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PNL-2486

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SAI-77-571-LJ

Critical Assessment of Methods for Treating Airborne Effluents from High-Level Waste Solidification Processes

by
J. D. Christian
D. T. Pence
Scientific Advances, Inc.

June 1977

Prepared for
Pacific Northwest Laboratory
Under Agreement No. B-36262-A-L

Pacific Northwest Laboratory
Richland, Washington 99352
Operated for the
U.S. Department of Energy by

Battelle

Memorial Institute

PNL-2486

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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract EY-76-C-06-1830

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

Price: Printed Copy \$____*: Microfiche \$3.00

*Pages	NTIS Selling Price
001-025	\$4.50
026-050	\$5.00
051-075	\$5.50
076-100	\$6.00
101-125	\$6.50
126-150	\$7.00
151-175	\$7.75
176-200	\$8.50
201-225	\$8.75
226-250	\$9.00
251-275	\$10.00
276-300	\$10.25

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CRITICAL ASSESSMENT OF METHODS FOR
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ABSTRACT

Off-gas treatment systems are reviewed for high-temperature processes which are being developed for the solidification of high-level liquid wastes from nuclear fuel reprocessing plants. A brief description of each of the processes is given and detailed analyses are made of the expected magnitudes of airborne effluent release rates from each system. The estimated release rates of the various processes are compared with present and anticipated regulatory limits. A number of recommendations are made for additional development studies to better understand and control certain airborne effluents from the solidification processes.

SUMMARY

Off-gas treatment systems are reviewed for high-temperature processes which are being developed for the solidification of high-level liquid wastes (HLLW) from nuclear fuel reprocessing plants. Brief descriptions of the individual processes and details of their off-gas systems are given in Section 2. Detailed analyses of the expected efficiencies of the individual systems for removing airborne radionuclide effluents generated by the processes are given in Section 3. A summary of the estimated feed-to-stack decontamination factors (DFs) for all the processes is given in Section 3.12.

The maximum permissible concentrations (MPCs) for individual isotopes in air for uncontrolled areas as tabulated in 10CFR20 were compared with the recently established EPA standards (40CFR190), using the anticipated processing conditions: design fuel burnup, fuel cooled $1\frac{1}{2}$ years from reactor discharge; processing rate of $6\frac{2}{3}$ MTHM/day; and a dispersion factor, χ/Q , from the stack to the site boundary of 1×10^{-7} sec m^{-3} . The results of the analysis show that the EPA release limits for α -emitting transuranics restricts the release rate of Cm-244 to some 3000 times less than that allowed by the 10CFR20 MPCs. The new EPA regulations make Cm-244 the radionuclide for which the most stringent control is required in a waste solidification process. Assuming 10% of the maximum allowable fuel cycle release limit for α -emitting transuranics are allowed to become airborne in the waste solidifier stack gas, an estimated feed-to-stack DF of 3×10^9 for particulate Cm-244 will be required.

Of the volatile and semivolatile isotopes, Ru-106 must be most strictly controlled. An estimated DF of 7×10^4 for

volatilized ruthenium will limit Ru-106 concentrations in air at a typical site boundary to 1/10 its MPC listed in 10CFR20. The ALARA clause may possibly result in even tighter controls. No specific release limit for Ru-106 has been established by EPA.

The EPA release limit for I-129 is approximately 2×10^4 times more restrictive than the 10CFR20 MPC. If 0.1% of total I-129 is in the HLLW, total release of iodine from the waste solidifier will amount to about one-fourth the total release limits for I-129 in the entire fuel cycle.

Complete release of NO_x from the HLLW solidifier into a fuel reprocessing facility stack with typical gas flow of $52 \text{ m}^3 \text{ sec}^{-1}$ is estimated to result in a concentration of NO_x in air at the site boundary, of about 0.5 ppb, two orders of magnitude below the EPA standard for ambient air quality. Whether NO_x control will be required will probably depend on local regulations.

A summary of estimated overall process DFs for each of the processes evaluated is presented in Table 19. In all but one case, the DFs exceed those deemed necessary for Cm-244 and Ru-106, indicating that adequate airborne effluent control is probably possible for a full-scale HLLW solidification facility. The types of treatment systems and the desired redundancy depend on a number of practical considerations such as the required throughput, type and expected age of cooled fuel, location of the facility, and the applicable effluent regulations. The information provided in this report, including the uncertainties and limitations in the various treatment system designs, should be useful in designing an appropriate treatment system for a particular need.

A number of conclusions and recommendations for study resulted from the review. Some important ones are as follows.

Evaporators used for concentrating HLLW may affect overall system DFs, depending on where the evaporator off gas enters the solidifier off-gas treatment system. Aerosol entrainment from evaporators may be approximately 0.005% and ruthenium volatility may be between 0.001 and 0.01%.

The required blowback frequency of primary sintered metal filters may be reduced by placing shrouds around the filter elements. HEPA filters used for final filtration have potential for releasing particulate material under accident conditions. A study to determine the applicability of small pore SMFs as substitutes or for backup filtration is recommended.

Because of the high Ru-106 activity and the difficulty of controlling release of Ru-106 from HLLW during solidification, it is recommended that ruthenium adsorbers, either silica gel or ferric oxide-based material, be used for ruthenium control in the off-gas system of any process. A catalytic bed NO_x converter may also be an effective device for removing volatilized ruthenium as well as other potentially volatile species; studies are needed, however, to verify the effectiveness of this device.

In-depth studies of optimum operating conditions of temperatures, superficial gas velocity, and residence times are needed for the ruthenium adsorbers so that maximum DFs can be obtained. Silica gel may provide substantially higher DFs than normal if used at near ambient temperature, and its use in low temperature dry streams should be investigated.

Ruthenium volatility during solidification can generally be suppressed by denitrating the feed. The effectiveness for the high temperature ceramic melters needs to be determined. The ruthenium behavior in a wiped-film evaporator needs to be determined, since operating conditions may enhance the volatility. If a problem exists, ruthenium suppression by denitration with formic acid should be investigated.

When ruthenium volatility is high in a process, potential exists for plugging off-gas pipes. Deposits in problem areas may be minimized by maintaining wall temperatures at 250° to 350°C, avoiding decreasing temperature gradients, and diluting the oxygen in the off gas with an inert gas.

In addition to general needs for measuring ruthenium flowpaths in specific processes, behaviors of other long-lived, potentially volatile isotopes need to be determined. Those of concern include Se-79, Te-127m, Sb isotopes, and, particularly, Tc-99.

In order to improve predicted efficiencies of off-gas effluent treatment systems, more extensive studies are generally needed to determine component efficiencies for removing particulates and volatilized isotopes as functions of concentrations and sizes down to those expected in the most downstream location in the system where a particular device might be used. Measurements are also suggested for selected integrated systems containing combinations of effluent treatment devices.

A problem with testing overall systems performances is the difficulty in sampling and measuring miniscule quantities of materials in the cleaned off gas. Fundamental and development studies are needed for the development of improved methods and techniques for these measurements.

In conclusion, adequate airborne effluent treatment design must ensure absolute containment of particulates at all times and reasonable control of the fission product semivolatiles. Such systems must function satisfactorily over the full range of operating and postulated accident conditions. Designs that satisfy these requirements appear possible with present technology but verification of performance, especially on a large pilot-scale, is clearly needed.

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1. INTRODUCTION

The major processes for the solidification of LWR high-level liquid wastes (HLLW) which are ready for demonstration or which require short-term (less than 5 years) development prior to demonstration consist of drying and calcination and of vitrification⁽¹⁾. In many cases, vitrification is coupled to a drying-calcination facility. The processes are listed in Table 1.

Most of the basic processes are being developed at more than one country or laboratory. Generally, the methods or procedures developed for a given process are different at the different sites. A description of most of them is given in the Technical Alternatives Document (TAD)⁽¹⁾. A review of the ruthenium removal aspects of the off gas systems for many of the processes has been given by Christian⁽²⁾.

These processes have had varying degrees of development and testing of off-gas treatment systems for the removal of particulates and volatilized fission products from the off-gas stream. The stages of their developments are discussed in this document. Off-gas treatment systems for more advanced technology systems, such as metal matrix, glass ceramic, sintering, and coated-pellet processes, which require more than 5 years development prior to engineering detail design, are not considered here. For the most part, these processes have not been advanced to the point where off-gas cleanup requirements have been addressed.

The reviewed systems are described in Section 2 and expected performances of the off-gas systems for removing process airborne effluents are given in Section 3. General conclusions and some recommended development studies which are suggested from the review are discussed in Sections 4 and 5.

TABLE 1
MAJOR SOLIDIFICATION PROCESSES

Process	Developing Countries and/or Laboratories ^a
Fluidized-Bed Calcination	USA: ICPP, PNL Eurochemic (LOTES Process)
Spray Calcination	USA: PNL Germany (VERA Process)
Pot Calcination or Vitrification	USA: PNL England (FINGAL/HARVEST Process) France (PIVER Process) Italy India
Phosphate Glass Formation	USA: PNL
Rotary Kiln Vitrification	France (AVM Process)
Drum Drier-Pot Vitrification	Germany (FIPS Process)
Continuous Ceramic Melter	USA: PNL Denmark France
Wiped Film Evaporator ^b	USA: PNL

^aICPP = Idaho Chemical Processing Plant

PNL = Battelle Pacific Northwest Laboratories

^bCoupled with vitrifier or pot calciner

2. REVIEW OF OFF-GAS TREATMENT TECHNOLOGIES FOR HIGH-LEVEL WASTE SOLDIFICATION PROCESSES

A review and brief description of integrated off-gas cleanup systems which have been used for the major processes are given in this section. In addition, some individual components that have been generally tested are mentioned, particularly materials which are used for volatilized ruthenium removal.

Each of the major processes is considered individually. Where more than one country or laboratory has developed a particular process, the off-gas systems for all of them are described in a group.

Each process generates water vapor and NO_x as the waste feed is heated, dried, and calcined or vitrified, and these gases contribute to the burden of any of the off-gas systems. Other major gas stream constituents include particulate solids and aerosols, air, oxygen, volatilized ruthenium and cesium, and, in some cases, kerosene combustion products. The extent of formation for other semivolatile species, such as technetium, is not known. Any residual iodine in the waste will be vaporized.

2.1 FLUIDIZED-BED CALCINATION

This process, carried out at temperatures between 400° and 800°C , generates a considerable amount of fine particulate material and some volatilized ruthenium which are carried with the off-gas stream. It is also characterized by a large off-gas flow, created by the required fluidizing air, atomizing air and combustion products. The off-gas cleanup system must, therefore, be capable of handling large gas volume flow rates and efficiently remove substantial quantities of particulate solid material and volatilized ruthenium.

The quantities of fines and volatile ruthenium generated depend on the operating conditions and, to a certain extent, on the feed composition and concentration. The process has been developed along quite different lines at the Idaho Chemical Processing Plant (ICPP) and at the Battelle Pacific Northwest Laboratories (PNL). Eurochemic is developing a modified process in which the bed is mechanically stirred, which reduces the amount of required fluidizing gas.

2.1.1 ICPP Fluidized-Bed Process

This process was initially developed at the Argonne National Laboratory (ANL)⁽³⁾ and the ICPP and was further tested with plant-scale equipment at the ICPP⁽⁴⁾. The plant (Waste Calcining Facility, WCF) has been used since 1963 to solidify radioactive defense wastes, and experiences with the use of the facility with these wastes have been documented⁽⁵⁻⁹⁾. A New Waste Calcining Facility (NWCF) with larger capacity and constructed with materials resistant to corrosion by the fluoride wastes now being processed is currently under construction^(10,11).

A schematic diagram of the calciner and off-gas cleanup system used for the ANL experimental facility is shown in Figure 1. Primary particulate removal was provided by sintered metal filters in the disengaging section above the calcine bed. Additional particulate and, also, some volatilized ruthenium removal were accomplished with a venturi scrubber which followed the sintered metal filters in the off-gas line. The venturi scrubber was followed by a cyclone which removed entrained moisture and aerosols, and then the gas passed through a bed of silica gel which adsorbed volatilized ruthenium. After the silica gel bed, the off gas was passed through a condenser. The noncondensable gases were passed through a stainless steel trap for entrained material, a centrifugal deentrainment device for moisture removal and, finally, through a HEPA filter.

Figure 1. ANL Experimental Fluidized-Bed Calcining Facility.

• The WCF off-gas cleanup system is a combination wet-dry system consisting of a series of unit operations designed for progressively smaller particles and is depicted in Figure 2. At the top of the calciner vessel is a baffle for deflecting particles. Entrained fine particulate material is partially removed by a cyclone fines separator at the exit of the calciner. The off gas is then cooled in a spray quench tower prior to passing through a venturi scrubber where most of the remaining particulates are removed along with some of the volatilized ruthenium. The scrub solution, which is maintained 4M in HNO_3 , dissolves most of the collected solids and is recycled to the feed at an average rate of 15% of the gross feed rate. Most of the water for the scrub solution used for recycle is condensed from the off-gas stream by control of the scrubbing solution temperature so that the condensation rate is approximately equal to the recycle rate.

At the end of the scrubber system is a scrubber separator vessel for separation of scrub water from the off gas which is followed by a cyclone for removal of mist and entrained aerosols. Following this, the off gas goes through a parallel bank of 1.2-m deep beds of silica gel at 0.12 m/sec. The off gas is heated between the demister cyclone and the silica gel beds to bring the temperature 5-10°C above the dew point so that the silica gel will be effective in removing volatilized ruthenium. A cyclone following the silica gel adsorber beds is included to remove any entrained moisture and particulates carried from the beds. Finally, the gas is passed through a parallel bank of roughing and HEPA filters after being heated to prevent moisture condensation.

The off-gas cleanup system for the NWCF will be virtually identical to that used for the WCF with some individual equipment refinements or improvements. Like the WCF, it will employ

Figure 2. Flowsheet of the ICPP Waste Calcining Facility Using In-bed Combustion for Heating.

in-bed combustion of kerosene for heating, and air fluidization. The principle changes are as follows. To minimize carry-over, the 1.5-m (5-ft) diameter bed section will have a 2.1-m (7-ft) diameter expanded deentrainment section above it as high as permitted by cell dimensions (ca. 2 to 3 m). The top of the deentrainment section will be a double venetian-blind baffle. Following the venturi scrubber, the off gas will pass into a centrifugal separator followed by a condenser where volatile ruthenium compounds will be partially removed along with some of the submicron dust particles. The off gas from the condenser will pass into a mist eliminator that will collect mist on a two-stage metal wire mesh filter.

The WCF and NWCF do not have provisions for NO_x or iodine removal as there is no requirement for NO_x removal at the facilities, and I^{129} levels in the defense wastes solidified are low.

2.1.2 PNL Fluidized-Bed Process

This fluidized-bed calciner was installed by PNL and began operation in late 1974 as part of their Waste Fixation Program (WFP); it is being used to study the calcination of simulated HLLW^(12,13). The process is a greatly modified version of conventional fluidized-bed calcination. A schematic diagram of the calciner is shown in Figure 3. In the process, termed the Continuous Inert-bed Process (CIB), an inert material (SiO_2) is used as a starting bed and is added continuously as product is withdrawn along with some silica. The operating conditions are such that most of the calcine is produced as fines which are elutriated from the bed; this maintains a low inventory of fission products in the bed. The calcine and silica discharged from the calciner are incorporated into glass in a melter below. As with the ICPP calciners, the fluidized bed is heated by internal combustion of kerosene.

Fluidized-Bed Calciner Material Balance

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	FLUIDIZING AIR	PLENUM	LOWER BED	UPPER BED	DISCHARGING SPACE	FUEL	FUEL ATOMIZING	FUEL	ATOMIZING AIR	INERT BED MATERIAL	FILTER VESSEL	BLOW BACK AIR	FILTERED OFF-GAS	CALCINE PRODUCED
TEMPERATURE °C	20	360	550	550	475	24	73	25	20	360	103	360		
PRESSURE psig	50	0.2	-0.2	-0.3	-0.4	80	80	5	90	-0.43	80	-0.9		
LIQUID RATE l/hr					4.5		25							
GAS RATE scfm	6.0		6.0				4.4		4.5			37		
GAS RATE acfm	1.46						0.74		0.68			91		
VELOCITY ft/sec			1.0	6.0	3.0									
SOLIDS RATE kg/hr														4.41

Figure 3. PNL Fluidized-Bed Calciner and Off-Gas System

The PNL fluidized-bed calciner is designed to produce a large quantity of fines to facilitate melting with glass frit. Since this is the desired product form, the fines are contained with filters rather than using a wet scrubbing-dissolution system in the off-gas train. The off-gas treatment system starts with a cyclone separator after the gases exit from the disengaging section of the calciner. This removes a portion of the particulates to the receiver. Above the cyclone outlet is a bank of sintered metal filters (SMF) with nominal pore size of 65 μm . After the initial coating with fines, the effective pore size is reduced to approximately 3 μm .

During operation of the melter for production of glass, appreciable quantities ($> 1\%$) of ruthenium may be volatilized. Laboratory studies are needed to determine the extent of this problem. The off gas from the melter exits with the calciner off gas. For the experimental studies, the off-gas cleanup downstream of the SMF consisted of a condenser and packed scrubber. Beyond the blower, the gases were blended with building ventilation air and filtered. An actual process facility will be assumed to include the HEPA filter after the scrubber. In some experiments, a HEPA filter was placed between the SMF and condenser; this was for collection of analytical samples only and not process purposes.

2.1.3 Eurochemic LOTES Process

Belgium authorities have requested the Eurochemic (European Company for the Chemical Processing of Irradiated Fuels) International Organization to condition the HLLW at its demonstration plant in Belgium to a safe form for storage. However, the Belgium authorities have not yet specified the acceptance criteria for terminal storage. Thus, Eurochemic has selected a granular calcine or glass product form for their solidified wastes to allow modification of the form if dictated by acceptance criteria which will be established in the future for terminal storage. They have chosen a fluidized-bed process for solidifying the wastes⁽¹⁴⁾. In order to minimize

fines entrainment the bed is stirred mechanically; this allows the flow rate of the fluidizing gas to be reduced by more than a factor of 10 from what is required without stirring and results in a reduction of the entrainment of fines by a factor of 2. At the same time, larger calcine granules are produced.

Another use of the stirred-fluidized bed is the production at 450°C of alumino-phosphate glass granule matrix for the waste. This process is called LOTES (for Low Temperature Solidification) and is depicted in Figure 4. The major part of the off-gas cleanup system is similar to the ICPP system. A difference is that the fines collected by the cyclone, rather than being mixed with the calcine product, are dissolved, along with those washed out by the venturi scrubber, and recycled to the calciner. The gases are not cooled prior to scrubbing.

Following the venturi-scrubber cyclone demister, water is condensed from the off gas, which then passes through another demister. No special ruthenium adsorbers are placed in the off gas stream. The final treatment of the off gas is by a HEPA filter.

2.2 SPRAY CALCINATION

Spray calcination was originally developed at Oak Ridge⁽¹⁵⁾ for decomposing uranyl nitrate to UO_3 . Based on that work, PNL applied the process in its Waste Solidification Engineering Prototype (WSEP) program to the calcination of HLLW and is currently developing the process further in the WFP. Germany is also developing a spray calciner for the solidification of the LWR HLLW (VERA process).

The product of a spray calciner is a powder. In all the processes, glass frits are added to the feed or product and a glass is formed either in a continuous melter below the calciner or in a pot. The off gases from the melting process go with the calciner off gases.

For materials, compositions and flows see attached table.

Figure 4. The LOTES Process.

The LOTES process (see Figure 4) materials, compositions and flows for cold testing at pilot scale

Stream No	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Stream	Feed	Feed atom. air	Kerosene	Keros. atom. air	Shroud air	Fluidiz. air	Calciner off-gas	Cyclone off-gas	Venturi scrub off-gas	Fines diss. make-up	Fines re- cycle	Condensate	Conden- ser off-gas	Product
Flow rate ^a	5	0.04	0.5	0.015	0.08	0.05	0.29	0.29	0.29	0.5	0.5	3.75	0.21	1.15 kg/h
Temp. °C	25	25	25	25	25	350	350	150	120	25	50	40	40	400
HNO ₃ M	1.7									12	8			
H ₃ PO ₄ M	2.1													
Al	1.4M						<60 g/h fines	<5 g/h fines			~0.7M			1.15 kg/h prod.
Sr mg/l	20													
Cs mg/l	33													
Ku mg/l	31													
Mg mg/l	341													
H ₂ % vol							52						71	
O ₂ % vol							12.5						17	
CO ₂ % vol							3.5						4.8	
H ₂ O							32						7.2	

^aLiquid streams are in l/h; gaseous streams in standard cubic meters/minute.

Total off-gas flow rates are less than for a fluidized-bed process, but the atomizing air does contribute significantly to the flow. As with the fluidized-bed calciner, the fraction of ruthenium volatilized is dependent on the mode of operation and can vary from less than 0.01 to 75%.

2.2.1 PNL Spray Calcination Process

In the waste solidification demonstration program for commercial nitrate wastes at PNL, two processes were developed for the spray calcination method^(16,17). In the standard process, phosphoric acid was added to the waste feed (1.3 to 1.8M) and the spray calcine product was continuously fused with the phosphate in a melter below the calciner. The calciner wall temperature was maintained at 700-720°C by external resistance furnaces, while the melter furnace was held at 1050-1100°C. Purex waste was modified with additives to simulate actual LWR and LMFBR processing wastes. In this process, ruthenium volatility was very high, from 35 to 75%.

The other mode of operation, called the in-pot melting modification, was finally adopted for the recommended process. In this process, the calcined waste was fused into a glass directly in the receiving pot. No phosphate was added to the feed, but frits (borosilicate or Na_3PO_3) for glass formation were added directly to the melting pot with the calcine. With the pot operated at 950°C, the total ruthenium volatilized during spray calcination and melting was between 0.5 and 2%.

Cesium and tellurium were the only other volatile fission products noted from the spray calciner, and they were volatilized to the extent of 0.002 to 0.3 and 1%, respectively.

