SESSION II

WASTE TREATMENT : VOLUME REDUCTION AND PREPARATION FOR STORAGE

Monday, August 7, 1978
CHAIRMAN: J. C. Dempsey

OPENING REMARKS OF SESSION CHAIRMAN:

The session we're starting is Waste Treatment: Volume Reduction and Preparation for Storage. By way of perspective, I've been a member of the Interagency Review Groups that have been mentioned in the previous session. The whole purpose is to come up with a work plan and to take care of the nation's wastes in a long-range way. High level waste, low level waste, transuranic waste, and all the rest. Whether processing liquids or solids, offgases are one of the technically vulnerable points in every case, from a technical as well as a control point of view. In that sense, we're working against a moving, or unknown, target because the regulations are being ratcheted in different ways. For example, EPA and NRC are meeting to prepare guides and regulations regarding what emissions will be permitted from DOE facilities. It is expected that this work will be completed about this time next year. So, all of the technology we will be talking about today should be considered in this context. We will be discussing incineration of low level transuranic waste, as well as calcination and vitrification of high level waste. There's no doubt about its being a national requirement. We have waste in-place and we must do something about it. The President has asked us to have a plan ready by October 1 in which all the aspects are outlined and what each agency has agreed upon as goals and timing. Of course, one of the major questions is, "When are you going to get it in the ground?" and that's one of the things we're concerned with. There is, as you know, a timetable that identifies calendar year 1985 as the starting date for a facility to accept DOE transuranic waste. And, to get there from here, the decision that must be made is whether to process all that waste by incineration. Therefore, 1985 looms very near when you consider that all this technology must be in-place and functioning by that time. I mention this to suggest that we have a new note of urgency about the technology that we will be talking about this afternoon.

The first paper is going to be by one of our colleagues from Canada. We're most interested to hear about their program, which apparently is very parallel to ours. The second paper is from the Allied Chemical Corporation in Idaho. It relates to the offgas treatment of high-level wastes. For several years Idaho has taken the lead in treating liquid wastes and is now moving to a still more elaborate treatment system. The third paper is also on the solidification of high-level waste; this time on vitrification, by Savannah River Laboratory. I'd just give you a bit of perspective here: I think it's public information that this program is also on the critical path of taking care of our nation's wastes. Solidifying these wastes is a major concern. Work has been going on for some time but now that the reports are coming in, we're sizing up the real magnitude of the problem. A plant to do this is now estimated well over 2 billion dollars and it will also be of concern in the Presidential report that is in preparation. All of us here have a vested interest in what Dr. Wilds has to say and it will perhaps impact on our children, as well. I think you'll agree that our final paper represents a fascinating and ingenious solution to a waste problem.

OPERATION OF LOW-LEVEL RADIOACTIVE WASTE INCINERATOR

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ABSTRACT

Ontario Hydro's radioactive waste incinerator designed to reduce the volume of low-level combustible wastes from nuclear generating station's was declared in-service in September 1977. Hitherto about 1500 m^3 of combustible waste have been processed in over 90 separate batches. The process has resulted in 40:1 reduction in the volume and 12.5:1 reduction in the weight of the Type 1 wastes. The ultimate volume reduction factor after storage is 23:1. Airborne emissions has been maintained at the order of 10^{-3} to 10^{-5} percent of the Derived Emission Limits. Incineration of radioactive combustible wastes has been proven feasible, and will remain as one of the most important processes in Ontario Hydro's Radioactive Waste Management Program.

I. INTRODUCTION

Ontario Hydro is currently operating over 4000 MW(e) capacity of CANDU (Canadian Deuterium Uranium) generating stations. Another 15,000 MW(e) capacity will also be available by 1990 (Figure 1).

The radioactive solid wastes from the generating stations are processed and stored at the Radioactive Waste Storage Sites of the Bruce Nuclear Power Development Services (BNPDS) Department. Generally over 80% of the Type 1 wastes from the generating stations are classified as processable (Figure 2). The present storage cost of Type 1 solid wastes in fully engineered trenches is $1060/$m^3$ ($\sim$$30/ft^3). Due to this high cost, there is considerable economic incentive to reduce the volume of the radioactive wastes prior to storage.

