. G. Mezga
- E. L. Albenesius
E. I. du Pont de Nemours
& Company, Inc.
Savannah River Laboratory
Aiken, SC 29801
- J. J. Cohen
Science Applications, Inc.
1811 South Rita Road
Suite 104
Pleasanton, CA 94566
- J. L. Crandall
Savannah River Laboratory
Aiken, SC 29801
- P. Dickman
Reynolds Electric Engineering Co.
Mercury, NV 98023
- 3 Transuranic Waste Systems Office
Rockwell International
Rocky Flats Plant
Golden, CO 80401
ATTN: P. G. Hagan
K. V. Gilbert
T. Scott

Lawrence Livermore Laboratory
Reference Library
P.O. Box 808
Livermore, CA 94550

G. B. Levin
EG&G Idaho
P.O. Box 1625
Idaho Falls, ID 83401

Los Alamos National Laboratory
Reference Library
P.O. Box 1663
Los Alamos, NM 87544

Savannah River Laboratory
Reference Library
Aiken, SC 29801

- 2 DOE Savannah River Operations
Office
P.O. Box A
Aiken, SC 29801
ATTN: E. S. Goldberg
T. B. Hindman

S. G. Harbinson
DOE San Francisco Operations
1333 Broadway
Oakland, CA 94612

- 2 Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
ATTN: J. H. Kittel
M. J. Steindler

- 2 Battelle Memorial Institute
Office of Nuclear Waste Isolation
505 King Avenue
Columbus, OH 43201
ATTN: N. E. Carter
S. Goldsmith

No. of
Copies

R. Williams
Electric Power Research Institute
3412 Hillview Avenue
P.O. Box 10412
Palo Alto, CA 94304

Environmental Protection Agency
Technological Assessment
Division (AW-559)
Office of Radiation Programs
U.S. Environmental Protection
Agency
Washington, DC 20460

J. L. Larocca, Chairman
Energy Research and Development
Authority
Empire State Plaza
Albany, NY 12223

R. G. Post
College of Engineering
University of Arizona
Tucson, AZ 85721

L. L. Hench
Dept. of Materials Science
and Engineering
University of Florida
Gainesville, FL 32611

R. Roy
202 Materials Research Laboratory
University Park, PA 16802

F. K. Pittman
3508 Sagecrest Terrace
Ft. Worth, TX 76109

ONSITE

5 DOE Richland Operations Office

E. A. Bracken
H. E. Ransom
J. J. Schreiber
M. W. Shupe
F. R. Standerfer

No. of
Copies

Westinghouse Hanford Company

A. G. Blasewitz

2 Rockwell Hanford Operations

J. K. Deichman
K. A. Gasper

54 Pacific Northwest Laboratory

S. M. Barnes
W. J. Bjorklund
H. T. Blair
W. F. Bonner
D. J. Bradley
R. A. Brouns
J. L. Buelte
J. G. Carter (5)
T. D. Chikalla
R. D. Dierks
R. W. Gales
M. S. Hanson (10)
A. J. Haverfield
L. K. Holton
J. H. Jarrett
Y. B. Katayama
S. E. King
D. E. Knowlton
C. A. Knox
W. L. Kuhn
L. T. Lakey
D. E. Larson
J. M. Latkovich
J. L. McElroy
G. B. Mellinger
R. E. Nightingale
K. H. Oma
R. D. Peters
G. L. Sevigny
D. H. Siemens
S. C. Slate
C. L. Timmerman
R. L. Treat
H. H. Van Tuyl
Technical Information (5)
Publishing Coordination (BG)(2)