A diagram of the calciner depicting the two process modifications is shown in Figure 5. Sintered metal filters were used to contain most of the particulate material as the off gas exited the calciner.

Downstream of the sintered metal filters, all three of the processes developed for the WSEP program (spray calcination, pot calcination, and phosphate glass) utilized the same off-gas cleanup system, termed the Auxiliary Process System (APS). A schematic diagram of the system connected to the solidifier is shown in Figure 6. In this system nitric acid was recovered and waste removed prior to discharging the gases to the stack.

In the WSEP auxiliary system, vapors from the solidification system were condensed for primary off gas decontamination, and the resulting condensate was re-evaporated in the evaporator (while concentrating solidifier feed in some cases). The vapors from the evaporator were decontaminated from entrained aerosols in the evaporator tower by impingement plates, bubble caps, and a mist eliminator before being vented to the evaporator condenser. The evaporator condensate was routed to an acid fractionator where nitric acid was recovered. The vapors from the fractionator were again condensed, and about 80% of the fractionator distillate was recycled to the evaporator as nitric acid strip water. The remaining 20% was collected as an intermediate level waste stream. The uncondensed gases were treated by high efficiency filtration, caustic scrubbing, and additional filtration before discharge to the atmosphere. As indicated in Figure 6, a HEPA filter was used after the solidifier condenser for some later runs and in-pot calcination runs (see Section 2.3.1).

The same off-gas treatment system will be used for radioactive demonstrations of the WFP spray calciner (which utilizes in-pot melting) except with a quench scrubber substituted for the solidifier condenser.

Figure 5. PNL WSEP Spray Solidification Processes.

Figure 6. WSEP Auxiliary Process System.

2.2.2 German VERA Process

This process has been developed using simulated LWR HLLW^(18,19). The spray calciner is heated to 420°C by introducing superheated steam at 650°C into the calciner. Steam is also used to atomize the feed. The HLLW is denitrated by reaction with formic acid to suppress ruthenium volatility during the calcination/vitrification. In earlier development work, the denitration was performed batchwise prior to feeding to the calciner. The principle nitrogen-containing gas product was N₂O when the HLLW was added to refluxing formic acid. This and CO₂ comprised about 95% of the total off gas from the VERA process excluding steam. The batchwise denitration did not destroy alkaline nor alkaline earth nitrates. In more recent development studies, denitration is carried out in the calciner by mixing the HLLW and formic acid in the feed nozzle. At the calciner temperature of 420°C, the principle gas products are CO₂ and N₂. Furthermore, the alkaline and alkaline earth nitrates are more completely destroyed, resulting in less NO₂ production from high temperature dissociation.

The first off-gas cleanup device is a bank of sintered stainless-steel filters with nominal pore diameter of 35 μm for stopping the calcine. Initially, these were in a vessel separated from the calciner and above the melter and receiver. In a more advanced concept recently developed, the metal filters are integrated into the calciner unit. The advanced VERA process includes the following improvements: in-calciner denitration by formic acid, the integrated filter system, and recycle of the condensed steam to the superheater and calciner. The flow-sheet, including the off-gas treatment system, is shown in Figure 7.

The process utilizes a semicontinuous melter in which the calcine and glass frit are received. A portion of the frit,

Figure 7. Simplified Flowsheet of the VERA Mock Up.

called "Celite," consisting largely of SiO_2 , is added to the HLLW feed to make the calcine less sticky . A freeze valve is opened to dispense the molten glass product into the receiving container, where it is annealed and sealed off.

After exiting the sintered metal filters, the steam is removed from the off gases by condensation. The remaining off gases, which contain mostly N_2 and CO_2 , are blended with vessel off gases and then simply passed through a condenser, scrubbers, and final condenser prior to venting to the ventilation system.

The condensed steam, which is separated from the contaminated off gas, is evaporated, reheated to 650°C , and recycled to the calciner. The complete condensation and recycling of the process steam provide the advantages that the activity level of the recycled steam is decreased by several orders of magnitude and the dilution of tritium by virgin process steam is avoided. This will be beneficial if it is decided to store the tritium .

Nitrates are known to enhance ruthenium volatility at calcination temperatures⁽²⁾. Because the feed is denitrated in the VERA process, ruthenium volatilization is less than 0.01%. No special equipment is included for removing volatilized ruthenium from the off gas.

2.3 POT CALCINATION

The pot calcination process, which was originally developed at Oak Ridge National Laboratory⁽²⁰⁻²³⁾ with simulated inactive wastes, has been tested with radioactive wastes at Battelle Northwest^(24,25). It consists simply of evaporation of the waste to as small a volume as possible without undue precipitation of solids and then complete drying and calcination at ca. 900°C in a separate

pot. In an alternate procedure, called the rising-level glass process, carried out in the same equipment at 950°C, concentrated feed containing glass forming additives is continuously added to the pot while the liquid is evaporated at the top. Calcination occurs in the middle, and a rising pool of glass is formed from the bottom. This is similar to the English FINGAL process⁽²⁶⁻²⁹⁾, now called HARVEST^(14,30); the HARVEST modification uses an annular vessel.

Italy has also developed a pot calcination/vitrification process^(31,32), and the French PIVER vitrification process^(33,34) utilizes a pot calciner/vitrifier.

The pot processes are generally characterized by low entrained solids in the off-gas stream (<1%) and a high percent of ruthenium volatilized from the pot (>10%). Because atomizing or fluidizing gases are not needed, the total off gas flow rate is relatively low.

2.3.1 PNL Pot Calcination Process

This process^(24,25), developed as part of the WSEP program, was based on the earlier work done at Oak Ridge⁽²⁰⁻²³⁾. In the calcination mode, approximately 10% of the total ruthenium was volatilized, and generally less than 1% of the nonvolatile solids was entrained in the off gas stream. Cesium did not appear to volatilize. It was observed that low sulfate wastes generated less volatilized ruthenium. Also, there was less evolution of ruthenium when early scaling of the pot wall (before approximately 25% of the total feed had been fed) occurred.

In the rising-level glass mode, the ruthenium volatility was 15%, and cesium was volatilized to the extent of 0.6%. (Total Cs carryover was 1.0%, including

solids entrainment). Based on $^{144}\text{CePr}^a$ in the pot condensate, the amount of entrainment was 0.38%, but other observations (including partial plugging of the pot throat and early plugging of an absolute filter beyond the solidifier condenser) indicated a much higher entrainment.

The calciner off-gas stream was decontaminated primarily by condensing the acid vapors and absorbing the nitrogen oxides in a condenser following the calciner at the head end of the WSEP APS (see Figure 6 and Section 2.2.1). Because of the low solids content, no sintered metal filters were utilized as a first-stage treatment. However, because of this, somewhat larger solids loading of the off-gas stream going to the WSEP auxiliary off-gas treatment system occurred and a HEPA filter was used following the solidifier condenser.

The condensate from the calciner condenser contained over 99% of the volatilized ruthenium and was returned to the evaporator.

A special self-cleaning off-gas line was used with the pot calcination process. Approximately 10 to 20% of the liquid boiled up from the pot was continually refluxed in the vertical off-gas line to keep it washed of entrained calcine (see detail, Figure 8). The reflux was not returned to the pot but was routed to the evaporator where it was recombined with the remainder of the pot condensate from the process condenser and distilled over to the acid fractionator.

While the pot process has been demonstrated and developed to readiness for commercial application, it is not currently considered an attractive process in the United States because of throughput limitations.

^a $^{144}\text{CePr}$ represents the equilibrium between ^{144}Ce and its short lived daughter, ^{144}Pr .

Figure 8. Pot Solidifier Self-Cleaning Vent Line and Fill Head.

The pot process and the associated off-gas treatment system developed at the PNL has been installed in India⁽³⁵⁾.

2.3.2 British FINGAL/HARVEST Process

The FINGAL rising-level-glass process was thoroughly developed with inactive wastes and tested with active waste feeds at Harwell from 1959-1969⁽²⁶⁻²⁹⁾. Based on experience with the process, some design and operating philosophy changes were proposed in 1972, and a modified process called HARVEST was designed, and a pilot-scale facility for inactive tests constructed at Harwell^(14,30). An active pilot plant is presently under construction at Windscale^(14,36). In order to accommodate projected wastes, several vessels are proposed for a plant. The processes make a borosilicate glass product at 1050°C. However, some newer mixed alkali borosilicate glass composition melting at temperatures as low as 900°C which have good leach resistant qualities are also under investigation⁽¹⁴⁾.

At the time of reporting (1976), no tests of the HARVEST process had been described, although the cold facility is in operation. The major differences between the two processes (FINGAL and HARVEST) were described in 1972 as follows⁽³⁰⁾.

	<u>HARVEST Process</u>	<u>FINGAL Process</u>
type of container	annular vessel	cylinder
inactive feed (glass frit additives)	slurry or dry feed	slurry
off-gas treatment	liquid scrubbing	filtration with iron oxide adsorption carried out in heated furnace (two per line of plant)
storage	water cooled in pond	air cooled in tunnel

In the later report⁽¹⁴⁾, however, the ruthenium adsorbers are again included in the HARVEST off gas system. This is discussed in detail below.

The basic flowsheet of the FINGAL process is shown in Figure 9. The calciner furnace is controlled at 1050°C (compared to 950°C for the PNL pot rising-level-glass process). The off gas is filtered by the small primary and large secondary filters in series. The filter material is granules of ferric oxide deposited on silica⁽²⁷⁾. The filters are maintained at 250°C to keep them dry; at this temperature, they also adsorb volatilized ruthenium when the superficial vapor velocity is less than 0.15 m/sec. Spent filter material from the primary filter is removed after each batch of glass is made and is fused with fission product waste in the succeeding calciner. The dust loading on the secondary filter is small; it retains a long service period and is not used for glass making.

The ruthenium filter design⁽²⁷⁾ is shown in Figure 10. In a later modification⁽²⁸⁾, the filter was changed to prevent dust gaining access to and depositing on the lid of the filter vessel. The modification consisted of reversing the flow through the filter, i.e., the dust laden gas was fed to the inside of the filter and passed outwards through the adsorber and absolute filter paper so that when it emerged from the vessel it was clean.

The off gas from the secondary filter/adsorber passes directly to the condenser, and the oxides of nitrogen are absorbed by the nitric acid condensate in a packed column. A caustic scrubber removes traces of acid fumes before the effluent gas passes through a final absolute filter.

Figure 9. Simplified Flowsheet of FINGAL Process.

Figure 10. Ruthenium Filter for FINGAL Process.

Ruthenium volatilized during the process is ca. 30% of the total quantity fed. Initially, these large quantities of ruthenium transported in the vapors resulted in deposits of RuO_2 in the exit throat of the calciner which caused plugging. This was prevented by decreasing the temperature there to between 250° and 400°C . This was accomplished by increasing the length of the calciner above the process furnace from 15 cm to 30 cm and cooling the top with air. Also, the upper elements were not brought up to 1050°C until the product was within a few cm of the zone.

The original flowsheet for the HARVEST process is depicted in Figure 11. Here, the filter/adsorbers have been replaced by a spray condenser/absorber. In the FINGAL process, each pot was connected to its own set of filter/adsorbers. In the HARVEST process, a single liquid scrubbing system is used for all pots on line in the plant.

As in the FINGAL process, the off gas from the solidification unit is maintained in the temperature range 250 - 400°C between the container and the condenser/absorber to prevent the deposition of volatile ruthenium. The condenser (spray type) is used for gas cleaning, cooling, and condensation of water vapor and other volatiles and removes the major fraction of oxides of nitrogens.

This section of the plant is equipped with a pump to recirculate spray liquor and a cooler to remove the heat absorbed from the off gas. The off gas then passes to a caustic scrubber to remove final traces of oxides of nitrogen^a. It is then subjected

^aThough not specifically used for that purpose, caustic scrubbing is also effective in removing small concentrations of volatilized ruthenium⁽³⁷⁾.

Figure 11. Flowsheet for HARVEST Highly Active Waste Solidification Process.

to low temperature dehumidification followed by heating and filtration prior to discharge to the atmosphere.

In the more recent description of HARVEST⁽¹⁴⁾ a heater and ruthenium adsorber follow the spray condenser and scrubber. An outline of the chemical flowsheet and a flow diagram of the process are given in Figures 12 and 13.

2.3.3 French PIVER Process

This process, which has been demonstrated with high activity waste in an industrial pilot plant, produces a borosilicate glass. Unlike other pot calcination-vitrification processes, the evaporation, calcination and fusing of glass are carried out in a fixed refractory alloy pot, and then the product is drained through a freeze valve at the bottom into the storage vessel. The process is similar to the PNL pot calcination process in that evaporation of the waste is completed before the melting of the glass agents (which are added with the waste feed at the start). The borosilicate glass is formed at 1100°-1150°C.

The process^(33,34) is shown in Figures 14 and 15. In order to minimize the number of melting pots required for a plant, the HLLW from the storage tanks is concentrated by a factor of two to 400 g/MTHM by evaporation prior to feeding to the calciner⁽³³⁾. Also, the nitric acid is partially destroyed prior to calcination, to $2M\ H^+$, by reaction with formaldehyde in order to reduce the ruthenium volatilized from the pot. Even so, approximately 15% of the ruthenium is volatilized, along with a small amount of cesium. Each pot calcines HLLW from 0.5 MTHM.

Water in the off gas is removed by a condenser as it exits from the calciner. The gas is then scrubbed in a packed column and passed through two ruthenium filters in series. The ruthenium filters are ferric oxide coated on glass beads and are maintained at 500°-600°C. The condensate

Figure 12. Block Chemical Flowsheet of HARVEST Process

Figure 13. The HARVEST Process.

Figure 14. Block Flow Diagram of PIVER Process.

Figure 15. PIVER Vittrification Unit.

contains approximately 90% of ruthenium that escapes from the pots. The condensate is concentrated in an evaporator (ruthenium recovery unit) and the nitric acid concentrate is reduced to 2 M with formaldehyde. The concentrate containing the ruthenium is neutralized and sent back to the vitrification unit during a special or periodical operation.

Large quantities of vapors are produced during the intermediate concentration of the HLLW (when nitric acid is destroyed by formaldehyde), during calcination, when nitrates are decomposed, and during concentration and denitration of condensate wastes. All the nitrogen oxide vapors are sent to absorption columns (nitric acid recovery unit). The liquid nitric wastes obtained are evaporated. The concentrate, of which there is only a small quantity, is recycled to the feed evaporator. The distillate is treated in a conventional type unit for the rectification of nitric acid, which produces a very low activity 11 N acid. This is recycled back to the irradiated fuel re-processing plant for re-use.

Final treatment of all the gaseous waste coming from the various process units, including air from air-lifts and from sweeping the storage tanks, and the off gases from all active equipment is provided as follows. They are scrubbed with acidified water in a first column and with sodium hydroxide in a second column. Finally, they are passed through an absolute filter unit, mixed with building ventilation air, and released.

2.3.4 Italian Pot Vitrification Process

The quantities of waste to be solidified in Italy are relatively small, and so the pot vitrification process is considered to be practical there. It has been developed in the

laboratory for both phosphate and borosilicate glasses, and tested on a bench scale with simulated fission product solutions⁽³¹⁾. The process, shown schematically in Figure 16, consists of concentration of the wastes along with partial denitration with formaldehyde followed by addition of glass forming agents and additional denitration and/or concentration. The prepared feed, at a concentration of approximately 130 l/metric ton, is pumped to a pot where it is dried, calcined at 600°-800°C, and melted at a temperature dependent on the glass composition. A block schematic diagram of the laboratory equipment used in the development of the process is shown in Figure 17.

The off gases from the calciner pot are passed through a ferric oxide-silica filter/ruthenium adsorber heated to 300°C, prior to going through a condenser to remove water. (In the laboratory experimental tests, the ferric oxide-silica filter was used only in the borosilicate glass experiments). After condensing out the water, the gases are mixed with the off gases from the evaporator/denitration vessels and passed through two scrubbers in series containing 2 M NaOH, where some of the NO_x not removed by the condenser is scrubbed out. The caustic solution also removes some of the volatilized ruthenium.

When phosphate glasses were made, red phosphorus was added to the waste to destroy the nitric acid and, thus, reduce the ruthenium volatility during calcination. The reaction produced the H₃PO₄ required for glass formation. The gaseous reaction products are composed of 39% N₂, 29% NO₂ and 32% NO with traces of N₂O. The red phosphorous additive suppressed the ruthenium losses in the bench test to levels comparable to the entrainment of nonvolatiles (1 to 0.02%).

Figure 16. Schematic Diagram of Italian Pot Solidification Process.

LEGEND

1 Evaporator reactor	6 Pot	11 Condensate tank
2 Stirrer	7 Heating systems	12 Sigmamotor finger pump
3 Feed + glass forming liquid additives tank	8 Peristaltic pump	13 Packed scrubber
4 Glass forming solid additives	9 Condenser	14 Air inlet
5 Pot feeding vessel	10 Reflux condenser	15 Water pump
		16 Ruthenium filter

Figure 17. Schematic Flow Diagram of the Italian Bench-Scale Laboratory Vitrification Plant.

Separate laboratory measurements showed that when $P/HNO_3 = 1.1$, the ruthenium volatilization was 0.75%. When no phosphorus reductant was used, the phosphate vitrification resulted in volatilized ruthenium losses as great as 80%.

When borosilicate glasses were made, ruthenium volatilized was ca. 13%, and the ruthenium filter was used to trap it. A bench-scale plant has been constructed for tests with radioactive wastes. Its flow diagram (Figure 18) is similar to that for the laboratory apparatus with HEPA filters added prior to the exhaust.

2.4 PHOSPHATE GLASS FORMATION

A phosphate glass process was originally developed, using simulated waste, at Brookhaven National Laboratory⁽³⁸⁻⁴⁰⁾, and then Battelle's Pacific Northwest Laboratories performed hot pilot-plant development studies of the process in the WSEP program^(17,41,42). The Italian pot calcination/vitrification process has also been developed for phosphate glasses (see Section 2.3.4).

2.4.1 PNL Phosphate Glass Process

In this process^(17,41,42), the waste which contains all of the melt-making phosphate additives is concentrated by a factor of 2 to 10 and partially denitrated (60 to 90% of nitrate removed) at 120° to 140°C to a thick, syrupy, aqueous phosphate slurry. The slurry is fed to a separate continuous melter where final volatilization of the water, nitrates, and other volatile constituents is accomplished, and the material is heated to 1000° to 1200°C to form molten glass. The molten glass flows through an overflow weir or a freeze valve into the receiver-storage pot below. After the pot is filled, it is cooled, sealed, and taken to storage. The process is shown schematically in Figure 19.

Figure 18. Schematic Flow Diagram of the Italian Bench-Scale Plant for the Radioactive Vitrification Tests.

Figure 19. Phosphate Glass Solidification Process.

From 2 to 10% of the total ruthenium fed to the solidifier was volatilized and/or entrained from the solidifier during the tests; entrainment of nonvolatiles varied from 0.2 to 0.3% during the first series of tests⁽⁴¹⁾ but was only 0.04 to 0.07% during the final series⁽⁴²⁾. Volatilization and entrainment of ruthenium from the denitrator/evaporator ranged from 0.5 to 0.9% while entrainment of nonvolatiles was 0.001 to 0.06%.

Cesium evolution from the melter was slightly higher than could be accounted for by entrainment. Cesium volatilization ranged from 0.05 to 0.1%. Approximately 3% of tellurium present in the feed was volatilized. Runs made with non-radioactive feed at Brookhaven indicated that 50 to 100% of selenium can be expected to volatilize, although this is not expected to present a problem because of the small quantities present.

The predominant off gases generated in the glass making step in the melter are water, nitrogen oxides, sulfur oxides (when present in the waste), and, to a lesser extent, phosphates. This stream is routed through a platinum - 5% iridium off gas line to the melter condenser. The temperature of the gases passing through this line was maintained in the range of 400 to 475°C to prevent condensation and thereby minimize corrosion in the line.

The off gases from the denitrator/evaporator and from the melter (or melter condenser when used for sulfate removal) were routed to the APS (see Section 2.2.1) for cleanup.

2.5 ROTARY KILN VITRIFICATION

France is developing this process^(14, 43-47) as a successor to its PIVER pot process (Section 2.3.3) for the formation of borosilicate glass from its wastes. It is a continuous

process called the AVM process, providing increased capacity for the glass making. An industrial plant (approximately 2 ton/day capacity) has been constructed at Marcoule, and it is scheduled to process radioactive wastes beginning July 1977⁽⁴⁷⁾.

A schematic diagram of the process is shown in Figure 20. The HLLW is preconcentrated to increase throughput. The calcination additives include azodicarbonamide which aids in breaking up the calcine by a "popcorn" action and an organic compact called Ferupore which helps in denitration and reduces ruthenium volatilization. The prepared waste is fed to a heated tube which is on a 3% incline from the horizontal and which rotates at 30 rpm. The walls of the tube are heated in sections electrically; the temperature varies from 225°C at the feed point to a maximum of 600°C. The feed is calcined in this device, and the calcine product falls into a melting pot where it is blended with glass frit. Total decomposition of the residual nitrates occurs in the pot, and a glass is formed at 1150°C. When the pot is filled, the glass is drained through a thermal valve into the final receiving/storage containers. Off gases from the melter pass to the treatment system through the calciner.

The primary wastes to be vitrified at the Marcoule plant will be from the reprocessing of natural uranium fuels from graphite gas reactors, and so, will contain fluoride. The off gas from the melting furnace, and the calciner contains, in addition to steam and nitrogen oxides, some volatile products (boron, cesium, ruthenium, fluorine compounds) and dusts. The dusts are trapped by a wet scrubber (labeled dust cleaner in Figure 20) that sprays the stream with acid solution which is continuously returned to the calciner via the feed system. Water is then condensed out for concentration

Figure 20. The Continuous Rotary Kiln Process Used at the Marcoule Vitrification Plant (AVM).

and recycling to the waste feed system to the calciner. The scrubber and condenser will provide some removal of volatilized ruthenium. While the quantity of ruthenium passed into the off gas from the calciner and melter has not been reported, it is likely to be a few percent of the total quantity fed.