The volume reduction processes selected are incinceration for combustible wastes having less than 5 mR/h on contact, and compaction for wastes unsuitable for incineration. The low-level radioactive waste incincerator is located in the Waste Volume Reduction Facility (WVRF) of the BNPDS Department. The incinerator was commissioned in May 1977 and declared in-service in September of the same year.

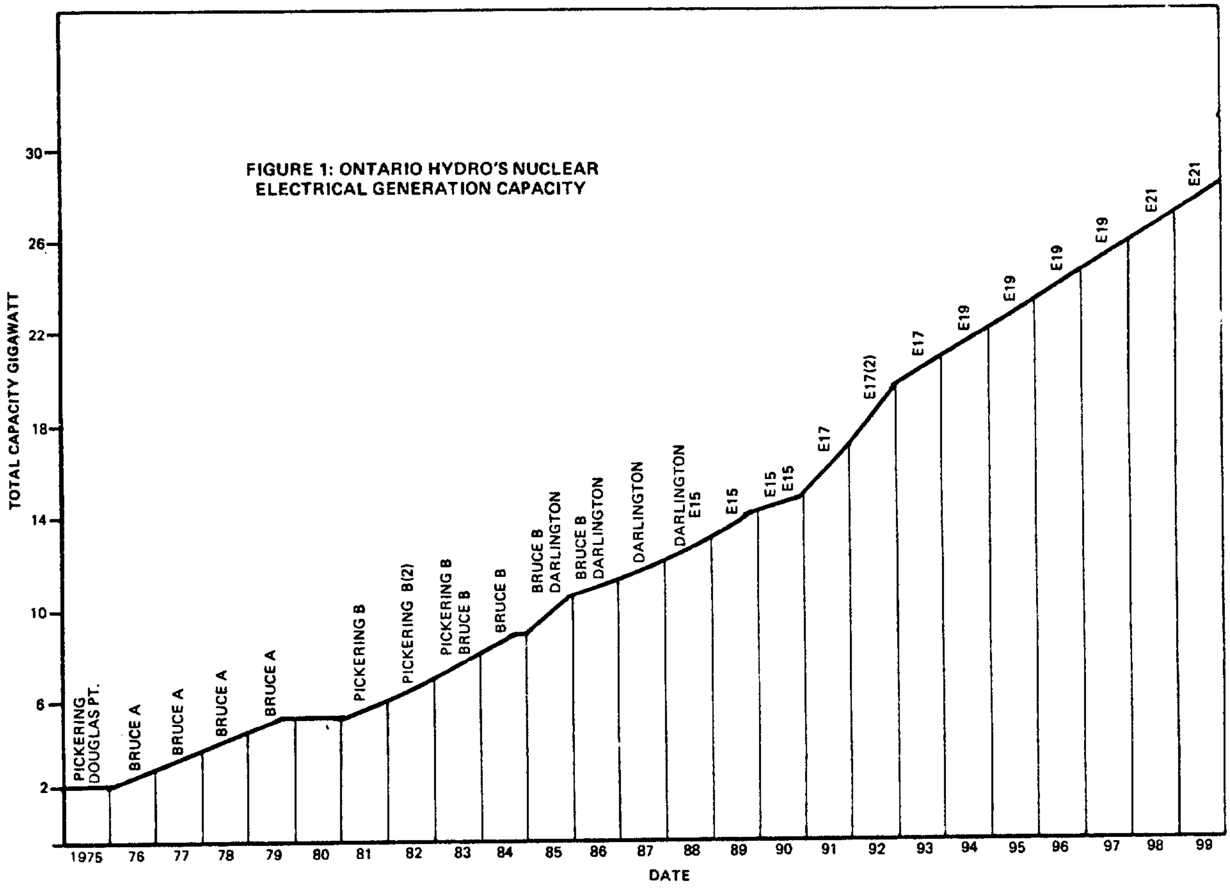