The remainder of the off-gas treatment equipment beyond the condenser is an absorption column, a washing column, and absolute filters^(14,45). The absorption column referred to is⁽⁴⁸⁾ heated ferric oxide coated on silica for removal of ruthenium (see discussion of the PIVER process, Section 2.3.3). As with the British HARVEST process (Section 2.3.2) spent ruthenium sorber material is formed into a glass in the melter.

2.6 DRUM DRIER - POT VITRIFICATION

This so-called FIPS (Fission Product Solidification) process is being developed in Germany^(14,49) for wastes from the reprocessing of HTR graphite fuels using the THOREX reagent. Among other considerations, the design of the FIPS process was partially based on the desire to minimize the volumes of off gas requiring treatment because very efficient cleanup of the off gas was required. Also, effective retention of tritium was required, so that processes involving dilution of fission product solution water were excluded.

The FIPS process is depicted in Figure 21. The fission product waste solution is concentrated by approximately a factor of 2 until the nitric acid concentration is ca. 5 M and then is transferred to another vessel where it is partially denitrated by formaldehyde for the purpose of controlling ruthenium volatilized during drying and vitritication. During the denitration, the solution is further concentrated by a factor of about 3. The off gas from the denitration contains NO_x and is routed to nitric acid recovery units. The treated

Figure 21. The FIPS Process.

fission product solution is blended with borosilicate glass-forming additives, and the resulting slurry is dried using a drum drier at 130°C. The drum dips into the slurry and rotates at 2 rpm. A thin film adheres to the surface of the drum which is maintained at a temperature of about 130°C. The drying time is about 20 seconds. The dried waste from the drum is scraped into a ceramic-lined, graphite-clay crucible where it is melted at 1100-1200°C by induction heating and forms a glass by the rising level in-pot method. Nitric acid is recovered in the off-gas treatment system.

The process was developed using cold, simulated wastes, and a small hot cell apparatus was constructed and tested with LWR hot wastes. During melting, some ruthenium volatilized, up to 1%. Some aerosol entrainment from the denitrator also occurred.

The off gases from the concentration units and the denitrator are blended and passed through a condenser where some HNO_3 is recovered. They are then blended with the melter off gas and passed through two nitric acid recovery units in series where oxygen is added at each stage to convert NO_x to HNO_3 in the scrub columns. Finally the gas is subjected to a caustic (1 M NaOH) scrub and released through an absolute filter.

During melting a small nitrogen gas flow streams through the furnace, passes a small gap between the feed pipe and the crucible, and is withdrawn with the melter off gas. The gas stream prevents the distribution of fine dust in the furnace outside the crucible as well as any oxidation of vessel materials. (This probably also assists in minimizing ruthenium volatilization from the melter, due to formation of RuO_4 via oxidation).

The vapors from the drum drier are passed through a condenser for water removal and then recycled back to the drier. Ultimately, residual gases pass through the melter and exit there to the scrubbers.

2.7 CONTINUOUS CERAMIC MELTER

Joule-heated, ceramic-lined melters are gaining wide use in the glass industry. Off-gas effluents are low, the melter has long life, and superior quality glass is produced. Application of this type of process to the solidification of HLLW was first investigated in Denmark⁽⁵⁰⁾ and, then, extended development work was done and is continuing in the United States at the PNL^(1,13). Because a joule-heated, ceramic melter can attain higher temperatures than other melters, higher silica content glasses, which generally have better chemical stability than glasses with lower silica content, can be formed.

Recently, France has begun investigation of a joule-heated, ceramic melter using induction coupling to the glass to provide the needed melting energy⁽¹⁾. Reports of advanced developments of this process are not available, and it will not be described here.

Germany is using a continuous joule-heated, ceramic melter for its PAMELA process in which glass beads are formed and then cast in a metal matrix.

In a continuous ceramic melter, the HLLW solution, with glass frits added to make a slurry, is evaporated, calcined, and vitrified directly in the melter. If desired, throughput can be increased by pre-evaporating some of the water from the waste solution in a wiped film evaporator (see Section 2.8). Or calcine from a spray calciner, for example, can be vitrified into the borosilicate glass in the continuous ceramic melter.

The concept for a joule-heated, continuous ceramic melter is shown in Figure 22⁽¹⁾. Joule (ionic) heating of the glass is accomplished by passing a current between electrodes submerged in the melt. Alternating current creates internal friction heating due to ionic (principally Na^+) motions. Start-up is accomplished by using a sacrificial heating element to bring the temperature of the glass up to where ionic conduction is adequate to produce heating.

The molten glass is contained by a ceramic liner surrounded by water-cooled plates. The glass formed is drained through an overflow line into a storage canister.

2.7.1 Denmark Continuous Ceramic Melter

The joule heated melter used in the Danish program⁽⁵⁰⁾ is shown in Figure 23. It was tested with a synthetic waste solution which was fed directly to the melter and a borosilicate glass was produced at 1100-1200°C. The solution used did not simulate a fission product nitrate solution but contained stainless steel sulfate and aluminum dissolved in sodium hydroxide.

Little attention was given to the off-gas system design. Initially, only a condenser was used to remove water vapor. However, the off-gas pipe to the condenser often plugged. Therefore, a prefilter of design shown in Figure 24 was tested. The off gas was made to pass through the glass frit as it was added to the feed. The design, in which a scraper was utilized to push used frit prefilter material into the melter, was not completely satisfactory. The layer of filter medium beneath the lowest scraper depth was slowly blocked by dust and intolerable pressure drops developed in less than a week. The filter was efficient for keeping the off gas to the condenser clear.

Figure 22. Continuous Ceramic Melter.

Figure 23. Danish Ceramic Melter.

Figure 24. Continuous Prefilter for Danish Ceramic Melter.

2.7.2 PNL Continuous Ceramic Melter

The program for development of this process was initiated in 1973⁽⁵¹⁾, and four laboratory scale melters were designed and tested⁽⁵²⁻⁵⁵⁾. Based on these studies, an engineering-scale melter, shown in Figure 25, was designed and constructed⁽⁵⁶⁾. This has been tested using simulated waste calcine with glass frit and using simulated HLLW solution with glass frit additives and has produced 3.6 kg of glass at 1150°C⁽⁵⁷⁻⁵⁹⁾.

No special attention has been given to development of an off gas cleanup system to date. Inherently, the process has a small total gas volume flow rate and, so, cleanup devices can be relatively small and inexpensive. The engineering tests indicated that, in the direct feeding mode, when the pool was covered with the waste solution (2.4 cm thick), less than 0.5% of the waste was entrained in the off-gas stream. No measurements have been reported of ruthenium behavior in the process.

2.7.3 German PAMELA Process

This process⁽¹⁴⁾, being developed by the Gelsenberg Company, in collaboration with Eurochemic, will be used to solidify HLLW from the processing of LWR and HTR fuels. The process, including the off-gas treatment system, is depicted in Figure 26. The liquid waste is denitrated with formaldehyde and concentrated by a factor of 5 in the same vessel. Glass-forming reagents are added and the feed is transferred to the ceramic melter. Thus far phosphate glasses have been made, and, so H_3PO_4 is the additive, but plans are to extend the studies to include making borosilicate glass. Following vitrification in the ceramic melter, glass beads are produced by allowing the liquid to drip from nozzles as

Melting Cavity Dimensions 0.36m wide, 0.76m long, 0.30m deep
 Outside Dimensions 1.28m wide, 1.36m long, 0.89m high

Figure 25. PNL Engineering Scale Ceramic Melter.

Figure 26. The PAMELA Process.

droplets onto a rotating disc. The glass beads are incorporated into a metal matrix by blowing them into the molten metal with an inert gas. The final product is called VITROMET.

There is no dust formation from the process. The off gas from the melter is blended with the denitration/concentrator off-gas, and then the treatment is similar to that for the FIPS process (Section 2.6) except the final caustic scrubber is replaced with an additional HNO_3 recovery unit. Off-gas treatment, then, consists of recovering of nitric acid with condensation of water and final filtration. Oxygen is added for oxidation of NO_x at the inlets of the two HNO_3 recovery units following initial condensation.

A bench-scale unit has been in operation since the end of 1974; it has been used to process 150 l of Purex high-level waste obtained from Eurochemic into 10 kg of phosphate glass beads. Also, two hot VITROMETS have been prepared. Engineering for a pilot plant facility will begin in 1977.

2.8 WIPED FILM EVAPORATOR

Wiped film evaporators have been developed for use in industry for processing heat sensitive materials; they are characterized by low retention times of feedstock. Studies⁽¹⁾ are underway at the PNL in the United States to determine the applicability of wiped film evaporation of LWR HLLW for producing concentrated slurries⁽⁶⁰⁻⁶²⁾ or dried powder⁽⁶³⁾ which can be fed to and vitrified in a ceramic or metallic melter. Little attention has been given to off-gas treatment development to date. The process is reviewed here to provide an indication of what the characteristics of the off gas may be.

The concept of a wiped film evaporator is shown in Figure 27. The feed may contain additives to control the characteristics of the final product. The wipers, which have

Figure 27. Wiped Film Evaporator.

a clearance of 0.7 mm from the wall, rotate at approximately 160 rpm. The walls are heated with steam at 8.2 atm gauge pressure (177°C), or they may be heated with circulating oil. The product, shown in Figure 27 as a concentrated slurry, may also be formed as a free flowing dry powder. The product outlet is connected to the inlet of a melter or pot calciner for final treatment of the waste.

The process has been demonstrated for simulated HLLW with the production of a 50 percent slurry and with evaporation to a free flowing solid. The direct conversion of the slurry concentrate to a borosilicate glass has been demonstrated with a metallic melter, in-can melter, and ceramic melter.

The off-gas stream contains condensable water and nitric acid, noncondensable gases, and volatile or entrained solids.

When the evaporator concentrate was dripped into the melter, radiant heat from the melter dried the slurry to a solid onto the feed tube and resulted in plugging of the tube. Also, there was solids carryover from the melter into the off-gas system; this was apparently aggravated by high water concentrations in the evaporator product. An attempt was made to recycle the melter off gas and its entrained solids back to the evaporator, including routing the off gas back up through the evaporator concentrate discharge nozzle. However, this only hastened the plugging of the tube with dried concentrate. A more successful technique was to pump the melter off gas with a steam ejector up through a Raschig ring-packed column and into a condenser. The condensed steam and melter off gas then dropped back down through the packed column, scrubbing the rising gases. The refluxed condensate, with its load of solids, then drained out of the scrubber unit and into the evaporator feed inlet nozzle.

An additional change was to drip the slurry into the melter canister through a 3-m long, 20-cm diameter (same diameter as the melter) pipe. In this mode, the glass frit was added along with the slurry to the melter. Again, melter off gas was routed to the evaporator through the scrubber/separator described above. A solids carryover of 50g/hr was observed for a processing rate of 26.5 l/hr of HLLW.

2.9 MISCELLANEOUS OFF-GAS TREATMENT SYSTEMS AND RUTHENIUM SORBENTS

The processes described so far have been developed and tested with integrated off-gas treatment systems on the laboratory, pilot plant, or plant scale. In this section a few individual devices (sorbents) developed or tested for volatilized ruthenium removal are discussed. Ruthenium-106 is one of the most dominant radioisotopes (in terms of curies/liter) in HLLW. Thus, removal of volatilized ruthenium from the off gas from a waste solidification facility requires particular attention. This is enhanced by the fact that, generally speaking, volatilized ruthenium is more difficult to quantitatively remove from an off gas than is particulate material.

Hanson and Kaser⁽⁶⁴⁾ have recently considered off-gas treatment needs for waste solidification facilities and proposed a system design which is also reviewed in this section.

2.9.1 PNL Proposed Off-Gas Cleaning System

Hanson and Kaser of Battelle's PNL have reviewed the individual types of control for particulates, NO_x, iodine, and ruthenium in the off gas from waste solidification processes and have proposed a design for a general off-gas treatment system that might be applicable to any waste solidification

process⁽⁶⁴⁾. The proposed system is depicted in Figure 28. Their design philosophy includes assumption of high solids loading or potential loading in the off gas, removal of water (with at least partial removal of HNO_3), removal of iodine from the effluent stream, and removal of NO_x . The option is left open whether to recover nitric acid or reduce the NO_x to N_2 with ammonia over a catalyst bed.

The first stage of treatment is removal of particulates with a venturi scrubber. If a solidification process such as spray calcination or continuous inert-bed, fluidized-bed calcination is chosen which produces a powder, sintered metal filters (SMF), as depicted in Figure 28, are positioned in line before the scrubber system. The venturi scrubber is then considered a back-up device for the SMF. In the case where a cyclone is used as the primary solids removal device, as in a conventional fluidized-bed process, the venturi scrubber is required for secondary removal of fine material.

The venturi scrubber operates by recirculating the scrub solution through a cooler. Dissolved and suspended solids in the acid scrub are periodically routed back to the evaporator-feed system for the calciner. A knockout pot in the off-gas stream exiting the scrubber removes entrained aerosols. If necessary, a fiber-type mist eliminator may be placed after the knockout pot.

Partial removal of water occurs in the venturi scrubber. The remaining condensables are removed by a condenser following the knockout pot/mist eliminator. A single-pass, down-draft shell and tube condenser with the process fluid on the tubeside is suggested because of its easy maintenance and ability to handle moderate solids loadings. The downdraft flow provides good aerosol deentrainment and some self-cleaning.

Figure 28. PNL Proposed Waste Solidifier Off-Gas Treatment System.

Liquid from the knockout pot and the condenser, in excess of that needed to operate the venturi scrubber, is processed through the HLLW evaporator and recirculated to the calciner.

Oxides of nitrogen are next removed from the off gas, either by oxidation and scrubbing out as HNO_3 , as shown in Figure 28, or by reducing them to N_2 with NH_3 over a catalyst bed. If HNO_3 is scrubbed out, a subsequent condenser is required to remove entrained water for return to the scrubber.

Final off-gas cleanup involves removing the small fractions of volatilized ruthenium and particulates, which pass through the devices described so far, and the iodine. Since iodine removal methods may also tend to remove some ruthenium (thereby poisoning the iodine adsorber) and ruthenium removal methods trap little iodine, the ruthenium is trapped first. Either silica gel or heated ferric oxide is proposed for use as the ruthenium adsorbent. The former requires preheating the gas to a temperature just above the dew point. A filter is used following the adsorber to remove entrained dust from the adsorber prior to passing the gas through the heated iodine adsorber. Potentially useful iodine sorbents suggested for application include metal-exchanged zeolites, silver impregnated amorphous silicic acid, aluminum and silver oxides, and silver and other metal cation impregnated alumina.

Final particulate filtration with HEPA filters is included to prevent any particle or entrained droplets from leaving the system.

Off gas from the HLLW evaporator is passed through a condenser, where water (and some HNO_3) is removed and sent to the waste acid evaporator, and then blended with the calciner off gas before the NO_x removal. Similarly, the waste-acid

evaporator off gas is treated with a condenser, which recovers the HNO_3 , and blended with the calciner off gas stream for final NO_x removal.

2.9.2 Ruthenium Sorbents

The types of sorbents that have been investigated for the removal from an off-gas stream of ruthenium volatilized from evaporation and high temperature solidification of nitric acid waste solutions were recently reviewed by Christian⁽²⁾. An earlier, quite thorough literature review was given by Courtois⁽⁶⁵⁾ who gave particular attention to ruthenium removal in a fluoride volatility process.

Two types of sorbents are predominantly used for volatilized ruthenium adsorption: silica gel and ferric oxide based materials. These have both been mentioned in the various sections on waste solidification processes. Hanson et al.⁽⁶⁶⁾ and Rhodes^(67,68) performed some early studies on ruthenium sorption onto silica gel. Decontamination factors of 1000 were obtained. Total loadings as high as 2000 g Ru/m^3 silica gel were obtained without ruthenium breakthrough. The superficial vapor velocity has no effect on the adsorption of ruthenium in the range 0.2 to 0.5 m/sec. Approximately 90% of the adsorbed ruthenium species can be washed off with hot water.

A DF of 1000 can be obtained in the vicinity of 70-100°C. Temperatures of this order are normally required for the off gas from a fluidized-bed calciner in order to stay above the dew point. Alleman and Barton⁽⁶⁹⁾ obtained a DF of 100,000 at 25°C with a flow velocity of 0.03 to 0.2 cm sec^{-1} through a 6.4 cm deep bed.

Edwards⁽⁷⁰⁾ also investigated silica gel as a ruthenium adsorber. Newby and Barnes⁽⁷¹⁾ recently evaluated a number of potential ruthenium adsorber materials for a fluidized-bed calciner system. Of a number of materials investigated,

Davison Chemicals Grade 40 silica gel, hydrous zirconium oxide, and ferric oxide (heated) were found to provide DFs of 1000 or greater. Silica gel was recommended for use in a facility because of its regenerability (by washing with hot water) and low temperature of operation.

Hydrous zirconium oxide gel, while regenerable, tends to cake if inadvertently exposed to moisture below the dewpoint and, so, is not recommended for use. Other materials investigated which were unacceptable for application were phenolic-based ion exchange resins, styrene-divinyl-benzene ion exchange resins, acid resistant molecular sieves, porous glass, impregnated alumina, a copper sulfide ion exchanger, and a zirconium oxide hydrate-dithionate ion exchanger. These either gave unsatisfactory ruthenium decontamination ($DF < 1000$) or were not chemically resistant to the simulated calciner off gas.

Rastogi et al.⁽⁷²⁾ investigated the retention of volatilized ruthenium on iron oxide coated silicious bed materials. At a flow velocity of 0.046 m/sec and a column temperature of 350°C, efficiencies of 99.9% ($DF = 1000$) were obtained.

In addition to their thorough study on silica gel, Hanson et al.⁽⁶⁶⁾ also performed laboratory investigations of several other potential adsorbent materials, including calcined alumina, activated alumina, polyethylene, molecular sieves, and stainless steels. Sixty-six-cm deep beds of activated alumina and Linde Type 4A and 5A molecular sieves at 115°C provided reasonably good DFs, but these materials were chemically attacked by the calciner off gas. Calcined alumina under similar conditions provided a DF of only 110. Marlex (trademark for Phillips' family of polyolefins) at 110°C provided DFs from 200 to 426 with a 58 cm column and was

stable in the simulated calciner off gas stream. No breakthrough of ruthenium was observed at a loading of 14 g Ru/m^3 . Loaded material cannot be regenerated. Type 301 stainless steel at 115°C did not remove ruthenium from the gas stream. Carpenter-20 Yorkmesh at 80°C provided DFs of 130-225 with a bed depth of 34 cm.

Ortins de Bettencourt and Jouan^(73,74) recommend use at $450\text{-}500^\circ\text{C}$ of glass granules coated with ferric oxide for volatile ruthenium trapping. This is what was incorporated into the French PIVER (Section 2.3.3) and rotary kiln (Section 2.5) processes.

Courtois⁽⁶⁵⁾ reviewed literature data on sorbents which might be effective in removing $\text{RuF}_5(\text{g})$ from a dry gas stream. One group included inorganic fluorides which complex the RuF_5 and are not discussed here. Others reviewed were materials which had been investigated for the sorption of $\text{RuO}_4(\text{g})$. Some of the studies are discussed elsewhere in this document, and the results are not repeated here. Of the remaining materials reviewed by Courtois, many are impractical for application, primarily because of the low DFs (substantially less than 1000) obtained for volatilized ruthenium. The specific materials reviewed are steel, alumina, crystalline sodium and calcium aluminosilicates, activated charcoal, iron oxide, iron oxide supported on silica, (other) metallic oxides, polyethylene, and silica gel. Those results of studies on materials which may provide high DFs (approaching 1000) for ruthenium and which are not discussed elsewhere in this document are reviewed here.

Crystalline sodium aluminosilicate provides a DF of 715 at 115°C but a capacity of only 7 g Ru/m^3 . Crystalline calcium aluminosilicate gives a DF of 800 at 115°C and a capacity of 3.9 g Ru/m^3 . The materials are not suitable for

recovering ruthenium by leaching, but they appear to adsorb compounds other than those of ruthenium.

Activated charcoal traps 0.2 g of RuO_4 per gram of charcoal before saturation is reached⁽⁷⁵⁾. However, several minutes later, the charcoal explodes with a flame. No DF was given.

Rastogi and Sehgal⁽⁷⁶⁾ report that iron oxide at 300°C is not efficient for retention of volatilized RuO_4 . However, as mentioned earlier in this Section, Newby and Barnes⁽⁷¹⁾ obtained good retention at 400°C of ruthenium volatilized at 400°C from a nitric acid solution.

Rastogi and Sehgal⁽⁷⁶⁾ did obtain good retention when iron oxide was supported on silica. The volatilized ruthenium species is reduced to RuO_2 on the surface where it is fixed. The fixed RuO_2 catalyzes the decomposition of the gas species. For efficiencies on the order of 99% the temperature should be greater than 200°C^(77,78). Efficiency of the filter increases with increasing temperature. Bancroft et al.⁽⁷⁹⁾ found that, for temperatures between 300 and 800°C, increasing the gas linear velocity by a factor of 20 (from 0.009 to 0.18 m/sec) does not affect the fixation of RuO_4 . These are quite slow velocities, however, and the results are in line with those found⁽⁷¹⁾ for ferric oxide in which the efficiency at 0.21 m/sec was significantly less than that at 0.12 m/sec. The British⁽⁸⁰⁾ found no temperature effect between 150 and 250°C.

At 200°C, 73% of RuO_4 decomposes in the first 2 cm of bed⁽⁷⁸⁾. At 320°C, the capacity is greater than 57,000 g of RuO_4 per m^3 (or 29,000 g Ru/m^3) of filtering material⁽⁷⁶⁾.

3. EVALUATION OF OFF-GAS TREATMENT SYSTEMS FOR HIGH-LEVEL WASTE SOLIDIFICATION PROCESSES

The off-gas treatment systems described in Section 2 are critically analyzed in this section for their measured or expected abilities to remove process airborne effluents.

The types of effluents of concern include radioactive particulates and aerosols, volatilized ruthenium and cesium, vaporized radioiodine, and NO_x . Selenium and tellurium have also been observed as vapor species in the off gas of some high temperature solidification processes. Technetium and antimony are potentially volatile species in a high temperature process, but no results of studies of their behaviors or their removal from an off-gas stream have been reported. Water vapor is a major off-gas constituent which can affect the design and performance of an off-gas treatment system.

Following an assessment of criteria for evaluating the cleanup systems, each process is analyzed for its measured or expected abilities for removing particulate material and volatilized species from the off gas. The evaluations take into account the quantities of these effluents released from the solidifier unit and removal efficiencies of the off-gas components, and then the estimated stack releases are compared with allowable release rates.

The various effluent removal efficiencies of many of the off-gas treatment systems have not been measured. To estimate overall system performances, characteristic decontamination factors (DFs)^a across typical individual components for the various species of concern are reviewed. The individual component approximate DFs are used when necessary when integrated off-gas systems are considered.

^aDecontamination factor across a device = concentration in influent stream divided by concentration in effluent stream.

3.1 AIRBORNE EFFLUENT REMOVAL REQUIREMENTS

In order to evaluate the adequacy of an integrated off-gas cleanup system, an estimate of required decontamination factors for the various off-gas constituents is needed. This, in turn, requires knowledge of processing rates for each constituent and of maximum allowable release rates. Processing rates can be fairly reliably estimated. However, allowable release rates are not well defined. A brief discussion of each is given here to aid in assessing the performances of the various off-gas treatment systems. The discussions are based on conditions and present and anticipated requirements in the United States.

3.1.1 Processing Rates

The flowsheet for the reference waste solidification facility described in the Commercial Waste Management Statement (CMWS), which is being prepared for ERDA and coordinated by the Battelle PNL, is based on a fuel and waste processing rate of 6 2/3 metric tons of uranium or equivalent heavy metal (MTHM)^a per day. This rate will be assumed here for the purpose of evaluating off-gas treatment systems for waste solidification facilities.

The assumptions of the CMWS, and which are also used here, are that the HLLW is solidified at an age of 1 1/2 years from the time that the fuel is discharged from the reactor, and that the fuel burnup is 28,700 MWd/MTHM^b. The concentration of the HLLW fed to the calciner is assumed to be 379 g/MTHM (100 gal/MTHM). The relative abundances (activities) of potential gaseous and major solid airborne radioactive effluents which are fed to a waste solidification facility are listed in Table 2 for these circumstances.

Masses of the volatile and potentially volatile species are given so that capacities of cleanup devices may be evaluated

^aMTHM = Metric tons of heavy metal in fuel as charged to reactor.

^bMWd = Megawatt days.

TABLE 2
RADIOACTIVE PRODUCTS INTRODUCED TO WASTE SOLIDIFIER FROM HLLW^a

Isotope	$t_{\frac{1}{2}}$, yr	Quantity	
		Ci/MTHM	g/MTHM
Volatile:			
H-3	12.33	33	3.5×10^{-3}
Total H	-----	33	3.5×10^{-3}
Kr-85	10.73	8×10^{-3}	2×10^{-5}
Total Kr	-----	8×10^{-3}	3×10^{-4}
I-129	1.59×10^7	3×10^{-5}	0.2
Total I	-----	3×10^{-5}	0.3
Potentially Volatile:			
Se-79	6.5×10^4	0.34	4.9
Total Se	-----	0.34	44
Tc-99	2.13×10^5	13	7.4×10^2
Total Tc	-----	13	7.4×10^2
Ru-103	0.1084	72	2.2×10^{-3}
Ru-106	1.01	1.8×10^5	54
Total Ru	-----	1.8×10^5	2.0×10^3
Rh-103 _{mb}	56 min	72	
Rh-106 _b	29.9 sec	1.8×10^5	
Te 123m	0.3275	1.5×10^{-2}	1.8×10^{-6}
Te 127m	0.298	4.2×10^2	4.5×10^{-2}
Total Te	-----	4.2×10^2	5.2×10^2
Sb-124	0.1648	0.68	3.9×10^{-5}
Sb-125	2.73	5.7×10^3	5.5
Sb-126 _{mb}	19.0 min	0.54	6.8×10^{-9}
Sb-126 _b	12.4 days	0.53	6.4×10^{-6}
Total Sb	-----	5.7×10^3	15
Cs-134	2.06	1.2×10^5	91
Cs-135	2.3×10^6	0.31	2.7×10^2
Cs-137	30.1	9.1×10^4	1.1×10^3
Total Cs	-----	9.3×10^4	2.4×10^3

TABLE 2 (Continued)

RADIOACTIVE PRODUCTS INTRODUCED TO WASTE SOLIDIFIER FROM HLLW^a

Isotopes	$t_{\frac{1}{2}}$, yr	Quantity	
		Ci/MTHM	g/MTHM
Potential Solids (Major Activities, Only ^c):			
Ce-144	0.7787	2.4×10^5	
Pr-144 ^b	17.28 min	2.4×10^5	
Sr-90	29	6.0×10^4	
Y-90 ^b	64.0 hr	6.0×10^4	
Cm-244	17.9	7.0×10^3	
Total Solids		1.1×10^6	6.5×10^{4d}

^a28,700 MWd/MTHM burnup, 1½ years after discharge from reactor, 379 g/MTHM. Isotope quantities are from the CWMS which is in preparation. They were tabulated by M. J. Steindler, Argonne National Laboratory, using the ORIGEN Code developed at Oak Ridge National Laboratory.

^bThese isotopes are supported by longer-lived parents.

^cIn addition to those listed as potentially volatile (RuRh-106 and Cs-137).

^dIn calcined form; if intermediate level liquid waste (ILLW) is blended and calcined with HLLW, 1.0×10^5 g. calcine/MTHM will be formed. ILLW will contribute negligible activity to the calcine.

where necessary. Rh-103m and Rh-106 are short lived daughters of Ru-103 and Ru-106, respectively, and their activities will essentially follow the path of the ruthenium.

The concentrated HLLW is assumed to contain, in the form of HTO, 8% of the total tritium present in the spent fuels. At the present time, there are no special requirements for tritium control at reprocessing and waste solidification facilities. Therefore, present designs will allow release of all of the tritium. Future plants may be required to recover tritium, however.

The Kr-85 assumed to be present in HLLW represents only 10^{-6} of the total Kr-85, and its total release will be negligible compared with releases from a fuel reprocessing plant, even with krypton recovery.

The iodine in the HLLW represents 0.1% of that present in spent fuel; it will be 100% vaporized in any high temperature solidification process. Ruthenium, which is the most predominant species in the HLLW in terms of Ci/MTHM, may become volatilized during solidification to the extent of 0.002% to virtually 100%, depending on the process and conditions of temperature, mode of heating, cover gas composition, etc. Because of its high total activity, the control of the volatility and removal from the off gas of any quantity volatilized is very important. In any practical process, the volatility will have to be kept quite low, certainly less than 10% and preferably less than 1%.

Several percent of the selenium and tellurium in the feed have been observed to be volatilized in a phosphate glass process. A small amount of cesium may be volatilized in very high temperature processes (near 1000°C). It, too, is a major activity constituent of HLLW.

Almost all of the dissolved and suspended constituents of HLLW will be converted to solids during calcination/vitrification. The only potentially volatile species that can affect the solids mass and activity is ruthenium; if its volatility is reasonably low (<10%), the change in solids composition will be insignificant.

The gross calcined solids activity will be 1×10^6 Ci/MTHM.

Those solids and potentially volatile species listed in Table 2 represent almost all of the activity present in the HLLW, although there are many other species present. Cm-244, while representing only 0.6% of the total activity, has a very small allowable release rate, and, so, influences the solids cleaning requirements for released off gases (see Section 3.1.2). It is listed in Table 2 for later consideration.

Decomposition of the nitrates will produce NO_x in the off gases from the high temperature solidification processes. The HLLW feed will contain approximately 2×10^3 moles NO_3^- per MTHM. If ILLW is blended with the HLLW, the feed will contain approximately 3×10^3 moles NO_3^- /MTHM. The quantity of NO_x evolved from a calciner will be on the order of 60 to 100 parts NO_2 equivalent per million parts stack gas by volume for a typical $52 \text{ m}^3 \text{ sec}^{-1}$ stack gas flow. Some of this would be removed by off-gas cleanup devices.

3.1.2 Allowable Release Rates

The Nuclear Regulatory Commission (NRC) has established a Code of Federal Regulations, 10CFR20⁽⁸¹⁾, which provides standards for protection against radiation hazards arising out of activities under licenses issued by the NRC. The Environmental Protection Agency (EPA) is also developing standards for the NRC to follow in regulating uranium fuel cycle facilities which, in some cases, may be more restrictive than the 10CFR20 standards. The EPA standards⁽⁸²⁾ are based in part on considerations of total radioactive releases from the complete uranium fuel cycle. The general standards established by the EPA with certain exceptions will limit the annual dose equivalent of an individual public member from discharges from uranium fuel cycle operations to 25 millirems to the body, 75 millirems to the thyroid, and 25 millirems to any other organ. Specific limits have been established of 5×10^4 Ci for Kr-85, 5×10^{-3} Ci for I-129, and 5×10^{-4} Ci for combined Pu-239 and other alpha-emitting transuranic radionuclides with half-lives greater than one year as maximum quantities of these

isotopes which may enter the general environment from the entire uranium fuel cycle per gigawatt-year of electrical energy produced by the fuel cycle. The EPA also anticipates that standards for C-14 will be made shortly with considerations of proposals for other long-lived radionuclides following at a later date.

The NRC has not yet established the manner in which the annual dose equivalents allowed by the EPA are to be allocated among the various fuel cycle facilities. Also, the EPA has not established specific standards for the majority of the radioisotopes. The 10CFR20 standards issued by the NRC presently provide the only available numbers for calculating relative process cleanup requirements for various isotopes and are used here for screening those isotopes which may require control and for establishing outside (maximum) limits of release rates for them. The specific standards established by the EPA for Kr-85, I-129, and the transuranic elements are also taken into consideration where practical in assessing off-gas cleanup requirements.

The NRC standards are in part presented in the form of maximum permissible concentrations which may be averaged over one year, maximum, above natural background of radionuclides which may be built in the atmosphere to which an individual may be continuously exposed. The maximum permissible concentration given for each isotope is based on the assumption that it is the only radionuclide released in the area in significant quantity of activity. If there is a mixture of radionuclides, the limiting values are derived from the relationship

$$\sum \frac{C_i}{(MPC)_i} \leq 1 \quad (1)$$

where C_i is the concentration of the i^{th} radionuclide and $(MPC)_i$ is the maximum permissible concentration from the Code for the i^{th} radionuclide when not in a mixture.

An "as low as is reasonably achievable" clause in 10CFR20⁽⁸¹⁾

establishes additional restrictions on release rates. It requires that, if reasonably practical and economical means are available for substantially reducing the releases below those permitted by the tabulated MPCs, they must be used.

The concentrations given for individual isotopes for an uncontrolled area may be taken to be the maximum allowed at the site boundary of a nuclear facility. The maximum permissible concentrations in the gas released from the stack may be related to those specified for the site boundary by the dilution factor which results between the release point of the stack and the site boundary. Dilution factors are site specific and depend on meteorological conditions, atmospheric stability and other time dependent parameters, radial direction and distance from stack, stack height, etc. Atmospheric dispersion data are normally reported in terms of χ/Q , where χ is concentration at a point on the ground resulting from release rate, Q , at plant stack. The dilution factor is related to this term by the equation

$$D = \frac{1}{(\chi/Q) \times F}$$

where D = dilution factor and F = stack gas flow rate.

Use of χ/Q values for a site boundary permits one to calculate maximum allowable rates of release of radionuclides from the tabulated maximum permissible concentrations in an uncontrolled area. For conservative comparisons of expected or measured release rates with those permissible, the most conservatively high value for χ/Q for the boundary of a site should be used. Russell and Galpin⁽⁸³⁾ have tabulated maximum offsite annual average χ/Q values for the NFS (West Valley), AGNS (Barnwell), and GE (Midwest) fuel reprocessing sites. More recently, Kullen et al.⁽⁸⁴⁾ reported estimates of tritium release rates at these plants and related these to % MPC (percent maximum permissible concentration), from which one can infer χ/Q values using the 10CFR20 value for tritium in an uncontrolled area (2×10^{-7} Ci m⁻³). The values obtained from the two reports are summarized in Table 3.

TABLE 3
DISPERSION DATA FOR U.S. COMMERCIAL REPROCESSING PLANTS

Facility	$\chi/Q, \text{ sec m}^{-3}$	
	Maximum Offsite Annual Average, Ref. 83	Ref. 84
AGNS (Barnwell)	5.7×10^{-8}	2×10^{-7}
NFS (West Valley)	4.1×10^{-8}	3×10^{-6} inversion 2×10^{-6} average
GE (Midwest)	2.8×10^{-8}	4×10^{-8}

The only large discrepancy between the two sources is for the NFS plant; the larger values may reflect more recent data. The Barnwell facility is generally used as a reference case when considering waste streams, for example in the CWMS. A value for χ/Q of $1 \times 10^{-7} \text{ sec m}^{-3}$ at the site boundary will be assumed for assessing release rates of radionuclides from a waste solidification facility. For the Barnwell facility, which will have a total stack gas flowrate of $52 \text{ m}^3 \text{ sec}^{-1(85)}$, this corresponds to a dilution factor of 2×10^5 .

MPC values are reported in 10CFR20 for soluble and insoluble species of the different isotopes, and for permanent gas species submerged in a semispherical infinite cloud. For each of the isotopes listed in Table 2, the limiting MPC, i.e., the smallest of the soluble or insoluble and of the gaseous concentration limits, is given in Table 4. As a minimum for prudence the maximum release rate at a facility should not exceed 1/10 the maximum permissible rate, and this minimum criterion will be used in evaluating the off-gas treatment systems. Assuming a χ/Q from stack to ground at site boundary of $1 \times 10^{-7} \text{ sec m}^{-3}$, 1/10 the maximum permissible release rate was calculated for each of the isotopes and tabulated in Table 4. Then, using the daily input of each isotope to the waste solidifier (data from Table 2), 10 times the minimum required feed-to-stack decontamination factor (DF) was calculated and tabulated. Also, 1/10 the

TABLE 4

MAXIMUM PERMISSIBLE RADIOACTIVE RELEASE QUANTITIES FROM WASTE SOLIDIFIER

Isotope	Limiting MPC, $\mu\text{Ci/ml}^a$	1/10 Maximum Permissible Release Rate at Stack, Ci/day ^b	10x Minimum Required Feed- to-Stack DF ^{b,c}	1/10 Maximum Allowed Volatility, %, for Complete Release
Volatile:				
H-3	2×10^{-7}	2×10^4	1×10^{-2}	8×10^3
Kr-85	3×10^{-7}	3×10^4	2×10^{-6}	5×10^7
I-129	2×10^{-11}	2	1×10^{-4}	8×10^5
Potentially Volatile:				
Se-79	1×10^{-10}	9	3×10^{-1}	4×10^2
Tc-99	2×10^{-9}	2×10^2	5×10^{-1}	2×10^2
Ru-103	3×10^{-9}	3×10^2	2	6×10^1
Ru-106	2×10^{-10}	2×10^1	7×10^4	1×10^{-3}
Rh-103m	2×10^{-6}	2×10^5	3×10^{-3}	4×10^4
Rh-106	$>1 \times 10^{-10}$	>9	$<1 \times 10^5$	$>7 \times 10^{-4}$
Te-123m	1×10^{-10}	9	1×10^{-2}	8×10^3
Te-127m	1×10^{-9}	9×10^1	3×10^1	3
Sb-124	7×10^{-10}	6×10^1	8×10^{-1}	1×10^2
Sb-125	9×10^{-10}	8×10^1	5×10^2	2×10^{-1}
Sb-126m	$>1 \times 10^{-10}$	>9	$<4 \times 10^{-1}$	$>2 \times 10^2$
Sb-126	$>1 \times 10^{-10}$	>9	$<4 \times 10^{-1}$	$>2 \times 10^2$
Cs-134	4×10^{-10}	3×10^1	2×10^4	4×10^{-3}
Cs-135	3×10^{-9}	3×10^2	8×10^{-3}	1×10^4

TABLE 4 (Continued)
MAXIMUM PERMISSIBLE RADIOACTIVE RELEASE QUANTITIES FROM WASTE SOLIDIFIER

Isotope	Limiting MPC, $\mu\text{Ci/ml}^a$	1/10 Maximum Permissible Release Rate at Stack, Ci/day ^b	10x Minimum Required Feed- to-Stack DF ^{b,c}	1/10 Maximum Allowed Volatility, %, for Complete Release
Cs-137	5×10^{-10}	4×10^1	1×10^4	7×10^{-3}
Potential Solids (Major Activities in Addition to Those Above):				
Ce-144	2×10^{-10}	2×10^1	9×10^4	
Pr-144	$>1 \times 10^{-10}$	>9	$<2 \times 10^5$	
Sr-90	3×10^{-11}	3	2×10^5	
Y-90	3×10^{-9}	3×10^2	2×10^3	
Cm-244	3×10^{-13}	3×10^{-2}	2×10^6	

^aLimiting MPC = smallest of maximum permissible limits for soluble, insoluble, and gaseous species.

^bAssumes χ/Q from stack-to-ground at site boundary = $1 \times 10^{-7} \text{ sec m}^{-3}$.

^cDF = decontamination factor; feed rate: HLLW from 6 2/3 MTU/day of fuel irradiated to 28,700 MWd/MTHM and cooled 1 1/2 years.

maximum allowed volatility for each potentially volatile species is listed assuming that the volatilized material is completely released in the stack gas.

The required DF values less than unity and the maximum allowed percent volatilities greater than 100 listed in Table 4 are, of course, physically meaningless; but they are included to provide an indication of the safety factor that exists for those isotopes.

For the minimum criterion of maintaining concentrations below 1/10 of the 10CFR20 MPC values, the 1/10 maximum permissible release rate (MPRR) at the stack may be approached for only a single isotope while all others (including releases from other activities at the fuel reprocessing plant) are much less than their 1/10 MPRR. Overall,

$$\frac{\sum_i (RR)_i}{\sum_i (MPRR)_i} \leq 1/10, \text{ i.e., } \frac{\sum_i C_i}{\sum_i (MPC)_i} \leq 1/10$$

must be adhered to (RR = release rate). Of the gaseous species which may be released from a reprocessing operation (H-3, C-14, Kr-85, I-129), only Kr-85 would approach or exceed 1/10 MPRR. Total release of H-3, C-14, and I-129 would result in 14, 3×10^{-5} , and 13%, respectively, of their 1/10 MPRRs. Total release of the krypton would result in a concentration at the site boundary of 20% MPC or twice 1/10 MPC and would require that all other releases be considerably below their 1/10 MPRR's. If 90% of the Kr were separated from the dissolver off gas, restrictions on other releases would be less severe. This case will be assumed in assessing the off-gas releases from the waste solidifier. It is also essential that less than 0.001% of the Ru-106 be allowed to escape from the fuel reprocessing off gas to the stack (0.001% release would result in 60% of its 1/10 MPRR).

Curium-244 is, by an order of magnitude, the worst isotope present in HLLW in terms of overall required feed-to-stack DF in order to meet 10CFR20 concentration limits. Thus, if a solidifier

off-gas system is designed to remove particulates sufficiently to meet the Cm-244 needs, it will be adequate for removing all other solid materials which are formed. The minimum required feed-to-stack DF is 2×10^6 for meeting 1/10 the MPC at the site boundary. (Curium is formed as a solid in the calciner and is not volatile).

The volatile species present in HLLW may be totally released according to the assumptions and criteria of Table 4. The potentially volatile species Se and Tc may also be completely volatilized and released. For all of these components, then, no critical assessment will be provided for the individual waste solidifier off-gas treatment systems except to note their flowpaths when known.

The short-lived rhodium daughters of Ru-103 and Ru-106 will not, themselves, be volatile, but any volatilized ruthenium will result in airborne activities of the rhodium daughters identical to the ruthenium activities. However, the required removal for ruthenium is also sufficient for its accompanying rhodium, and no special consideration is required for the rhodium.

While the semivolatile isotopes may become vaporized in the waste solidifier to a small extent, most are quickly condensed and are removed in the cooler regions outside the calciner. In fact, observations concerning their volatilities have been made by analyzing scrub solutions and condensates. Thus, even though some processes may result in significant volatilization of some of these isotopes, they should not result in significant airborne gas species released to the stack, and no special consideration is required in terms of meeting 10CFR20 MPCs. Ruthenium is the one exception. Under certain conditions it can remain as a stable gaseous form even in the cooler regions of the off-gas train and be released as a gas. Because of this and because its minimum required feed-to-stack DF is large, particular attention will be given to ruthenium flowpaths for the various waste solidification processes.

The above evaluation based on 10CFR20 MPCs has brought out the important points that Ru-106 and Cm-244 require greatest attention in terms of controlling their releases in waste

solidification processes. No direct comparison can be made for ruthenium to the EPA standards⁽⁸²⁾, but a specific limit is provided by the EPA for transuranic elements. It permits maximum combined release of all alpha-emitting transuranic elements with half-lives greater than 1 year of $0.5\text{mCi/GW}_{\text{e}}\text{yr}^{\text{a}}$ from the entire fuel cycle. Curium-244, at $7.0 \times 10^3 \text{ Ci/MTHM}$, is the most abundant transuranic isotope in terms of Ci/MTHM, by a factor of 8.4 over other transuranic elements, present in 1.5 year HLLW. If one assumes that most of the transuranic effluents will be generated from the solidification process and provides a safety factor of 10, the maximum release rate of Cm-244 in the solidifier gas effluents that will be permitted by the EPA standard is calculated to be $1.3 \text{ }\mu\text{Ci/MTHM}$. This is based on an fuel requirement of $40 \text{ MTHM/GW}_{\text{e}}\text{yr}$, the value used in the CWMS. This release rate corresponds to $8.3 \text{ }\mu\text{Ci/day}$, a factor of 3.1×10^3 less than permitted by 1/10 MPC of 10CFR20. This would require a feed-to-stack DF of 6×10^9 , compared with 2×10^6 required by the 1/10 MPC of 10CFR20.