FIGURE 1: ONTARIO HYDRO'S NUCLEAR ELECTRICAL GENERATION CAPACITY

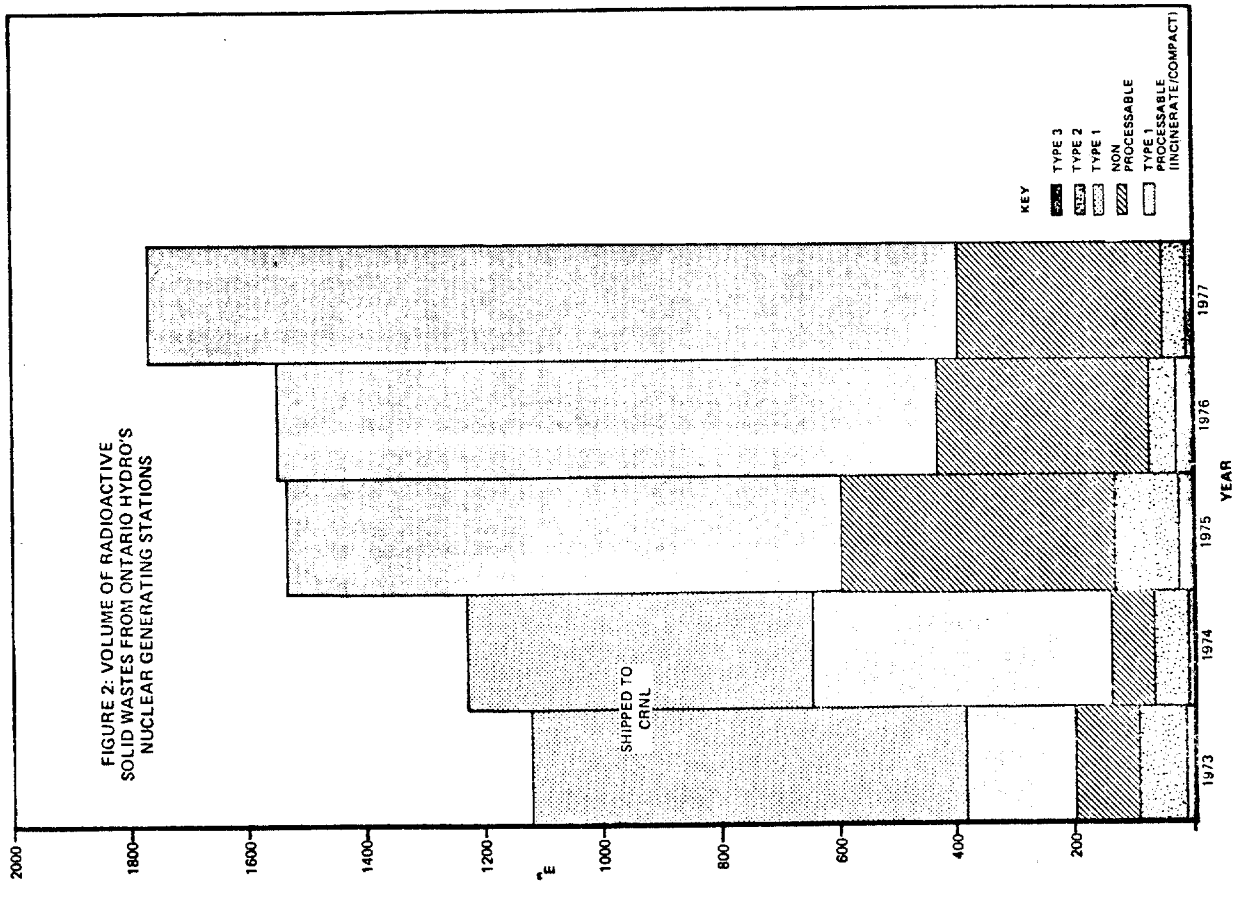

FIGURE 2: VOLUME OF RADIOACTIVE SOLID WASTES FROM ONTARIO HYDRO'S NUCLEAR GENERATING STATIONS

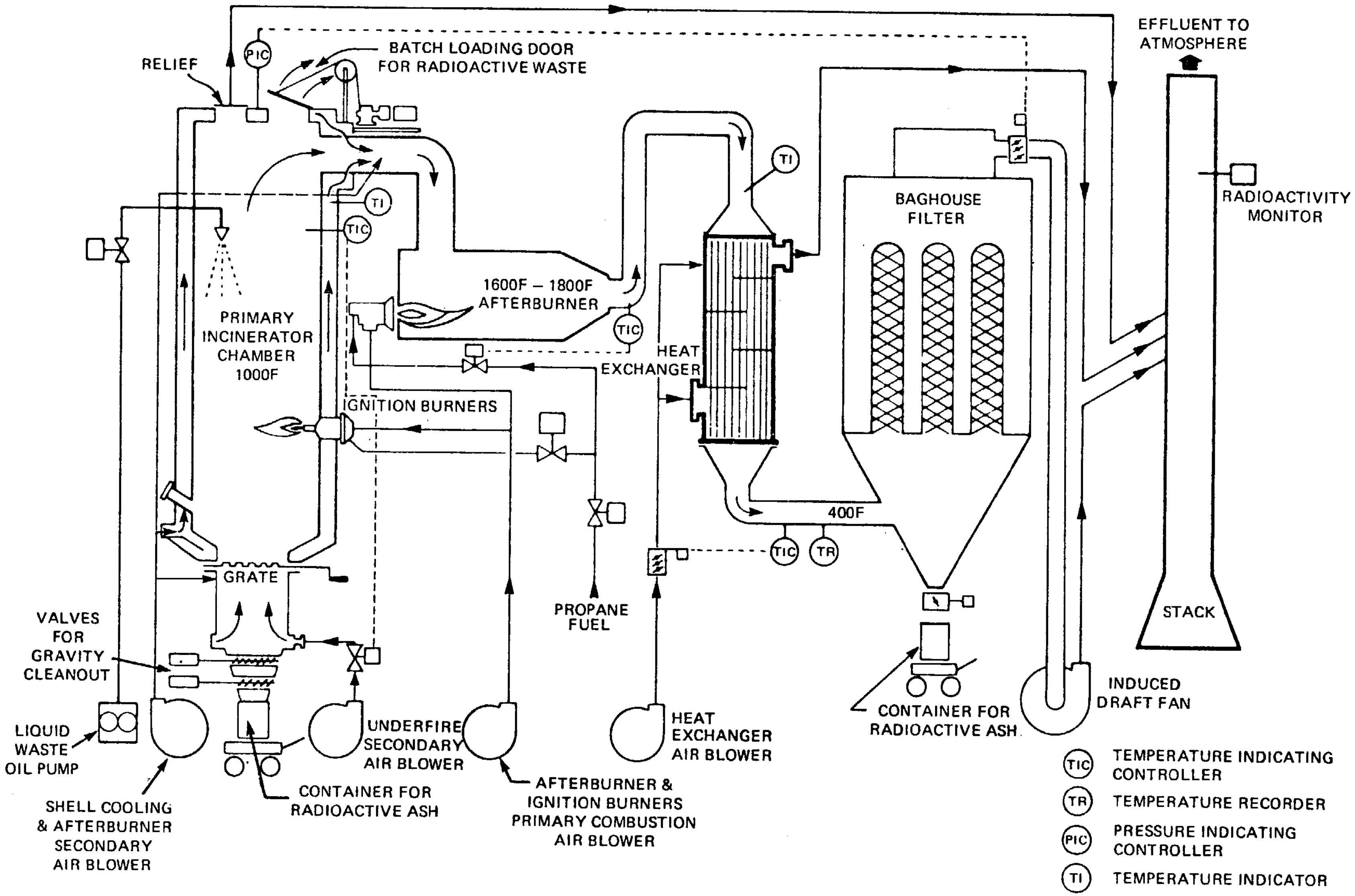

FIGURE 3 INCINERATOR SCHEMATIC

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The wastes processed in this system may contain disposable cotton and plastic coveralls, gloves, cardboard, paper, wood pieces, oil absorbers, and mop heads, etc. Specific activity of the wastes is on the order of 10^{-4} Ci/m^3. The wastes are generally packed in clear polyethylene bags with an average weight of about 5 kg/bag.

2.0 RADIOACTIVE WASTE INCINERATOR SYSTEM DESCRIPTION

Controlled air incineration is used to minimize radioactive particulate emissions(Figure 3). The incinerator's design capacity is 17 m^3/burn (600 ft^3/burn). About 2200 kg of wastes can be processed in each burn cycle.