Similar assumptions and calculations for Kr-85 and I-129 show that the EPA standards for releases of these isotopes from a fuel reprocessing facility are more restrictive than the 10CFR20 MPCs by factors of approximately 40 and 2.4×10^4 , respectively. This will not, of course, impose any requirements for removal of Kr-85 from waste solidifier off gases, but is marginal in requiring removal of I-129. One-tenth the EPA standard for I-129 will permit a release of approximately $13 \text{ }\mu\text{Ci I-129/MTHM}$ for the entire fuel cycle. The iodine in the HLLW is assumed to represent 0.1% of the total iodine formed in the fuel and corresponds to a concentration of $30 \text{ }\mu\text{Ci/MTHM}$. This is one-fourth of the total EPA approximate release limit for I-129. No presently developed waste solidification system includes iodine

^a GW_{e} = gigawatt electrical.

removal. Individual evaluations of iodine control are, thus, not made in the review.

The above comparisons for Cm-244 indicate that significantly tighter demands will be placed on containment of particulates in a waste solidification process when the EPA standards become effective (December 1, 1979). While the EPA restrictions on releases for ruthenium and other volatile and potentially volatile species other than Kr-85 and I-129 are not presently established, it is likely that they too may be more severe than the 10CFR20 MPC limits impose. However, conjecture cannot be made at this time, and the 10CFR20 MPCs are used for evaluations of the process gas effluent characteristics in this review, with the recognition that they may be too liberal in the future. The ALARA clause in 10CFR20 may, of course, require release limits for a particular species below those established by the EPA as well as by the 10CFR20 MPC if reasonably practical and economical means are available for implementing smaller releases. In practice, the ALARA clause must be used in designing a nuclear facility, in addition to the 10CFR20 MPC and the EPA standards.

To summarize, the minimum required feed-to-stack DFs for radionuclides which are used in evaluating the different processes is 6×10^9 for entrained particulates and aerosols and 7×10^4 for volatilized ruthenium. These DFs will result in release rates of particulates equal to 1/10 the rates allowed by the new EPA standards and in concentrations of ruthenium at the site boundary corresponding to 1/10 the 10CFR20 maximum allowable concentration for Ru-106.

Nitrogen oxide emission limits are as nebulous as those for the radionuclides. The Environmental Protection Agency specifies 0.05 ppm by volume for ambient air quality^(86,87). For a concentration in the stack gas of 100 ppm (see Section 3.1.1) and a dilution factor of 2×10^5 from stack-to-ground (assumed earlier in this section) complete release of the NO_x would result in a concentration in air of 0.5 ppb, two orders of magnitude

below the standard. Local requirements may place additional restrictions on the release of NO_x . For example, San Diego County restricts the concentration in a stack gas to 250 ppm maximum, which is near the actual maximum possible concentration in a reprocessing facility stack gas. This concentration may be approached for a new facility only if it results in no significant change in present air quality. Thus, it is likely that in some locations, the NO_x from a calciner will have to be removed or destroyed.

3.2 DECONTAMINATION FACTORS OF INDIVIDUAL OFF-GAS SYSTEM COMPONENTS

Off-gas treatment devices are employed for removal from the off-gas stream of entrained particulates, volatilized ruthenium, NO_x , and water vapor (in some systems, NO_x and H_2O are released to the stack). As discussed in Section 3.1.3, the devices required for these purposes are also effective in removing any other semivolatile isotopes such as selenium, technicium, tellurium, antimony and cesium, although the degrees of effectiveness are not known.

Devices used primarily for particulate separation and removal from a gas stream include cyclones, sintered metal filters (SMF), scrubbers, particularly venturi scrubbers, and HEPA filters. The scrubbers create aerosols which are largely removed by following demister and de-entrainment devices. Primary ruthenium removal is provided by silica gel or ferric oxide adsorbers. Scrubbers and condensers may provide partial removal of volatilized ruthenium so that the adsorbers will not be overloaded. The NO_x can be removed in part by scrubbing and some nitric acid recovered; more substantial removal is accomplished by reduction to N_2 and H_2O by NH_3 over a heated catalyst bed. Water, if recovered, is removed by condensers; scrubbers can provide cooling and partial condensation, also.

Although a particular device may be used for removal of a specific type of effluent, it may also provide partial removal for other constituents. For example, a venturi scrubber used for particulate removal will also remove approximately 90% of

the volatilized ruthenium entering it. Condensers will remove particulates and volatilized ruthenium. And, a catalytic reduction of NO_x will probably also reduce and remove volatilized ruthenium.

The performance characteristics of individual or groups of off-gas treatment devices have been measured for some process systems, but not for all. Thus, it is necessary to evaluate the existing data for the components so that efficiencies of untested systems can be estimated. It is true that the efficiency of a device may depend on its location in the system or on the solidification process and, therefore, off-gas composition. Thus, the estimates can only be approximate.

Typical decontamination factors for volatilized ruthenium, for particulate material, and for NO_2 and NO across various off-gas cleanup devices are tabulated in Table 5. They are estimates based on published data for the many solidification processes described in Section 2. The DFs for volatilized ruthenium were taken largely from the review by Christian⁽²⁾. Newby, Thomas and Barnes obtained preliminary results for volatilized ruthenium removal across an NO_x converter consisting of ammonia blended with the gases and passed over a zeolite catalyst bed and their results⁽⁸⁸⁾ were used.

Decontamination factors across the scrubbers and condenser include the associated demister device. These aqueous condensate devices probably provide DFs of up to 10^3 for particles greater than $1\text{ }\mu\text{m}$ in diameter, but removal efficiencies fall off quite rapidly for smaller particles; their tendency to generate submicron aerosols can contribute to particulate loadings beyond them. The conservative DFs of ca. 100 tabulated for particulates approximate actual experiences with these devices.

The DF across a sintered metal filter (SMF) is probably greater than 10^3 for particles with diameters greater than $5\text{ }\mu\text{m}$ and about 10 to 10^2 for particles with diameters less than $5\text{ }\mu\text{m}$. Overall DF for a SMF with a spray calciner in the WSEP program⁽¹⁶⁾ was 10^3 . Thus, perhaps as much as 10% of the particles were

TABLE 5

TYPICAL DECONTAMINATION FACTORS ACROSS OFF-GAS CLEANUP DEVICES

Component	DF			
	Particulates	Volatilized Ru	NO ₂	NO
Cyclone	10 ^a	1	1	1
Venturi Scrubber	100-600 ^{a, b}	10 ^{a, b}	2	1
Tube and Shell Condenser	10 ² -10 ^{3b}	2x10 ^{2a, b, h}	2	1
NO _x Absorber	10	10	5 ⁱ	1
Brink Fiber Mist Eliminator	10 ²	1	1	1
Packed Spray Tower	10 ³	10 ²	4	1
NO _x Converter	2	3.8x10 ^{2d}	10 ^{2g}	10 ^{2g}
Ruthenium Sorber: Silica Gel	8 ^{a, c}	10 ^{3a, e}	1	1
Fe ₂ O ₃ on Glass	2 ^j	(1 to 5)x10 ²	1	1
Sintered Metal Filter	10 ^{3f}	1	1	1
HEPA Filter	10 ^{3a}	1	1	1

a Reference 37

b Reference 64

c Includes cyclone deentrainment device following 1 m deep bed of 6 to 12 mesh silica gel. Median size of influent particles coming from venturi scrubber ranged from 0.3 μ m to less than 0.01 μ m in diameter and had a mean size of 0.1 μ m. Particles collected beyond the silica gel bed ranged from 0.2 μ m to 0.02 μ m diameter and had a mean size of 0.04 μ m⁽⁴⁾. No other reports have been made of small particulate removal by beds containing large particles. No removal is assumed for beds other than silica gel, except those specifically designed for filtration. Any differences of operational DFs from these assumed values of 8 for silica gel and 1 for other beds will not significantly affect the overall estimated system performances.

d Reference 88

e Reference 2

f References 16, 89

g References 90, 91, 92

h 100 for fluidized-bed calciner.

i A caustic scrubber has only a minor effect on the NO_x removal efficiency⁽⁶⁴⁾ and is assumed, also, to provide a DF of 5 for NO₂.

j 10³ if designed for filtering.

probably smaller than 5 μ m in diameter. Bjorklund⁽⁸⁹⁾ also obtained DFs exceeding 10³ for SMFs connected to a fluidized-bed calciner or a spray calciner.

In some processes, DFs for total (as opposed to volatilized) ruthenium are reported for various devices. While the values are useful for evaluating the particular process, they cannot be used in conjunction with ruthenium volatility data for estimating ruthenium releases for other processes.

The NO_x converter is a heated catalyst bed over which the blended mixture of NO_x in the off-gas stream and NH₃ are passed. It provides DFs for NO₂ and for NO exceeding 100⁽⁹⁰⁻⁹²⁾.

3.3 FLUIDIZED-BED CALCINATION

3.3.1 ICPP Fluidized-Bed Process

Christian and Rhodes⁽³⁷⁾ have analyzed the operating data from the WCF and evaluated the projected decontamination factors for particulates and for volatilized ruthenium when commercial HLLW is calcined in a similar facility. The results are summarized in Table 6. A second series HEPA filter is included in addition to the off-gas components shown in Figure 2.

The NWCF off-gas system will also contain a condenser with its associated mist eliminator. This will provide additional DFs (see Table 5) of approximately 100 each for volatilized ruthenium and for particulates.

The scrubber and condenser will remove very little NO_x because, with in-bed combustion heating, the predominant NO_x emerging from the calciner is NO which is difficult to remove with an aqueous system⁽⁸⁾.

A plant of the design reviewed by Christian and Rhodes⁽³⁷⁾ would yield DFs exceeding the minimum requirements (Section 3.1.2) by factors of 30 and 7 x 10³ for particulates and volatile ruthenium, respectively. The design does not provide for removal of NO_x. In a commercial facility, removal would probably be required. If this is done by oxidizing and scrubbing for conversion to nitric acid, the overall DF may be increased by a factor of approximately 100 for the particulates and 10 for

TABLE 6
ESTIMATED DECONTAMINATION FACTORS FOR COMMERCIAL
HLLW IN ICPP FLUIDIZED-BED CALCINER^a

Component	DF		
	Particulates	Volatilized Ru	NO _x
Calciner	4	5×10^4	1
Cyclone	10	1	1
Quench Tank and Venturi Scrubber ^b	600	10	1
Silica Gel Adsorber ^c	8	810	1
HEPA Filter	1000	1	1
HEPA Filter	1000	1	1
Overall Feed-to-Stack	2×10^{11}	5×10^8	1

^a With second HEPA filter added as recommended in reference 37.

^b Includes scrubber separator and demister devices following scrubber.

^c Includes cyclone deentrainment device following adsorber bed.

volatilized ruthenium, respectively, while a DF of 5 would be provided for NO_x. A catalytic converter (placed at the tail end of the system) could provide an additional DF of ca. 380 for volatile ruthenium. The latter option would likely be used because the NO is difficult to oxidize and remove with a scrub system⁽⁸⁾.

The overall system is efficient for cleaning the off gas. Because of the large gas flow rates required for fluidization and atomization, the equipment required is large and, therefore, capital costs high. In summary, the system of Figure 2 with a second final HEPA filter and an NO_x converter would probably provide approximate overall feed-to-stack^a DFs of 2×10^{11} , 2×10^{11} , and 1×10^2 for particulates, ruthenium, and NO_x respectively.

^aFeed used here is the HLLW transported to the calciner feed system.

The silica gel is regenerable by washing with hot water; approximately 90 percent of the sorbed ruthenium can be removed by the washing treatment. The wash water is recycled to evaporators and calcined with the HLLW. The capacity of the silica gel has not been determined but is known to exceed 200 g/m^3 (see Section 2.9.2). A pair of parallel adsorbers for a commercial facility would contain approximately 3.2 m^3 of silica gel so the capacity for ruthenium will be greater than 6400 g. The quantity of ruthenium reaching the adsorbers under normal operating conditions will be only 0.004 g/MTHM. Thus, the adsorbers should not require regeneration for removal of ruthenium. Washing might be required for other purposes, such as removing organic deposits accumulated from the unburned hydrocarbons in the off gas.

A desirable feature of the silica gel in this system is its low temperature of operation compared with ferric oxide adsorbers. The gases pass to the HEPA filters following the adsorber. The filters cannot tolerate temperatures higher than ca. 150°C without use of special adhesives. If heated ferric oxide were used in place of the silica gel, cooling of the gases would be required between the adsorber and the filter.

3.3.2 PNL Fluidized-Bed Process

Isokinetic sampling of solids downstream of the sintered metal filters has shown the solids concentration to be less than $3.5 \times 10^{-2} \text{ g/m}^3$ of noncondensable gases. Based on the concentration of particulate solids generated in the vessel divided by the concentration of non-condensable off-gases, this represents a DF of 10^3 to 10^5 for the combined pseudo-cyclone-SMF system⁽¹³⁾ (see Figure 3). Thus, an additional DF for particulates across the remainder of the off-gas treatment system of 6×10^6 is required. Ruthenium volatility for the process has not been measured. Since it will be connected to a vitrification unit, the ruthenium volatility will probably be on the order of 1%. An off-gas system must, thus, provide an overall DF for the volatile ruthenium of approximately 700.

The DFs, beyond the SMF, across the components of the off-gas system used for the experimental development of the calciner (Figure 3) are estimated in Table 7. The packed scrubber DF for particulates is conservatively estimated to be 10^2 because it is not followed by a demister. As discussed in Section 2.1.2, a final HEPA filter is assumed to be in place following the packed scrubber.

TABLE 7
ESTIMATED DECONTAMINATION FACTORS FOR COMMERCIAL HLLW
IN PNL FLUIDIZED-BED EXPERIMENTAL OFF-GAS SYSTEM

Component	DF	
	Particulates	Volatilized Ru
Calciner-Cyclone SMF	10^3	10^2
Condenser	10^2	10^2
Packed Scrubber	10^2	10^2
HEPA Filter	10^3	1
Overall Feed-to-Stack	10^{10}	10^6

A single measurement with ruthenium in the feed at 1/10 the normal concentration showed a DF from feed-to-condensate of 10^4 , identical to the value predicted for the calciner and condenser in Table 7⁽¹²⁾. Cesium transport was measured; analysis of condensate and off-gas samples showed less than 1 ppm Cs when 0.05M Cs was in the feed. The DF for Cs across the calciner, SMF, and condenser was 10^4 to 10^5 . The predicted DF for particulates to that point is 10^5 . A small amount (on the order of 0.01%) of the Cs may have been vaporized and reached the condenser as a vapor where it was removed. The total volatility may have been slightly higher with some of the Cs plating out ahead of the condenser. In support of this suggestion, when a HEPA filter was placed between the SMF and condenser, the small amount of fines material collected on it contained a larger percentage of Cs than did the bed material⁽⁹³⁾.

As in the ICCP fluidized-bed calciner, it is likely that NO_x

emerging from the kerosene-heated fluidized-bed will be largely NO, which will pass through most of the off-gas system. Perhaps half of it will be oxidized and scrubbed out.

In summary, the system with the experimental off-gas train and a final HEPA filter will provide approximate feed-to-stack DFs of 10^{10} , 10^6 , and 2 for particulates, ruthenium, and NO_x, respectively.

3.3.3 Eurochemic LOTES Process

The stirred fluidized-bed, which is heated by in-bed combustion of kerosene, will generate approximately half as many fines as in the ICPP calciner which will elutriate from the calciner. A summary of the expected DFs across the components from the feed tank to the stack is given in Table 8. The individual DFs are taken to be the same as those experienced for the plant scale WCF at the ICPP⁽³⁷⁾ (see Table 6).

TABLE 8
ESTIMATED DECONTAMINATION FACTORS FOR COMMERCIAL
HLLW IN LOTES PROCESS

Component	DF		
	Particulates	Volatilized Ru	NO _x
Calciner	2	10^4	1
Cyclone	10	1	1
Venturi Scrubber and Deentrainment Cyclone	300	10	1
Condenser and Demister	100	100	1
HEPA Filter	10^3	1	1
Overall Feed-to- Stack DF	6×10^8	1×10^7	1

The DF for the venturi scrubber is conservatively estimated to be one-half that for the WCF because no quench spray tower precedes the scrubber. The ruthenium volatility from the calciner is assumed to be 0.01%.

As with the ICPP fluidized-bed process, the emerging NO_x will be largely NO . Only a small amount, less than 50%, will be scrubbed out from the off-gas stream. The particulate DF is inadequate for meeting EPA standards, but can be improved to an acceptable level by adding a second HEPA filter.

3.4 SPRAY CALCINATION

3.4.1 PNL Spray Calcination Process

During the WSEP tests the ruthenium volatilized from the calciner/melter equipment was approximately 2% of the quantity fed to the system when the in-pot melting modification was utilized with no phosphate in the feed. During the tests, the ruthenium concentration in the feed was 10% of that expected for commercial wastes. Iron was substituted for the remainder of the Ru. Cesium volatilized to the extent of 0.002 to 0.3% and tellurium volatility was 1%^(16,17). Nonvolatile particulate entrainment from the system through the SMF was less than 0.1% ($\text{DF} > 10^3$). The WSEP Auxiliary Process System (Figure 6) adequately removed these constituents from the off-gas. The overall DFs from feed-to-stack ranged from 10^9 to 10^{10} for ruthenium and from 10^{11} to 10^{13} for nonvolatiles; most typical values were 10^{10} and 10^{12} for ruthenium and particulates, respectively^(16,17).

Decontamination factors were determined through each stage of the APS⁽¹⁶⁾. The overall DFs from the calciner feed to the recovered nitric acid in the fractionator (see Figure 6) were typically 10^2 to 10^3 for ruthenium and 10^4 to 10^6 for cerium, which represents nonvolatile particulates. Comparable DFs to the recovered water (accumulated fractionator distillate) were greater than 10^5 for ruthenium and greater than 10^9 for cerium. The overall DFs to the off-gas scrubber were greater than 10^4 for ruthenium and ranged from 10^7 to 10^9 for cerium. Comparable DFs to the off-gas leaving the scrubber were 10^7 to 10^9 for radioruthenium and 10^{10} to 10^{11} for radiocerium.

The data were not separated for the vapor and solid airborne ruthenium species, so that DFs for ruthenium cannot be attributed to one form of species or the other. The installation in later runs of a modified solidifier condenser containing Pall rings for improved vapor-liquid contact

followed by a high efficiency filter reduced the ruthenium carry over beyond the evaporator. Spraying water into the condenser was only modestly successful in scrubbing out additional uncondensed ruthenium and nitrogen oxide gases.

The solidifier condenser removed 33 to 73% of the nitrogen oxides that volatilized from the solidifier while the remaining 67 to 27%, probably present as NO, were carried through the condenser in the gas phase. The nitrogen oxides entering the scrubber neutralized the scrubber at a fairly constant rate. When the solution (2M NaOH) became completely neutralized, no more nitrogen (NO_x) would accumulate in the scrubber. From 8 to 39% of the equivalent feed nitrogen accumulated in the scrubber while approximately 15% of the NO_x was lost to the stack.

The radioruthenium concentration in the final aqueous effluent (fractionator distillate) was as high as 4×10^4 greater than allowable values in 10CFR20. Consequently, additional cleanup would be necessary before discharging to the environment; alternatively the effluent could be recycled in a fuel reprocessing plant.

The APS system for off-gas treatment was used also for the pot calcination and phosphate glass processes developed in the WSEP program. The performance of the system was similar for the three processes with minor differences. A summary of the general operating data for the three processes is given by McElroy et al.⁽¹⁷⁾ and is presented here for reference.

As discussed above, the radioactivity removed from solidifier off-gases was distributed to three aqueous streams. The bulk of it remained in the evaporator bottoms where it could be recycled to the solidifier feed. About 0.1% of the ruthenium was found in the fractionator bottoms (recovered HNO₃) and less than $10^{-4}\%$ in the fractionator distillate. Also about $10^{-4}\%$ of the cerium was found in the fractionator bottoms and about $10^{-7}\%$ in the fractionator distillate. The radioactivity in the fractionator distillate exceeded 10CFR20 values

for concentrations in water by factors of 10^3 to 10^5 . The overall feed-to-stack DF for gaseous effluents was approximately 10^{10} for radioruthenium and 10^{12} for radiocerium for all three processes.

A summary of information on typical effluents resulting from waste solidification in WSEP is presented in Table 9.

3.4.2 German VERA Process

Denitration of the feed by reaction with formic acid in the spray calciner will suppress the ruthenium volatilized to less than 0.01%, thereby minimizing requirements for special attention to its removal from the off gas. The NO_x will be largely destroyed by conversion to N_2 .

A summary of estimated DFs across the system (Figure 7) is given in Table 10. Individual DFs from Table 5 were used as a starting points for the estimates.

It is difficult to evaluate the performances of the series scrubbers and condensers. Decreasing efficiencies are estimated because of the likely increasing difficulty in removing the smaller size and quantity of matter passing to successive stages. At the same time, entrained aerosols down to $1\text{ }\mu\text{m}$ in diameter are probably quite efficiently removed by the scrubbers; thus, the effect of no mist deentrainment devices will be largely overcome by the presence of the succeeding scrubbers. The final condenser may produce some aerosol mist which will pass to the ventilation system and result in a decreased condenser net efficiency.

The second condenser is estimated to have a decreased efficiency because of the rather low water content of the gases reaching it. Thus, its "washing" effect will be diminished

When overall DFs on the order of 10^{12} are predicted, the uncertainties must be considered to be large because of the difficulties in measuring or estimating DFs across components when the impinging material concentration is miniscule. Nevertheless, the large magnitude of the estimated overall DF provides the indication of more than adequate off-gas cleanup.

TABLE 9

TYPICAL EFFLUENTS RESULTING FROM SOLIDIFICATION OF HIGH-LEVEL RADIOACTIVE
WASTE IN WSEP PROCESSES^(a,e)

Stream	Major Constituent	Radium/ruthenium Ci/Ci in Feed ^b			Radio-cerium Ci/Ci in Feed ^b			Potential Disposal
		PC	SS	PG	PC	SS	PG	
Solidifier Condensate	1 to 6M HNO ₃	2x10 ⁻¹	6x10 ⁻¹ (1x10 ⁻²) ^c	8x10 ⁻²	6x10 ⁻³	7x10 ⁻⁴	2x10 ⁻³	Recycle to solidifier feed or to fuel reprocessing plant waste concentrator.
Fractionator Bottoms	7 to 10M HNO ₃	1x10 ⁻³	4x10 ⁻³	2x10 ⁻³	2x10 ⁻⁶	5x10 ⁻⁶	8x10 ⁻⁷	Recycle for reuse in fuel reprocessing plant.
Accumulated Fractionator Distillate	0.01 to 0.1M HNO ₃	1x10 ⁻⁶ (4x10 ⁻⁴) ^d	1x10 ⁻⁵	4x10 ⁻⁶	1x10 ⁻⁸	1x10 ⁻⁹	1x10 ⁻⁸	Recycle for reuse in fuel reprocessing plant or provide further decontamination
Scrubber Bottoms	0 to 2M NaOH	1x10 ⁻⁵	4x10 ⁻⁵	3x10 ⁻⁶	~10 ⁻⁸	~10 ⁻⁸	~10 ⁻⁸	Intermediate level waste treatment or combine with high level aqueous waste.
Final Off-Gas from Scrubber	Air	~10 ⁻⁸	~10 ⁻⁸	~10 ⁻⁸	~10 ^{-9d}	~10 ⁻¹¹	~10 ⁻¹¹	To building ventilation filters.
Final Off-Gas to Stack	Air	~10 ⁻¹⁰	~10 ⁻¹⁰	~10 ⁻¹⁰	~10 ⁻¹²	~10 ⁻¹²	~10 ⁻¹²	To atmosphere.

^aBased primarily on average of typical values for all WSEP runs.

^bTotal curies of radionuclide accumulated in auxiliary tank during entire run/total curies of radionuclide in feed to solidifier during entire run.

^cFor in-pot melting runs SS-12 and SS-13.

^dAverage value for last three pot calciner runs.

^eReference 17.

PC = pot calcination, SS = spray solidification, PG - phosphate glass solidification

TABLE 10

ESTIMATED DECONTAMINATION FACTORS FOR COMMERCIAL
HLLW IN VERA PROCESS

Component	DF		
	Particulates	Volatilized Ru	NO _x
Calciner and SMF	10 ³	10 ⁴	20
Condenser	10 ² to 10 ³	10 ²	1
Condenser	20	20	1
Scrubber	10 ²	20	1
Scrubber	50	10	1
Scrubber	10	10	1
Condenser	20	20	1
Feed-to-Stack	10 ¹² to 10 ¹³	10 ¹²	20

The building ventilation system will likely provide HEPA filtration for final removal of entrained particulates in addition to that resulting from the system shown in Figure 7. Because of the suppressed ruthenium volatility, more ruthenium will go to, and be removed by, the first condenser in the form of particulates than volatilized ruthenium. Approximately 0.1% of the total solids activity or 10³ Ci/MTHM will be removed by the condenser and passed through the evaporator to the medium activity waste (MAW) stream. This is ultimately returned to the calciner after the MAW is concentrated by evaporation.

The sintered metal filters developed for the advanced VERA process are of smaller pore diameter than those tested at the PNL 35 μm⁽¹⁸⁾ vs. 65 μm⁽¹⁷⁾. The filters are integrated in the calciner with each filter candle surrounded by a shroud (see Figure 7). This arrangement permits use with blowback every

30 minutes⁽¹⁹⁾ compared with 1-to 5-minute blowbacks required by the conventional design⁽¹⁶⁾. Alternatively, fewer filter candles can be installed.

3.5 POT CALCINATION

3.5.1 PNL Pot Calcination Process

Based on the WSEP data summarized in Table 9, (see discussion in Section 3.4.1) the overall DFs from feed-to-stack for the process were 10^{10} and 10^{12} for ruthenium and particulates, respectively, when the APS was used for off-gas treatment (Section 2.2.1, Figure 6). The accumulated reciprocal DFs from feed through each of the off-gas units are also presented in Table 9 (DF = 1/reciprocal DF as presented in Table 9).

The condensate from the calciner condenser contained 99% of the volatilized ruthenium (approximately 10% of total ruthenium fed). The condensate was returned to the evaporator so that virtually all of the ruthenium was recycled to the calciner.

In the rising-level glass mode of operation, 0.6% the cesium was volatilized and was removed in the pot condensate. Solids carry over in this mode caused partial plugging of the pot throat and early plugging of an absolute filter beyond the solidifier condenser. Thus, the solids entrained from the calciner is evidently much larger than the quantity of 0.6% inferred from analysis of the condensate (Table 9).

Although the same off-gas treatment system (APS) was used for the pot calciner as for the spray calciner, in a plant a smaller-sized system could be used for the pot process (for an equivalent processing rate) because no atomizing air is required.

As in the spray calcination process, approximately 15% of the feed nitrogen may be expected to go to the stack, primarily as NO (see Section 3.4.1).

3.5.2 British FINGAL/HARVEST Process

The ruthenium volatility from the pot in these processes is 30% of that fed to the calciner⁽²⁷⁾. The off-gas treatment for the FINGAL process is different from that developed for

the HARVEST version and, so, they are considered separately here.

The dust carry over from the pot in the FINGAL process is $3.4 \pm 1.1\%$ ⁽²⁶⁾. Cesium is only entrained as a particulate, i.e., is not substantially volatilized. The removal of the dust and the volatilized ruthenium is accomplished largely by the primary filter/adsorber (Figures 9 and 10). Measured DFs across the primary filter are 500 for Ru⁽²⁷⁾ and 3×10^3 for particulates⁽²⁷⁾.

The secondary filter, having larger surface area and slower gas velocity flow through it, should provide higher DFs⁽²⁷⁾. The primary filter is made smaller because it must be disposed of by placing it in a pot and calcined with the HLLW. Because the secondary filter will handle low quantities of dust and ruthenium, it will have a long service life and, thus, disposal was not a primary consideration in its design. The secondary filter will provide a safeguard should the disposable (primary) filter fail.

The capacity of the ferric oxide filter material for adsorbing volatilized ruthenium is greater than 2×10^3 g Ru/cm³. The true capacity is not known since tests were not run to breakthrough. The primary filter is changed at the end of each pot filling⁽²⁸⁾.

Estimated decontamination factors across the various components are listed in Table 11. The DFs across the calciner and the filter/adsorbers are based on measurements discussed above. Those across the **other components** are based on estimates given in Table 5 with adjustments taking into account locations in the system.

Actual measurements⁽²⁸⁾, based on analysis of the condensate when active feed was calcined in the pilot facility, were made of DFs from the feed through the condenser. The DF for particulates was 3×10^{10} , the same as that calculated from the data and estimates in Table 11. The DF for ruthenium varied from 8×10^4 to 10^8 . The higher value was observed in early parts of the run. During the latter part of the run when the

TABLE 11

ESTIMATED DECONTAMINATION FACTORS FOR COMMERCIAL
HLLW IN FINGAL PROCESS^a

Components	DF		
	Particulates	Volatilized Ru	NO _x
Pot Calciner	30	3.3	1
Primary Filter/ Adsorber	2×10^3	5×10^2	1
Secondary Filter/ Adsorber	5×10^3	10^3	1
Condenser	10^2	10^2	2
NO _x Absorber	10	10	5
Caustic Scrubber	10^2	10^2	5
HEPA Filter	10^2	1	1
Overall Feed-to- Stack	3×10^{15}	2×10^{11}	50

^aSee text. Expected overall feed-to-stack DFs are 10^{15} for particulates and 10^{13} for ruthenium.

furnace was slowly raised, some ruthenium on the interior walls of the pot vessel was revolatilized, causing the effective DF to drop. In another run, the DF for ruthenium was 1×10^5 . The predicted DF from Table 11 is 10^8 , but this is evidently somewhat higher than can be expected in practice.

For all activity, the DF to the effluent gas beyond the HEPA filter was 10^{14} to 10^{16} . Since Ru-106 represents on the order of 10% of the total activity in the feed, the overall DF for the volatilized ruthenium must have been on the order of 10^{13} to 10^{15} , one to four orders of magnitude greater than estimated in Table 11.

When the primary filter is fused into glass in the calciner, less than 1% of the ruthenium on it becomes volatilized⁽²⁸⁾. This corresponds to only about 1/10 the total ruthenium generated from the calciner and, thus, does not affect operations.

In summary, the expected feed-to-stack DFs in the FINGAL process are 10^{15} for particulates, 10^{13} for volatilized ruthenium, and 50 for NO_x .

The HARVEST process, which replaced the FINGAL process, has not been tested with active waste feed. Data from the FINGAL development studies may be used to estimate effluents from the HARVEST operation. The estimated DFs are summarized in Table 12 (refer to Figures 12 and 13).

TABLE 12
ESTIMATED DECONTAMINATION FACTORS FOR COMMERCIAL
HLLW IN HARVEST PROCESS

Component	DF		
	Particulates	Volatilized Ru	NO_x
Pot Calciner	30	3.3	1
Spray Condenser	10^2	50	2
Caustic Scrubber	10^2	10^2	5
Caustic Scrubber	10^2	50	5
Ru Filter/Adsorber	10^3	5×10^2	1
HEPA Filter	10^3	1	1
Overall Feed-to-Stack	10^{13}	$10^8 - 10^9$	50

3.5.3 French PIVER Process

The ruthenium volatility in this process, as measured by ruthenium collected in the condensate (see Figures 14 and 15) is about 15%^(33,34). The volatility measured in this

manner decreases slightly from run to run. This is interpreted⁽³⁴⁾ as being due to the catalytic effect of deposited RuO_2 in the pipes on causing further deposition. The activity in the deposits is comprised of 80% Ru-106 and 10% Cs-137⁽³⁴⁾. Solids entrained is 0.05%. Total cesium carryover is 0.1%, so approximately 0.05% of the cesium is volatilized and removed in the condenser.

The condensate contains 90% of the ruthenium that escapes from the pot⁽³³⁾, i.e., the DF across the condenser is 10. The overall DF for all activity before the gases pass through the ruthenium filters is stated⁽³³⁾ to be 10^8 . However, this is not clear and may refer to the gases after they pass through the ruthenium filters, the error possibly occurring in translation when the text was written in English.

The off-gas treatment system depicted in Figures 14 and 15 is a design (untested) of an industrial facility. Experimental development was done with a slightly different arrangement and some DFs were measured while active waste was calcined⁽³⁴⁾. The sequence of components was condenser, ruthenium filter, alkaline venturi scrubber, water column scrubber, silica gel adsorber, and HEPA filter. The overall feed-to-stack DFs measured for this system were $5 \times 10^7 - 10^8$ and 10^{10} for ruthenium and cesium, respectively. Some measurements were made which permit one to calculate some individual component DFs. The results are summarized in Table 13.

The group DFs may be separated by estimation. Reasonable values are, for ruthenium, 10, $(0.5-1) \times 10^3$, and 1 across the aqueous scrubber, silica gel and HEPA filter, respectively. For particulate cesium, comparable values are approximately 10^2 , 2, and 5×10^2 . Across the condenser and ruthenium filter, the cesium DFs may be approximately 10 and 2, respectively.

Using these values, and experience from other processes (Table 5), estimated DFs for the industrial design plant (Figure 14 and 15) may be made. These are tabulated in Table 14.

TABLE 13
DECONTAMINATION FACTORS IN EXPERIMENTAL PIVER SYSTEM

Component	DF		
	Ruthenium	Cesium	Nonvolatiles
Pot	6.7	10^3	2×10^3
Condenser	10	{ 20	
Ru Filter	30		
Alkaline Venturi Scrubber	5	5	
Aqueous Column Scrubber	{ 5×10^3 to 10^4	{ 10^5	
Silica Gel			
HEPA Filter			
Overall Feed-to-Stack	5×10^7 to 1×10^8	10^{10}	

The ruthenium filters may be more efficient than listed for volatilized ruthenium, even though the listed DFs are greater than inferred from the experimental active system. It is stated⁽³³⁾ that the adsorbers function properly only at slow gas velocities. It is assumed here that the design will account for this so that good efficiencies can be obtained.

As in the British FINGAL/HARVEST process, the spent ruthenium filters will be fused into glass with the HLLW. The experimental filter contained 34 kg of the ceramic granules. The filter material is replaced after adsorbing 10 mg Ru/g material, or 340 g Ru total. This corresponds to approximately what would be volatilized and adsorbed from 1 MTHM of HLLW, which is calcined in two pots.

The condensate from the condenser is concentrated, neutralized to $0.5N \text{ H}^+$, and recalcined. During the calcination, about 1% of the ruthenium in the concentrate will probably become volatilized.

TABLE 14
ESTIMATED DECONTAMINATION FACTORS FOR INDUSTRIAL PIVER PROCESS

Component	DF		
	Particulates	Volatilized Ru	NO _x
Pot Calciner	2×10^3	6.7	1
Spray Condenser	10 to 10^2	10	2
Packed Scrub Column	10^2 to 10^3	10 to 10^2	4
Ru Filter	2	10^2	1
Ru Filter	2	10^2	1
Acid Recovery	10	10	5
Acidic Scrubber	10^2	10	2
Caustic Scrubber	10^2	10^2	5
HEPA Filter	10^2	1	1
Overall Feed-to-Stack ^a	10^{14} to 10^{16}	10^{11} to 10^{12}	4×10^2

^aOperation of waste evaporator will reduce particulate DF to 10^{13} to 10^{14} and ruthenium DF to 10^{10} to 10^{11} (see text).

Figure 14 indicates that the condensate from the waste concentrator is routed to the acid recovery unit which follows the ruthenium filter. Aerosol entrainment and ruthenium volatilized from the evaporator may cause the overall-feed-to-stack DFs to be slightly diminished from those calculated in Table 14. Experience with evaporator/denitrator units in the German FIPS process (see Section 3.8) indicates that aerosol entrainment may be approximately 0.005% ($DF = 2 \times 10^4$). Ruthenium volatility should be less than 0.01% ($DF = 10^4$) at acid concentrations less than 4 M^(2,94) and may be less than 0.001% under radiolysis conditions (see Section 4). The DFs across the evaporator condenser are approximately 10^2 to 10^3 for particulates and 2×10^2 for volatilized ruthenium (see Table 5) so the overall DFs from the evaporator to the acid recovery unit are 2×10^6 to 2×10^7 for

particulates and 2×10^6 to 2×10^7 for ruthenium. The comparable DFs to the acid recovery unit via the calciner are 8×10^6 to 8×10^8 and 7×10^6 to 7×10^7 for particulates and ruthenium, respectively. Thus, the evaporator may reduce the overall feed-to-stack DFs to approximately 10^{13} to 10^{14} for particulates and 2×10^{10} to 2×10^{11} for ruthenium.

During the experimental tests, two pluggings of the off-gas pipes occurred due to deposits of volatilized ruthenium species which decomposed to RuO_2 . One necessitated changing of a pot. The other was removed by injection of a caustic solution and heating by induction. In additional runs, several starts of the plugs were detected by an alarm system which measured the quantities of radioruthenium going into and exiting from the pipe. Acid rinse broke up the plugs.

3.5.4 Italian Pot Vitrification Process

The process has been tested in the laboratory and with a pilot scale facility using cold simulated HLLW⁽³¹⁾. With the phosphate glass vitrification, when red phosphorous was added to the waste, the ruthenium volatility was less than 1%, while 39% of the NO_x was destroyed.

When borosilicate glass was made, the ruthenium volatility was 13%.

Estimated DFs for the process (Figure 18) are given in Table 15. While it is claimed that the ruthenium filter will provide a DF of 10^3 , actual use in the bench scale process yielded DFs of only 5.3 to 260. A value of 10^2 is estimated here.

The particulate carryover from the calciner was measured at ca. 0.1% in the bench scale tests. DFs for particulates across the ruthenium filter were measured to be between 10^2 and 10^3 .

Effluents to the first caustic scrubber from the evaporator and its condenser are less than those from the pot condenser, so the evaporator integrated into the system will not affect the overall feed-to-stack DFs.

TABLE 15

ESTIMATED DECONTAMINATION FACTORS FOR COMMERCIAL
HLLW IN ITALIAN POT PROCESS

	Pot Calciner	Ru Filter	Condenser	Heated Demister	NaOH Scrubber	HaOH Scrubber	HEPA Filter	Overall Feed-to-Stack
Phosphate Glass:								
Particulates	10^3	10^2	$10^2 \times 10^3$	2	10^2	10^2	10^3	10^{13} to 10^{14}
Volatilized Ru	10^2	10^2	2×10^2	1	10^2	10^2	1	10^{10}
NO _x	2.5	1	2	1	5	5	1	10^2
Borosilicate Glass:								
Particulates	10^3	10^2	10^2 to 10^3	2	10^2	10^2	10^3	10^{13} to 10^{14}
Volatilized Ru	7.8	10^2	2×10^2	1	10^2	10^2	1	10^9
NO _x	1	1	2	1	5	5	1	50

On the average, 93% of the nitrates present in the feed for the borosilicate vitrification was recovered in the plant, yielding a DF of 15, of the same magnitude as predicted from the estimates in Table 15.

3.6 PHOSPHATE GLASS FORMATION

3.6.1 PNL Phosphate Glass Process

Based on the WSEP data summarized in Table 9 (see discussion in Section 3.4.1) the overall DFs from feed-to-stack for the process (Figure 19) were 10^{10} and 10^{12} for ruthenium and particulates, respectively, when APS was used for off-gas treatment (Section 2.2.1, Figure 6). The accumulated reciprocal DFs from feed through each of the off-gas units are also presented in Table 9 (DF = 1/reciprocal DF as presented in Table 9).

As discussed in Section 2.4.1, approximately 3% of the tellurium was volatilized and collected in the off-gas units, and most of the selenium may be expected to volatilize. Neither should present operational or release control problems because of the relatively small masses and activities involved (see Section 3.1).

The feed is partially denitrated prior to calcination, but this should not substantially affect the quantity of NO_x released to the stack (approximately 15% from the calciner, see Section 3.4.1) because NO_x will be released from the denitration unit. The off gas from the denitrator is blended with calciner off gas.

3.7 ROTARY KILN VITRIFICATION

Very few measurements of effluents in the French process (Section 2.5, Figure 20) have been made and reported. Most of the predictions of operability are based on experience with the PIVER process (Sections 2.3.3 and 3.5.3).

A small amount of dust will escape from the calciner. Approximately 0.75% of insoluble material will exit the

vessel; it consists mostly, approximately, 80% of MoO_3 and ZrO_2 ⁽⁴⁾. Approximately 3.5% of soluble lanthanum and cerium escapes to the scrubber which removes 3.4% leaving 0.1% that goes to and is removed by the condenser⁽⁴⁸⁾. The rare earths are transported from the calciner/vitrifier primarily by volatilization. Less than 0.1% of total calcine solids passes through the scrubber to the condenser⁽¹⁴⁾; i.e., less than 13% of that entering the scrubber. Thus, the calciner DF for particulates is approximately 130, and the scrubber DF is greater than 8.

The condenser has a DF for insoluble dust of greater than 10^2 and of 30 for the soluble material carried over⁽⁴⁸⁾.

Based on these data, data from the PIVER experiments (Section 3.5.3), and data from other process (Table 5), estimates of DF across the various off-gas components of the AVM system are made and summarized in Table 16. The ruthenium volatility from the kiln was assumed to be approximately 10%.

TABLE 16
ESTIMATED DECONTAMINATION FACTORS FOR COMMERCIAL
HLLW IN FRENCH ROTARY KILN PROCESS

Component	DF		
	Particulates	Volatilized Ru	NO_x
Calciner	1.3×10^3	10	1
Spray Scrubber	10 to 10^2	10 to 10^2	2
Condenser	10^2	10	2
Ferric Oxide Adsorber	2	10^2	1
Wash Column	10^2	10	2
HEPA Filter	10^3	1	1
Overall Feed-to-Stack	10^{10} to 10^{11}	10^6 to 10^7	8

3.8 DRUM DRIER-POT VITRIFICATION

Tests with a small hot cell apparatus were conducted in 1974^(14,49). The feed used in the tests had an activity of 330 Ci/l. During denitration (see Figure 21), some aerosol entrainment occurred, producing an activity in the condensate of 50 to 200 mCi/l. This corresponded to a DF across the denitrator of $(2 \text{ to } 8) \times 10^3$. The condensate was not rich in ruthenium, indicating that little ruthenium volatility occurred. The denitrator was a still with a packed column reflux condenser. The developers assume⁽⁴⁹⁾ that when large-scale equipment is constructed, a more feasible design can be utilized which will increase the DF by a factor of 10 or more. The condenser should provide DFs of approximately 10^2 to 10^3 for the particulates and aerosols and 10^2 for any volatilized ruthenium generated from the denitrator and concentrator; the ruthenium generated will be negligible compared with that released from the drier.

The condensate from the drying operation had a specific activity of 10 mCi/l, corresponding to a DF across the drier of more than 10^5 . The formation of dust was generally low.

During melting a small amount of ruthenium, on the order of 1% or less, was volatilized.

Taking the above data into account, and assuming that aerosol entrainment from a plant scale denitrator unit would be less than $5 \times 10^{-3}\%$ ($DF > 2 \times 10^4$), the fraction of activity in the feed that passes through the condenser and enters the first HNO_3 recovery unit is calculated to be 10^{-5} as particulate and aerosol (overall DF to that point of 10^5) and 0.01 as volatilized ruthenium ($DF = 10^2$). For the remainder of off-gas treatment system, the combined particulate aerosol DF will be approximately 10^4 across the two NO_x absorber units plus the caustic scrubber and 10^2 to 10^3 across the HEPA filter. For volatilized ruthenium the comparable DFs will be approximately 10^3 and 1. The overall feed-to-stack DFs will, then, be approximately 10^{11} to 10^{12} for particulates and 10^5 for volatilized ruthenium.