The primary chamber of the incinerator is loaded in batch prior to ignition. Temperature in the primary chamber during the burn is maintained at 538°C (1000°F) by adjustment of the underfire air. The pyrolyzed gases generated in the primary chamber are further oxidized in the after-burner at 871°C to 982°C (1600°F to 1800°F) with the aid of a propane burner. The high-temperature flue gas from the after-burner is then cooled to 204°C (400°F), the limiting temperature of the baghouse. Despite the system's characteristicly low particulate loading, a shaker type baghouse with Nomex bags is provided for further filtration prior to release. The incinerator is maintained at slightly negative pressure (-0.05 kPa(g) or -0.2 psig) by an induced draft fan.

Detailed design of the incinerator was discussed in a previous publication(1).

3.0 OPERATING EXPERIENCE

3.1 General

About 1500 m^3 of Type 1 combustible wastes have been processed in more than 90 burns since the middle of 1977. The majority of the wastes processed had a contact field of less than 2 mR/h. Until the end of 1977 50 hours were required to completely process a batch of waste. This included:

2 hours for loading the primary chamber with wastes;
2 hours for warming-up the after-burner;
24 hours for burning (from primary chamber ignition to after-burner shut-down);
20 hours for cooling (from after-burner shut-down to ash unloading);
2 hours for ash unloading into 200 L drums.

The process time has since been reduced to about 36 hours eliminating the cooling period. Hot ash is now unloaded directly into 2.5 m^3 rectangular carbon steel containers as soon as the burning cycle is completed.

The larger, rectangular container also have the advantage of holding several burns of ash, thus reducing the handling time, and providing maximum use of storage space.

TABLE 1

Radioactive Compositions of Incinerator Ash

SAMPLES OF ASH FROM EACH BURN	SPECIFIC ACTIVITY OF THE SAMPLE (mCi/m^3)	RADIOACTIVE COMPOSITIONS IN %							
		Ce-144	Cr-51	Cs-137	Zn-65	Co-60	Zr/Nb-95	Ru-106	Others
1	14.15	8.9	14.1	27.2	9.6	26.1	6.5	-	7.6
2	30.67	8.7	54	5.0	1.8	1.9	6.9		4.6
3	39.06	5.6	6.2	5.9	14.1	30.7	27.0		10.5
4	67.89	7.2	5.5	4.4	7.9	66.7	4.1		4.2
5	19.17	11	27	7	11	26	7		11
6	16	18	2.3	22.7	2.6	18.2	3.5		32.7
7	8	17	3	14	3	36	19		8
8	6	14	2	26	6	37	8		7

An average batch-load of waste (~16.4 m^3) produces about 0.4 m^3 of ash, giving an average volume reduction factor of 40 to 1. The average weight reduction factor is about 12.5 to 1. The ultimate volume reduction factor is 23:1 after storage of the 2.5 m^3 containers in engineered concrete trenches. One container occupies about 3.5 m^3 of trench space.

3.2 Characteristic of the Incinerator Ash And Heat Exchanger Deposit

Specific activity of the ash collected ranges from 5 to 100 mCi/m^3 depending on the type of wastes processed. Contact fields on most of the container surface is between 10 and 20 mR/h.

Analysis of the ash collected suggests that Co-60 is the predominant radionuclide. Other major radionuclides found are Ru-106, Cs-137 and Ce-144 (Table 1). This finding is consistent with the radionuclides found in other types of radioactive solid waste. It can be seen that these radionuclides are the activation and fission products generally found in the reactor systems. Since most of the solid wastes processed by the incinerator are generated during reactor maintenance, it is not surprising that they are contaminated with the above mentioned radionuclides.

Particle distribution analysis of a sample of ash collected in the baghouse suggests that 10% of the ash particles are under 10 µm and 50% under 30 µm. The largest particle found is about 2000 µm. The latter may be attributed to particle aggregation in the baghouse.

Samples of slag from the primary chamber, and deposits in the inside of the heat exchanger were analyzed for weight loss upon ignition at 1000°C, and the chemical composition. The results are summarized in Table 2.

Among the gamma-emitting radionuclides identified with the heat exchanger slag deposit, Cs-137, Zn-65, Cs-134 had notably higher concentrations than others such as Ru-106, Co-60.