The denitrator will release NO_x into the off-gas stream which passes through a condenser prior to being mixed with the off gas from the drier and melter. Those nitrates not destroyed in the denitrator will be dissociated in the drier, the off gas of which is also treated with a condenser. A small amount of NO_x will be evolved from the melter directly to the NO_x scrub columns. Thus, the overall DF for NO_2 to the entrance of the scrub columns will be approximately, that of a condenser i.e., 2. Through the three scrub columns an additional DF of $10^2 \times 10^2 \times 10 = 10^5$ may be obtained. The last scrubber does not add oxygen to convert any NO to NO_2 and may have a diminished DF. The feed-to-stack DF for NO_x may, then, be as high as 2×10^5 .

A concept for the process is to recycle waste water streams in the reprocessing plant and concentrate the tritium in the fission product solution (HLLW). The FIPS process can recover it undiluted.

3.9 CONTINUOUS CERAMIC MELTER

The behavior of ruthenium during glass forming at the high temperatures of a ceramic melter (1150°C) is a potential problem that has not been studied. Air and NO_x oxidation at this temperature can create significant partial pressures of $\text{RuO}_4(\text{g})$ and $\text{RuO}_3(\text{g})$ (2,95,96) via the following reactions

Although NO_2 formed by decomposition of nitrates will quickly dissociate at these temperatures, the dissociation creates oxygen; thus complete exclusion of air, while helpful, cannot totally eliminate formation of RuO_4 and RuO_3 . As the gases exit the hot zone of the melter, the formation equilibria can shift to the left, converting the gas species to $\text{RuO}_2(\text{s})$ that can either deposit or remain airborne as fine particulate material. The relative importances of these processes, including the kinetics

involved, are not currently known. If deposition occurs in the off-gas piping, plugging will be a potential problem.

For purposes of evaluating the processes, it will be assumed that 5 to 10% of the ruthenium in the feed volatilizes from the melter in the form of gaseous oxides and that one-half of this remains in the gas form while one-half is dissociated to particulate RuO_2 in the off-gas treatment system. Five% of the ruthenium as entrained particulate represents 0.8% of total solids activity.

3.9.1 Denmark Continuous Ceramic Melter

The off-gas treatment system (Section 2.7.1) is not considered designed for this melter. The incomplete off-gas system used for the experimental development of the melter consisted of a continuous prefilter (Figure 24) and a condenser. Large amounts of dust evolved from the melter to the filter, probably significantly exceeding the 0.8% represented as entrained particulate ruthenium. If one assumes that there is 5% entrainment of solids from the melter and that the DF across the filter is 10^2 , then the overall DF for particulates of the experimental system is approximately 10^6 (including 10^2 to 10^3 across the condenser). For volatilized ruthenium the DFs are approximately 40, 1, and 10^2 across the melter, filter, and condenser, respectively, with an overall DF of 4×10^3 .

3.9.2 PNL Continuous Ceramic Melter

An off-gas treatment system has not been designed for the PNL ceramic melter and it has only been tested on an engineering scale using simulated wastes. In the operating mode adopted (Section 2.7.2), less than 0.5% of the waste was entrained in the off-gas stream (DF across melter = 200). As discussed at the beginning of the Section, ruthenium, when present in the feed, may contribute an additional entrained particulate activity that would double the effective activity carry over.

3.9.3 German PAMELA Process

This process has been tested on the bench scale. Purex high-level waste was converted into phosphate glass beads; some of the glass beads were also cast into a lead matrix to form VITROMETS. No dust was formed in the process⁽¹⁴⁾.

No other data on effluents have been reported. The off-gas treatment system is similar to that for the FIPS process for which data have been reported (see Section 3.8). Information gained from those studies are used here as a starting basis for estimating effluents in the PAMELA process.

Decontamination factors for volatilized ruthenium across the off-gas components are difficult to estimate from data obtained from other processes because the principal ruthenium vapor species is probably different at the high temperature⁽²⁾. The difference arises because air oxidation becomes significant at the higher temperature and NO_2 , which stabilizes the gas species formed in lower temperature processes, is dissociated. The RuO_4 and RuO_3 formed will be less stable and more easily removed in the early stages of the off-gas train. But, as the gases pass through the system, NO will be oxidized to NO_2 so that the ruthenium species will behave more like that in other, lower temperature calcination/vitrification processes. It will be assumed that, beyond the denitrator/concentrator, where the gases are exposed to HNO_3 , the DFs for volatilized ruthenium are similar to those in the FIPS and other lower temperature processes.

Suppose 10% of the ruthenium is volatilized and then partially dissociates to RuO_2 (see introduction of Section 3.9). The denitrator/concentrator, through which the off gas from the melter passes (Figure 26) will provide a DF of approximately 10^3 for the RuO_2 . Because of the partially reducing conditions in the unit and the thermodynamic instability of the gaseous ruthenium oxides as they are cooled, the DF of the ruthenium-containing vapors will be of the same magnitude, 10^3 . Thus, the quantities of ruthenium passing from the melter through the denitrator/concentrator will be approximately 0.005% as

particulates and 0.005% as volatile ruthenium, primarily in the form created in lower temperature calcination processes.

The concentrator/denitrator should volatilize negligible additional ruthenium. The particulate and aerosol carryover will be approximately 0.005%, the same as the FIPS process. Overall, the fraction of activity from the melter and denitrator/concentrator that enters the condenser will be approximately 10^{-4} (DF = 10^4) for particulate and aerosol and 5×10^{-5} (DF = 2×10^4) for volatilized ruthenium.

The estimated DFs across the remainder of the system are listed in Table 17.

TABLE 17
ESTIMATED DECONTAMINATION FACTORS IN PAMELA PROCESS

Component	DF		
	Particulates	Volatilized Ru	NO _x
Melter and Denitrator/ Concentrator	10^4	2×10^4	1
Condenser	10^2 to 10^3	10^2	1 to 2
HNO ₃ Absorber	10^2	10	5
HNO ₃ Absorber	10^2	10	5
HNO ₃ Absorber	10	10	5
HEPA Filter	10^2 to 10^3	1	1
Overall Feed-to-Stack	10^{13} to 10^{14}	10^9	2×10^2

All the NO_x will be released to the condenser as a mixture of NO and NO₂; the relative amounts will determine the efficiency of the condenser for removing the NO_x mixture. After the condenser, it is assumed that the NO has been oxidized to NO₂.

3.10 WIPED FILM EVAPORATOR

As indicated in the description of the evaporator (Section 2.8) an overall off-gas treatment system has not been developed, other than the technique and equipment necessary to handle solids generated from the melter when simulated HLLW was treated.

The temperatures used for evaporation and drying in the wiped film evaporator may result in very high ruthenium volatilities. For example, when simulated HLLW is calcined in a fluidized-bed, indirect heating at temperatures less than 375° , down to 305°C , virtually all of the ruthenium is volatilized^(2,37). This potentially serious problem should be investigated for a wiped film evaporator. Prior denitration of the feed could reduce the ruthenium volatility if it is a problem.

3.11 PNL PROPOSED OFF-GAS CLEANING SYSTEM

The described system allows for alternate treatment for NO_x removal, depending on whether acid recovery is desired (see Section 2.9.1). The primary system considered (Figure 28) shows NO_x absorption for acid recovery. This case is used for the initial analysis here, and the effect of substituting an NO_x converter is then discussed.

The off-gas treatment system is designed to be general. For evaluation purposes, the base solidification process is considered to be a spray calciner with in-pot melter (Figure 5, Section 2.2.1) and with sintered metal filters at the gas exit. The ruthenium volatilized from the solidifier would be approximately 2% and particulate/aerosol transport beyond the SMF would be 0.1% (see Section 2.2.1).

Estimated DFs across the off-gas components are presented in Table 18. This is the only solidification process system in which iodine recovery is considered. It was included based on an assumption⁽⁶⁴⁾ of 2% of total iodine from spent fuel being in the HLLW, compared with 0.1% assumed in this report (Section 3.1.1).

TABLE 18
ESTIMATED DECONTAMINATED FACTORS FOR COMMERCIAL
HLLW ACROSS PNL PROPOSED OFF-GAS SYSTEM

Component	DF			
	Particulates	Volatilized Ru	NO _x	Iodine
Calciner and SMF ^a	10 ³	50	1	1
Venturi Scrubber and Knock-Out Pot	10 ³	10	2	1
Condenser	10 ² to 10 ³	2x10 ²	2	1
NO _x Absorber	10	10	5	1
Condenser	20	20	1.5	1
Ru Adsorber	1	10 ³	1	1
HEPA Filter	10 ² to 10 ³	1	1	1
Iodine Adsorber I	1	1	1	10 ³
HEPA Filter	10 ²	1	1	1
Overall Feed-to-Stack ^a	10 ¹⁴ to 10 ^{16b}	10 ¹⁰	30	10 ³

^aPNL Spray Calciner with in-pot melter

^bEvaporator reduces this to 10¹²-10¹⁴. See discussion in text.

The condenser following the NO_x absorber is for the purpose of removing any entrained liquid from the absorber solution. Because bulk water vapor is removed from the gases ahead of the absorber, the rate of water removal by the condenser following the absorber will not be high. Thus, the condenser's efficiency for removing other material will probably be somewhat diminished from that of the first condenser.

The overall DFs given (10¹⁵ to 10¹⁷ for particulates and 10¹⁰ for volatilized ruthenium) are for the path from feed to stack through the calciner. Another path that must be considered is through the evaporator off-gas lines, which enters the off-gas treatment system just ahead of the NO_x absorber.

Data from the German FIPS process (Section 3.8) indicates that aerosol entrainment from a well designed evaporator might be on the order of 0.005% (DF 2×10^4). Ruthenium volatility should be less than 0.01% at acid concentrations less than $4 \text{ M}^{(2,94)}$ (DF = 10^4) and possibly less than 0.001% (see Section 4.3.1). The DFs across the condenser for the HLLW evaporator are approximately $10^2 - 10^3$ for particulates and 2×10^2 for volatilized ruthenium (see Table 5), so the overall DFs from feed to NO_x absorber via the waste evaporator are 2×10^6 to 2×10^7 for particulates and 2×10^6 to 2×10^7 for volatilized ruthenium. The comparable values via the calciner are 10^8 to 10^9 for particulates and 10^5 for volatilized ruthenium. Thus, the evaporator will contribute negligible volatilized ruthenium to the off-gas stream at the NO_x absorber, but the aerosol and particulate entrainment will be a factor of 50 greater than that from the calciner route. The effect will be to reduce the feed-to-stack DF for particulates to $10^{12} - 10^{14}$.

If an NO_x converter is utilized in place of the acid recovery system, the following changes will occur. The NO_x absorber and the condenser following it will be replaced by the converter system. The DFs across the absorber and condenser are 200 for particulates and 200 for volatilized ruthenium. Across the NO_x converter, they are expected to be 1 for particulates and about 380 for volatilized ruthenium (Table 5). Thus, the replacement would result in a decrease in particulate DF of 200 and an increase in volatilized Ru DF of 2, so that the overall feed-to-stack DFs would be 10^{10} to 10^{12} for particulates and 4×10^{10} for ruthenium.

Because condensers are used before the gases reach the ruthenium adsorber bed, it would be possible to operate a silica gel bed at ca. 35°C . The DF at this temperature for volatilized ruthenium may be an order of magnitude greater than the value of 10^3 obtained at $70 - 100^\circ\text{C}$ (see Section 2.9.2). The latter temperature range is required to stay above the dew point of the off gas in the ICPP WCF because

water is not removed, and most laboratory studies have been performed at this temperature range. One study at 25°C showed a DF of 10^5 (69).

This proposed off-gas cleanup system is the only one with a backup device considered for primary sintered metal filters. The venturi scrubber was included in the design primarily for that purpose so that if a SMF should fail, the remainder of the off-gas treatment devices would not be flooded with particulates. A backup for the primary filters is advisable for any system in which high particulate loadings are present.

In the ICPP and Eurochemic LOTES fluidized-bed processes, the venturi scrubber follows the primary cyclone as a matter of necessity for routine operation because the cyclone passes significant quantities of dust.

3.12 SUMMARY

The expected overall feed-to-stack decontamination factors for the different processes considered are summarized in Table 19. The Denmark and PNL continuous ceramic melters and the PNL wiped film evaporator are not included because integrated systems have not been developed for them (see Sections 3.9.1, 3.9.2, and 3.10 for discussion of these devices).

Additional comments regarding the expected performances are given in Section 4.

Except where noted, the tabulated overall DFs do not include effect of evaporators used for concentrating the HLLW. See Section 4.3.1 for discussion of evaporators and their possible effects on overall DFs.

TABLE 19
SUMMARY OF ESTIMATED OVERALL FEED-TO-STACK PROCESS
DECONTAMINATION FACTORS

Process	Feed-to-Stack DF		
	Particulates	Volatilized Ru	NO _x
ICPP Fluid-Bed ^a	2x10 ¹¹	2x10 ¹¹	1x10 ³
PNL Fluid-Bed ^b	10 ¹⁰	10 ⁶	2
Eurochemic LOTES	6x10 ⁸	1x10 ⁷	1 to 2
PNL Spray	10 ¹²	10 ^{10c}	7
German VERA	10 ^{12d}	10 ¹³	20
PNL Pot	10 ¹²	10 ¹⁰	7
British FINGAL	10 ¹⁵	10 ¹³	50
British HARVEST	10 ¹³	10 ⁸ to 10 ⁹	50
French PIVER ^e	10 ¹³ to 10 ¹⁴	10 ¹⁰ to 10 ¹¹	4x10 ²
Italian Pot ^e Phosphate Glass	10 ¹⁴ to 10 ¹⁵	10 ¹⁰	60
Borosilicate Glass	10 ¹⁴ to 10 ¹⁵	10 ⁹	25
PNL Phosphate Glass	10 ¹²	10 ¹⁰	7
French Rotary Kiln	10 ¹⁰ to 10 ¹¹	10 ⁶ to 10 ⁷	8
German FIPS ^e	10 ¹¹ to 10 ¹²	10 ⁵	2x10 ⁵
German PAMELA ^e	10 ¹³ to 10 ¹⁴	10 ⁹	2x10 ²
PNL Proposed System ^{e,f}	10 ¹² to 10 ¹⁴	10 ¹⁰	10 ³

^aWith NO_x converter and second HEPA filter.

^bIncluding final HEPA filter.

^cData are for total Ru, but since total Ru DF is 0.01 times total Ce DF, one may assume the majority of released Ru is in volatilized form.

^dIf final HEPA filter is included in ventilation system, particulate DF will be increased by a factor of approximately 10².

^eWaste Evaporator (concentrator) included in integrated system.

^fPNL spray calciner with in-pot melter assumed. DF for iodine = 10³.

4. CONCLUSIONS AND DISCUSSION

Some general observations and conclusions that may be made regarding the waste solidification systems reviewed are summarized here. The remarks are categorized into general areas and topics of importance.

4.1 AIRBORNE EFFLUENT REMOVAL REQUIREMENTS

4.1.1 Regulatory Release Limits

Detailed calculations were made of estimates for feed-to-stack DFs that will be required to meet 10CFR20 maximum permissible concentration limits for uncontrolled areas and EPA standards which have been specified for certain isotopes. The analysis took into account the anticipated feed rates of the various isotopes for a typical 6 2/3 MTHM/day waste solidification facility. For correlation of the 10CFR20 MPCs with required DFs, an average χ/Q value from stack-to-site boundary of $1 \times 10^{-7} \text{ sec m}^{-3}$ was assumed; for a typical stack gas flow rate of $52 \text{ m}^3 \text{ sec}^{-1}$, such as will be used at the Barnwell facility, this corresponds to a dilution factor of 2×10^5 . The EPA standards for selected isotopes (Kr-85, I-129, and transuranic elements) are presented in the form of the maximum number of curies for each that may be released per $\text{GW}_{\text{e}}\text{yr}$ in the entire fuel cycle. A fuel burnup of $40 \text{ MTHM/GW}_{\text{e}}\text{yr}$ was used as a basis for calculating the resulting DFs that will be required for the isotopes. Assumptions were made that the only release of transuranics in the fuel cycle will be at the waste solidification facility, and that the only releases of iodine will be from the fuel reprocessing and waste solidification facility.

The results of the analysis indicate the radionuclide that will require the most stringent control is Cm-244. Of the

volatile isotopes, Ru-106 must be most strictly controlled during waste solidification. Ruthenium-106 has required special attention in the past when defense wastes have been solidified in the WCF at the ICPP. Because Ru-106 concentrations in commercial HLLW will be approximately 2700 times greater than in the ICPP wastes⁽²⁾, the importance of controlling its volatility and in removing from the off gas any that becomes volatilized will be much greater for commercial facilities.

The analysis also shows that the recently established EPA standards will result in significantly more stringent limits for releases of transuranic elements, which are predominantly in the particulate form, than those placed by the 10CFR20 MPCs. To limit the release of Cm-244 to the reduced levels, an additional reduction of 3000 is estimated. Thus the feed-to-stack DFs for particulates in waste solidifiers will need to exceed 10^9 .

The EPA standards for I-129 which are approximately 2×10^4 more restrictive than those imposed by the 10CFR20 MPC, may also require control for effluents from waste solidification processes if the I-129 is not adequately removed during reprocessing.

Specific EPA standards have not yet been established for radionuclides other than the transuranics, I-129, and Kr-85. The 10CFR20 MPC for Ru-106 requires an overall DF exceeding 10^4 . However, this does not include consideration of the ALARA clause which will likely result in even tighter controls.

The annual average 25 mr per person whole body exposure limit for the uranium fuel cycle established by the EPA has not been broken down into restrictions for each of the radionuclides nor for the various fuel cycle facilities. This will be a task for NRC, and when they complete their evaluation, it is quite possible that controls will have to be placed on other isotopes which may be volatilized in high-temperature waste solidification processes. Some isotopes that may be included in this category are: Tc-99, Se-79, Te-127m, and H-3.

4.1.2 General Needs for Various Processes

While all processes require control of particulates and volatilized ruthenium, the burden borne by the off-gas treatment system varies with the solidification system. Fluidized-bed and spray calciners place a large amount of particulates in the gas stream and, thus, require greater attention to particulate removal than do other processes. Furthermore, because these two processes have large gas flow rates, the size and, therefore, capital and operating costs of the individual effluent treatment systems will be greater than required for other processes.

Ceramic melters and pot calciners have inherently smaller off-gas flow rates so that relatively small-scale effluent treatment equipment will be needed. However, both have high potential for volatilizing the ruthenium. Pot processes are known to have high ruthenium volatilities. The extent of the problems in continuous ceramic melters has not yet been determined. Because of the large amount of radiation associated with the ruthenium and the need to remove it to such low levels, control systems will need to be rather complex when ruthenium volatilities are high.

4.2 SYSTEM PERFORMANCES

The expected airborne effluent releases from the various waste solidification processes currently in advanced stages of development have been assessed on the basis of past experiences with the processes and with the different types of off-gas treatment devices being used. Generally, the results of the analysis indicate that the 10CFR20 MPC limits for particulate isotopes and for ruthenium, and, also, the recent EPA standards for transuranium elements can be adequately met when high-level liquid wastes are solidified. This does not mean, however, that each of the systems will provide the effluent controls necessary to satisfy ALARA interpretations by regulatory groups.

With one exception, the DFS indicated in Table 19 all exceed the minimum requirements assumed in Section 3.1.2: $DF > 6 \times 10^9$ for particulates and $DF > 7 \times 10^4$ for volatilized ruthenium. See Section 4.1.1 for summary of the bases of the DFS. Again, these values may or may not be adequate when interpretations are made of the ALARA clause. The Eurochemic LOTES process could be improved to an acceptable level of particulate removal by adding a second HEPA filter. The overall DF for ruthenium in the process is significantly smaller than for many other processes. Again, this could be substantially improved by insertion of a ruthenium adsorber bed.

The ruthenium DF for the German FIPS process with its present effluent treatment scheme is unacceptable for application of that process in this country. A ruthenium adsorber bed would be required. Marginal ruthenium DFS are also provided by the experimental system used for development of the PNL fluidized-bed process and by the French rotary kiln process. It is recognized that the former is not a final design for an industrial facility and was only used for cold waste studies.

Some of the process off-gas treatment systems, particularly experimental ones, provide an "overkill" for removal of radionuclides and may not be practical as an industrial facility in terms of simplicity and cost. Others lack basic simple treatments, for example, ruthenium adsorbers. Generally a balance between overall gas cleanup and cost and practical operation must be attempted.

Generally, it is recommended that a solidification process and its operating conditions be selected that results in a small ruthenium volatility, preferably less than 0.1 %, because of its high activity in the feed and the difficulty in efficiently removing it from the off gas. Also, high ruthenium volatilities can present operating problems due to depositions in pipes (see discussion in Section 4.3.5).

Even though reasonable efforts were taken to evaluate the DFs of individual components, taking into account their locations in an integrated system, the estimated DFs in Table 19 must, in many cases, be considered to have large uncertainties associated with them. This is particularly true for the particulate DFs which, generally, have very large predicted values, on the order of 10^{12} or more. Some may be in error two or three orders of magnitude. This is because of the lack of data for individual component DFs when the quantity and size of the particulate loadings become very small and on the effect of relative arrangements of components on overall DFs. However, the fact that the estimated DFs are very large indicates the adequacy of the systems, even in the light of rather large uncertainties.

The sampling and measurement techniques used in past tests on systems have not been sufficiently comprehensive in most cases to allow complete evaluations. Little evidence exists of work on identifying the flowpaths of potentially volatile pure beta emitters such as Tc and Se which may require control, depending on their volatilities and the stabilities of the vapor species.