3.3 Radioactive Airborne Emissions

The stacks of both the radioactive waste incincerator and the incinerator building ventilation system are equipped with radioactivity monitors. Tritium, iodine and particulates emissions are continuously monitored for operational control. The building ventilation also includes exhaust air from the compactor when it is in operation. Since the incinerator is maintained at negative pressure, its contribution to radioactivity emission via the building ventilation exhaust is not significant during the burn cycle. Some low-level, localized contamination of the room air may occur during the incinerator loading and ash unloading periods.

TABLE 2

Analyses of Incinerator Slag and Ash

SAMPLES	% Weight Loss Upon Ignition at 1000°C After 100 Minutes	Chemical Elements Identified			Compounds Identified In Crystalline Phase
		Major	Minor	Trace	
Heat Exchanger Tube Deposit	10-11	Fe,Zn,S,Cl	Cu,Ni,K,Ca,Cr Ma,As	Si,Ti	ZnS,CuO
Primary Chamber Slag Deposit	1	Fe,Cu,Ca	Al,Si,S,Cl,K Ti,V	Ni,Zn	CuO
Heat Exchanger Ash Deposit	1	Fe,Zn,S	Cu,Ni,K,Ca Ti,V,Ma,As	Si	Fe_3O_4,ZnS,CuO

Emissions of radioactivity are usually expressed in percent of the Derived Emission Limits (DEL). The DEL of each radionuclide expressed in Ci/week is estimated from the maximum continuous release rate (Q) of that particular radionuclide. Q is in turn expressed as:

$$Q\ (\mathrm{Ci/sec}) = \mathrm{MPCa}/\mathrm{Ka} \qquad (1)$$

where MPCa = the Maximum Permissible Concentration of the radionuclide in air ($\mathrm{Ci/m^3}$)
Ka = long term mean dilution factor ($\mathrm{sec/m^3}$) as a function of the effective stack height, the distance from the source and the weather.

The MPCa, Ka and DEL of the major radionuclides emitted from the incinerator and its building based on various pathways are given in Table 3.

Using the lowest limits given in Table 3, the DEL's for the radioactive incinerator and its building are:

I-131	0.72 Ci/wk
H-3	1.4×10^5 Ci/wk
Particulates	1.8 Ci/wk

Airborne emissions from the incinerator and its building in 1977 and early 1978 have consistently been below 0.1% for particulates, 0.01% for I-131, 1% for H-3 (Figure 4). Airborne emissions in each burn via the incinerator stack are given in Figure 5. The variation from burn to burn is attributed to the origin and the type of wastes processed.

Tritium emissions have been consistently higher than other radionuclides mainly because of the higher tritium content in the wastes, and the volatile nature of tritium as tritium oxide upon incineration. Tritium concentrations in the reactor systems are increasing as a result of neutron activation of heavy water. The average tritium concentration at Pickering 'A' Generating Station's Moderator System was about 16 Ci/kg of heavy water at the end of 1977, compared to 11 Ci/kg at the end of 1975. Airborne emissions of tritium from Pickering 'A' were about 10 times higher than those from the Waste Volume Reduction Facility in 1977.

Emissions of I-131 and particulates have consistently been below 10^{-4} Ci for most of the burns. Analyses by the stack monitors suggest that Cs-137, Cs-134 and Zn-65 are the major radionuclides and constitute about 70% of the gross $\beta\gamma$ emission. It can be seen from Figure 5 that aside from tritium, emissions of radioactivity from the incinerator are sufficiently low that extensive flue gas treatment is not necessary with the type of wastes presently processed.

TABLE 3

Parameters Used for Airborne Emission Control

	Indirect Intake Via Food Chain (Ka = 5 x 10^{-7} sec/m^3)		Direct Intake Via Inhalation or External Irradiation (Ka = 1.3 x 10^{-6} sec/m^3 @ 1 km from source)	
Radionuclides	MPCa (Ci/m^3)	DEL (Ci/wk)	MPCa (Ci/m^3)	DEL (Ci/wk)
<u>I-131</u>	6 x 10^{-13}	0.72	3 x 10^{-11}	14
<u>H-3</u>	-	-	3 x 10^{-7}	1.4 x 10^{5}
<u>Particulates</u>				
Cs-137	5 x 10^{-11}	6.1	1.5 x 10^{-9}	700
Cs-134	1.5 x 10^{-11}	1.8	1 x 10^{-9}	470
Sr-90	1.5 x 10^{-12}	1.8	4 x 10^{-11}	19
Sr-89	1.5 x 10^{-11}	1.8	2 x 10^{-10}	93
Co-60	-	-	9 x 10^{-11}	42
Ru-106	-	-	4 x 10^{-11}	19
Unidentified Particulates	1.5 x 10^{-12}	1.8	4 x 10^{-11}	19