When a predicted DF is marginal in acceptability, that integrated waste solidification system should be tested to determine if it will meet minimum effluent suppression requirements. In addition to uncertainties in predicted individual component cleanup performances, a given solidification process may produce unexpected levels of effluents. For example, the Danish continuous ceramic melter apparently produced large quantities of dust which was entrained in the off gas, while the PNL continuous ceramic melter produced only a small amount, and the Germans claim that no dust is generated from the continuous ceramic melter in the PAMELA process. Volatile ruthenium generation (and removal) is a rather significant unknown for many processes.

When large overall or individual component DFs are predicted for routine operations, one must recognize the possibility, and resulting effect, of operational failure of a component in the integrated system. That is, the on-stream time is an important additional factor. For example, if a filter ($DF = 10^3$) should fail or the temperature of a ruthenium adsorber ($DF = 10^3$) has an excursion to a range where the adsorber is ineffective, for one day out of a year before the problem is corrected, the annual average DF will be degraded by a factor of 4. More significantly, the twenty four-hour release rate would be increased a factor of 1000 over the normal release rate. It is prudent to provide a sufficient overall safety factor so that unexpected individual failures or process upsets can be temporarily tolerated.

Sintered metal filters are utilized for primary containment of dust in all the processes which form a powder product. Only the PNL proposed off-gas cleaning system (Section 2.9.1) includes a backup high-load particulate removal device. While sintered metal filters are durable and quite reliable, the failure of a filter candle is possible and would result in high dust loading to downstream components. It would be desirable to protect those components which are not designed for high loadings of dust and to preserve system DF for particulates by providing a backup device, such as a second series SMF.

4.3 INDIVIDUAL DEVICES AND CONTROL PROCEDURES

The affect on the processes and the relative merits of some individual off-gas treatment devices and some methods used for effluent control are summarized here. A brief discussion of fundamental design information for particulate devices is included at the end of the section.

4.3.1 Evaporators

As indicated in Table 19 the integration of the waste evaporator (concentrator) into the off-gas treatment system is included in the description and estimates of overall DFs for a few of the processes. It was assumed that aerosol entrainment and ruthenium volatility from the evaporator are 0.005% and

0.001 to 0.01%, respectively. All the processes include pre-concentration of the waste prior to solidification. However, for some of them, the points of tie-in of the evaporator off gas to the off-gas treatment systems, if at all, are not indicated, and, so the affect of the evaporator on overall DFs could not be evaluated. If, as in the Italian pot process, the evaporator condenser off gas enters the system near the front end, the net releases to the environs will not be increased by the operation of the evaporator. If the integration is somewhat downstream in the off-gas treatment system, as in the PIVER process, the overall feed-to-stack DFs may be diminished from those calculated for the path via the solidifier.

Some evaporators may have their own off-gas treatment systems. Unless proper consideration is given to the possible effluents from the evaporator, it may result in an overall increase in net radionuclide releases to the stack.

The aerosol entrainment assumed from the evaporator (0.005%) is based on experience and estimates from the FIPS process (see Section 3.8) and is probably conservatively high. The ruthenium volatilized during evaporation will probably be less than 0.01% if the acid concentration does not exceed 4 $\underline{M}$ ⁽⁹⁴⁾. As the nitric acid concentration is increased, the ruthenium volatility could increase rapidly up to 1% at HNO_3 concentrations greater than 8 $\underline{M}$. However, presence of NO or HNO_2 , even in small quantities when air is largely excluded, can suppress the ruthenium volatilized to 0.003% when HNO_3 concentration is 8 $\underline{M}$ ⁽²⁾. Since radiolysis will likely form significant quantities of NO , it is possible that ruthenium volatility will automatically be controlled to less than 0.01%. Recent measurements performed at the Oak Ridge National Laboratory showed that radiolysis conditions do indeed prevent ruthenium from volatilizing during evaporation of LWR high-level raffinate, even at 9 to 10 $\underline{M}$ HNO_3 concentration⁽⁹⁷⁾.

4.3.2 Sintered Metal Filters

Two methods are described for the application of sintered metal filters for dust containment. The standard arrangement places the filters in a vessel separated from the calciner with filters fully exposed. This configuration requires blowback every 1 to 5 minutes. A new approach is that used in the advanced VERA process in which the filter candles are arranged around the walls in the spray calciner but are individually shrouded. This reduces blowback requirements to 30-minute intervals; alternatively, it may be possible to get by with fewer filters.

4.3.3 Scrubbers and Condensers

Hanson and Kaser⁽⁶⁴⁾ discuss the relative merits of different types of condensers and scrubbers for particulate removal. If the calciner has potential for high solids loading in the off gas, an open-type scrubber, such as a venturi, is recommended. If the potential for loading is small, then a shell-and-tube condenser or a packed-bed quench scrubber is suggested. A packed-bed quench scrubber yields high DFs because of its inherent scrubbing capability but has the disadvantage of relatively high pressure drops and plugging potential. It provides better acid absorption than a venturi scrubber.

4.3.4 Ruthenium Adsorbers

Ferric oxide is becoming widely recognized as a replacement for silica gel for volatile ruthenium removal. Both substances yield DFs of ca. 10^3 under the proper conditions, and both have high capacities. Since they are generally used for final ruthenium removal after the bulk of it has been scrubbed out of the off gas stream, regenerability is usually not an important consideration in the selection. In the past, silica gel has been used in the WCF where water vapor is not removed from the off gas and the dew point at the adsorber is 60 to 65°C; the adsorbers were operated at 65 to 75°C during the campaigns in which indirect heating was used. Most laboratory studies of ruthenium adsorption on silica gel have been carried out at

ca. 80°C. In processes where water vapor is condensed out, the silica gel adsorbers could be operated at a lower temperature where higher DFs might be obtained. One laboratory study at 25°C indicated a DF of 10^5 ⁽⁶⁹⁾. This advantage for a dried gas stream could not be obtained with ferric oxide which requires elevated temperatures for ruthenium adsorption. Further investigations into the use of silica gel at lower temperatures in dried systems is apparently warranted.

The type of ferric oxide adsorbers used in the French PIVER process which are operated at 500°C to 600°C may possess advantages for a fluidized-bed process in which kerosene is burned in the bed. The high temperature of the adsorber may prevent deposition of unburned hydrocarbons which sometimes occur on silica gel beds.

4.3.5 Ruthenium Control

Volatilized ruthenium can be removed from a gas stream by a combination of scrubbing and use of adsorber beds. The quantity volatilized can be controlled somewhat by operational procedures. In-bed combustion of kerosene controls ruthenium volatility in a fluidized-bed calciner to less than 0.01%^(2,37). When a fluidized-bed calciner is heated indirectly, the ruthenium volatility is high at low temperatures but decreases with increasing temperature^(2,37).

Denitration of the HLLW, either batchwise prior to calcining or continuously during calcination will suppress the ruthenium volatility from the calciner significantly. Generally, the volatility from denitrated feed is less than 0.01% in fluidized-bed and spray calciners. The effect of denitration on ruthenium in a continuous ceramic melter is not known.

In processes which have high ruthenium volatilities, ruthenium deposition in pipes can result in plugging as well as create high radiation fields which are difficult to eliminate for contact maintenance when required. Some techniques to prevent ruthenium deposits in problem locations have been

reviewed by Christian⁽²⁾. Briefly those which are somewhat effective are maintaining the wall temperatures at 250 to 350°C, avoiding decreasing temperature gradients, and, possibly, diluting the oxygen in the gas with an inert gas (N₂ or NO) which causes the depositions to occur at high temperatures. Use of inert and reducing gases in fluidizing and purge streams can also reduce the ruthenium volatility.

4.3.6 NO_x Converter

In addition to providing increased DF for NO_x removal over that by scrubbers, an NO_x converter may provide advantages in removal of volatilized ruthenium and, possibly, other semivolatile species from the off gas. Preliminary information indicates that the DF for ruthenium is approximately 380.

The combined advantages of improved DF for NO_x removal and enhanced removal of volatilized ruthenium (and possibly other semivolatile species) make an NO_x catalytic converter an attractive alternative to scrubbing out nitric acid. Even if the HNO₃ is reclaimed, the NO_x converter can be used as a polishing bed for NO_x and ruthenium.

NO_x removal early in the off-gas system could also result in appreciable aid in operating costs by eliminating downstream NO_x corrosion.

4.3.7 HEPA Filters

Final filtration for the processes is supplied by HEPA filters. While they are highly efficient for small particulate removal, HEPA filters do possess some operational drawbacks, particularly under accident conditions. Their efficiencies are dependent on low linear face velocity through the filter medium and the filters are subject to particle penetration at differential pressures exceeding 0.02 atm. A backup filtering device or system should be provided for protection in the event of adverse or accident conditions. The possibility of either providing backup filtering or of substituting the HEPA filter with a sintered metal filter might be considered.

See additional discussion in Section 5.4.1.

4.3.8 Fundamental Considerations for Particulate Removal

Theodore and Buonicore⁽⁹⁸⁾ have reviewed in some detail the fundamentals and design principles of industrial control equipment for particulate air pollutants. The general types of devices which are discussed in depth are gravity settlers, centrifugal separators, electrostatic precipitators, wet scrubbers, and fabric filters; the design of each is considered from both a theoretical and practical viewpoint. The important facts and conclusions regarding some selected devices which appear pertinent to the nuclear industry, including some currently in use as well as others, are summarized here. For additional details and discussion, the interested reader is referred to the comprehensive review of Theodore and Buonicore⁽⁹⁸⁾.

Conventional cyclones have body diameters three to five times the diameter of the inlet duct and are useful where large gas handling capacity and moderate collection efficiency is required. High-efficiency cyclones have smaller body diameters and usually must be arranged in a parallel bank of several elements to handle typical gas volumes. The collection efficiencies for different sized particles of the two classes of cyclones are given in Table 20. Pressure drops across cyclones are typically 0.005 atm.

TABLE 20
CYCLONE COLLECTION EFFICIENCY

Particle size (μm)	Efficiency (% by wt)	
	Conventional cyclone (%)	High-efficiency cyclone (%)
<5	-----	50-80
5-20	50-80	80-90
15-50	80-95	90-99
>40	95-99	95-99

Spray towers are suited for both particle collection and mass transfer (gas absorption) as are all wet scrubbers. They are capable of handling large gas volumes and are often used as precoolers to reduce gas stream temperatures. Particles larger than 10 μm can typically be removed with efficiencies up to 70%. The chief disadvantages of spray towers is their relatively low scrubbing efficiency for dust particles in the 0 to 5 μm range.

Packed-bed scrubbers, while normally used for removal of gaseous pollutants, are also highly efficient for removing particulates. For the collection of particles as small as 3 to 5 μm , packed countercurrent scrubbers have been found to be the most efficient. To remove particles as small as 0.25 μm in diameter, high energy cocurrent flow must be used. Operating pressure drops in packed-bed scrubbers are typically 0.008 to 0.03 atm per meter of bed depth but rapidly increase for the high efficiency scrubbers. Countercurrent scrubbers are normally 1 to 3 meters deep; concurrent flow beds are shallower.

As mentioned earlier, the major problems in using packed-bed scrubbers for particulate removal are plugging of the packing and the maintenance problems subsequently incurred. A general rule of thumb is to allow a maximum of 0.5 g of dust per standard cubic meter of gas to enter a packed tower. Application of moving-bed scrubbers to particulate removal often minimizes, if not eliminates, the plugging problem. Pressure drops in moving-bed scrubbers typically range from 0.007 to 0.01 atm per stage, and collection efficiencies may be in excess 99% for particles down to 2 μm .

Atomizing inertial scrubbers include venturi type, impingement plate, and disintegrator scrubbers. They are generally characterized by the ability to handle relatively high dust loadings in large gas flow rates. Efficiency in the 90 to 95% range can be obtained for particles greater than 5 μm in diameter.

The efficiency of a combined venturi-impingement scrubber is relatively high for particulates as small as 0.5 μm in diameter.

The pressure drop usually ranges from 0.02 to 0.037 atm.

The collection efficiency of a venturi scrubber is dependent on pressure drop; pressure drops range from 0.01 to 0.2 atm. A 0.025-atm pressure drop venturi can typically remove particles as small as 2 μm with virtually 100% efficiency, while a 0.15-atm pressure drop venturi is often required to remove particles as small as 0.3 to 0.4 μm . When the pressure drop across the venturi scrubber used in the waste cladding facility at the ICPP was ca. 0.15 atm, the particles exiting it had a reported median diameter of 0.1 μm ⁽⁴⁾.

The venturi itself is only a gas conditioner and must be followed by a separating section for the elimination of entrained water droplets.

Impingement-plate scrubbers provide collection efficiencies of 90 to 98% for 1 μm particles with pressure drops ranging from 0.0025 to 0.2 atm.

Impingement-plate scrubbers are designed for collection of small, submicron particles and require prior removal of larger particles. They have high operating costs due to the energy required to drive impellers; the need for a seal for the impeller drive shaft makes their application in a nuclear facility questionable.

Electrostatic precipitators can provide high collection efficiencies for submicron particles, as small as 0.01 μm , with low pressure drops (< 0.01 atm). They can handle large gas flows, to 10^3 actual m^3/sec . The disadvantages include large space requirements for installation, high initial and operating power costs, and formation of a poor waste product for disposal.

4.4 SUMMARY

In summary, most of the vitrification processes and their associated off-gas treatment systems are practical in terms of limiting the radioactive gaseous effluents. The choices

of process and off-gas treatment system depend on a number of factors, including required throughput and trade simplicity/cost and overall effluent releases. The information summarized in this report contains data which can be used in an objective design and evaluation. The detailed considerations have revealed a number of areas where additional experimental data are needed for accurate prediction of system performances for effluent control. Some recommended development studies are outlined in Section 5.

5. RECOMMENDED DEVELOPMENT STUDIES

The evaluations have led to the recognition of a number of areas where additional information is needed in order to predict and/or control airborne effluents from the processes and to assess the adequacies of the controls. The studies which are recommended are outlined below.

5.1 RELEASE LIMITS

With regard to established maximum allowable release rates, additional studies should be made to determine the desired local and global maximum release rates for the long-lived and the moderately long-lived volatile and semivolatile radio-isotopes, because they can accumulate globally as the number of nuclear facilities increases. Limits are needed so that any necessary additional controls can be established. Of particular concern are the isotopes I-129 ($t_{1/2} = 1.59 \times 10^7$ yr), Tc-99 ($t_{1/2} = 2.13 \times 10^5$ yr), and Se-79 ($t_{1/2} = 6.5 \times 10^4$ yr), and, for fuel reprocessing plants, C-14 ($t_{1/2} = 5730$ yr) which will tend to accumulate in the biosphere once released. Also, accumulations of H-3 ($t_{1/2} = 12.33$ yr) and Cm-244, the worst particulate, ($t_{1/2} = 18$ yr) and, for fuel reprocessing facilities, Kr-85 ($t_{1/2} = 10.73$ yr) should be avoided because large quantities in the environs would remain for several generations. Future studies should include in-depth investigations of the biological hazards of these isotopes and of the potential pathways to man. These data can then be coupled with evaluations of long-term projections of nuclear facility installations to provide rational estimates of maximum release rates that can be permitted cumulatively for facilities worldwide and for individual installations.

While global accumulations must be concerned with long-lived isotopes, local releases of shorter-lived isotopes must

also be adequately controlled to protect the immediate population. Those included in this category are other potentially volatile species, such as selenium, tellurium, and antimony, as well as ruthenium. More quantitative data are needed on their health effects and environmental transport.

5.2 INDIVIDUAL ISOTOPE BEHAVIORS

The process behavior and control of most of the semivolatile species considered in Section 5.1 are not generally understood. Studies of the volatilities and of the removal efficiencies in the off-gas system of these semivolatile species, particularly Tc-99, are needed so that their releases can be predicted and, if necessary, controlled. The removal efficiencies of off-gas treatment devices for volatilized cesium ($t_{1/2} = 30$ yr for Cs-137) should also be investigated, because it can enter the gas stream as a vapor species in some vitrification processes.

As discussed in Section 2.4.1, tellurium and selenium volatilities may be high for phosphate glass processes. Thus, the flowpaths of these elements should particularly be investigated in processes in which phosphate glass is made, such as the PAMELA process and the Italian pot process.

Because of its high activity in the feed and lack of extensive data on its behavior during high temperature vitrification processes, the volatility of ruthenium during vitrification in the selected processes should be determined. This is particularly important for the ceramic melter processes. Because of the possible instability of any volatilized ruthenium in these processes, the flowpath in the off-gas treatment system should be investigated. The behaviors of other potentially volatile species should particularly be determined for the ceramic melter which operates at very high temperatures. As indicated in Section 3.10, the operating conditions for a wiped-film evaporator are optimum for possibly causing ruthenium to become volatilized. Thus, the ruthenium volatility behavior in a wiped film evaporator, with and without feed denitration with formic acid or formaldehyde, must be

investigated prior to its application to concentration of commercial wastes.

5.3 CONTROL TECHNOLOGY FOR SEMIVOLATILES

In general, the potential problems of semivolatiles other than ruthenium becoming airborne are not presently well understood. Thus, specific recommendations for their control cannot be made at this time. Specific studies for ruthenium control are recommended below.

5.3.1 Process Control of Ruthenium

If ruthenium transport into the off gas of a ceramic melter is found to be a problem, the effect of denitrating the feed, either batchwise, or continuously in the melter, should be investigated to see if it has a significant suppression effect for the high temperature conditions. For calcination/vitrification processes in general, where ruthenium volatility is normally on the order of 1% or greater, the effect on the volatility of in-calciner denitration with formic acid should be determined. If the suppression effect is significant, the off-gas removal system may be simplified. Also, in-calciner denitration may possibly convert nitrogen-containing gas species to predominately innocuous and noncorrosive N_2 or N_2O (see Section 2.2.2).

5.3.2 Ruthenium Adsorbers

Limited studies indicate that ruthenium adsorption by silica gel may be greatly enhanced over that normally obtained at ca. 70°C by maintaining the silica gel near 25°C. The possible application of silica gel for removing ruthenium from the off gas in dried streams at low, near ambient, temperatures should be investigated.

Additional measurements should be made of capacities of ruthenium adsorber materials, particularly the ferric oxide-based ones which can be used near the head end of the off-gas system, where the temperature is high and where it would be

exposed to relatively large concentrations of ruthenium in the gas stream.

More extensive studies regarding the optimum operating conditions, particularly temperature and superficial vapor velocity, for the ferric oxide-based adsorbers are needed. The recommended temperatures range from 250°C for the British filter/adsorber to 600°C for the French devices. While DFs for ruthenium of 10^3 have reported^(71,72), values exceeding 10^2 are difficult to obtain (see Sections 3.5.2, 3.5.3, and 3.5.4). Thus, it is important to establish acceptable ranges of operating parameters.

Further investigation is needed to determine the effectiveness of an NO_x converter for removing volatilized ruthenium from the off gas, including DF, capacity, and how catalyst properties for NO_x reductions are affected.

5.4 GENERAL AIRBORNE EFFLUENT TREATMENT

Some recommendations related to the general treatment of airborne effluents are discussed below. Individual devices are first considered and then some comments are made regarding studies with integrated off-gas systems.

5.4.1 Individual Devices

Final filtration for the process systems is supplied by HEPA filters. They do possess several drawbacks, particularly under accident conditions (see Section 4.3.7). Because of their limited loading capacity, they contribute significantly to the volume of solid wastes. These problems could possibly be minimized with the appropriate use of sintered metal filters, but they must first be proven effective in laboratory and pilot-scale studies. Sintered metal filters can be obtained with pore diameters as small as 5 μm and have claimed efficiencies approaching those of HEPA filters for particles as small as 0.1 μm . It is suggested that an in-depth study be made of their applicability to the nuclear industry, especially for reprocessing and high-level waste solidification processes.

As implied earlier in Section 4, projected system DFs are difficult to make because individual component DFs are not well established. Studies are needed to determine component efficiencies for removing particulates and volatilized ruthenium as functions of concentrations and particulate and aerosol sizes down to those expected in the most downstream location in the system where a particular device might be used. Aerosol re-entrainment from wet devices should be included when measuring DFs across the components. The theoretical limits for efficiencies and particle sizes that can be removed should be established for the various types of equipment.

5.4.2 Integrated Systems

Beyond thorough studies of individual devices, more extensive investigations might determine the combined efficiencies of probable arrangements of two or more components. The configurations must be limited to a few reasonable ones, because a very large number of combinations ($n!$) can exist for three or more components.

When studying component or system performances, consideration must be given in the design of the experiments to the possible effects on DFs of scaling up equipment to plant sizes. Although it is frequently possible to simulate face velocities, residence times, etc. that would be expected in a plant, small-scale equipment does not always provide identical conditions or results that a large system would. Where possible, scale-up effects should be estimated, or at least the limitation on data imposed by them acknowledged. This problem also makes it difficult to extrapolate off-gas component data from a plant-scale pot process, for example, which has a small off-gas flow rate, to a process with large off-gas flows, such as spray or fluidized-bed calciners.

5.5 SAMPLING AND MEASURING

A problem with testing overall system performances is the difficulty in sampling and measuring the miniscule quantities

of materials in the cleaned off gas. For particulate DFs in the range of 10^{11} to 10^{14} , the concentrations of high-activity isotopes in the process off gas will be on the order of 10^{-8} to 10^{-13} $\mu\text{Ci}/\text{cm}^3$. For volatilized ruthenium DFs of 10^7 to 10^{11} , the volatilized ruthenium activity in the off gas will be on the order of 10^{-6} to 10^{-10} $\mu\text{Ci}/\text{cm}^3$. These levels of concentrations cannot be measured by counting methods⁽⁹⁹⁾. Concentration and more sensitive detection methods must be utilized. Hower et al. have recently reviewed and discussed sampling and measuring problems for nuclear reprocessing and waste solidification facilities⁽⁹⁹⁾. A thorough evaluation of the problem requires extensive in-depth considerations. The interested reader is referred to this study for detailed discussion. A number of recommendations for development studies are included in the report.

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