TABLE 4

Economic Analysis of the Radioactive Waste Incinerator

<u>Annual Cost Without Incineration</u>	
Waste Processable/y	2000 m^3
Storage Cost (\$1060/m^3)	\$2,120,000
<u>Annual Cost With Incineration</u>	
Ash Volume/y (Volume Reduction factor = 23:1)	87 m^3
Storage Cost (\$1060/m^3)	\$ 92,000
Annual Fixed Cost of the Incinerator (Total Capital Cost = \$3.7M, Capital Recovery Factor = 0.24 depreciated in 6 y, 11% interest rate)	\$ 875,000
Annual Operating and Maintenance Cost Under Normal Conditions (Estimated)	\$ 600,000
Total Annual Cost With Incineration	\$1,567,000
Annual Savings from Incineration	\$ 553,000

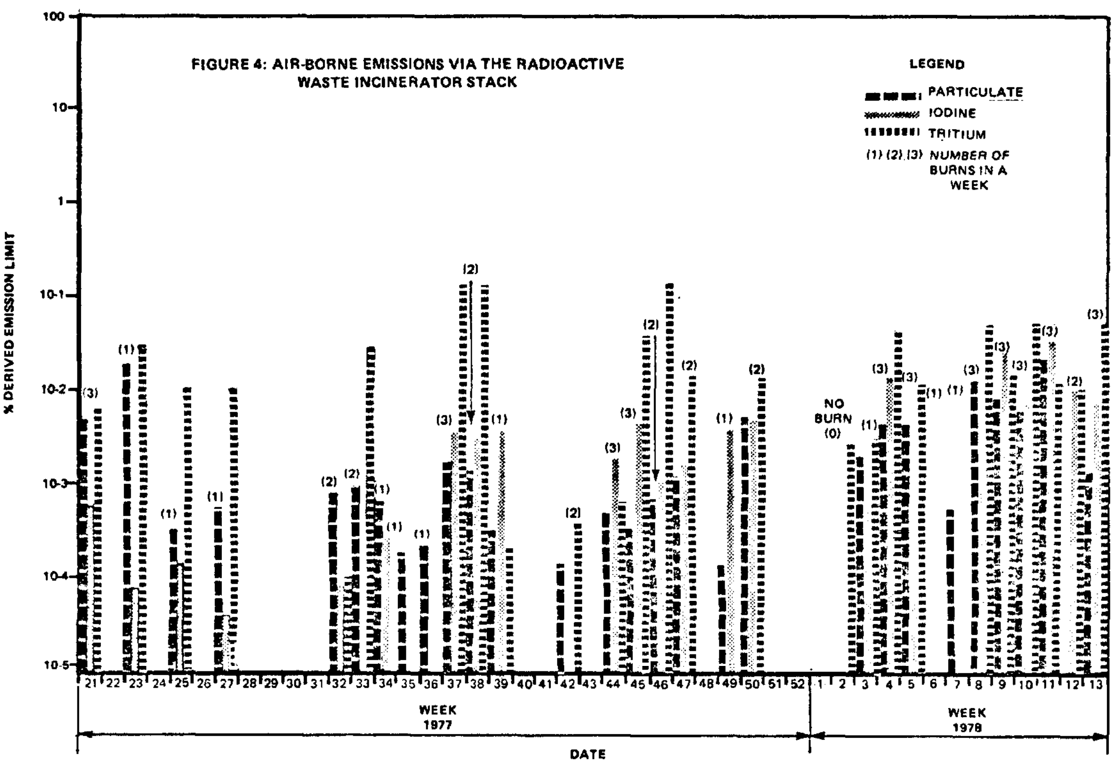

FIGURE 4: AIR-BORNE EMISSIONS VIA THE RADIOACTIVE WASTE INCINERATOR STACK

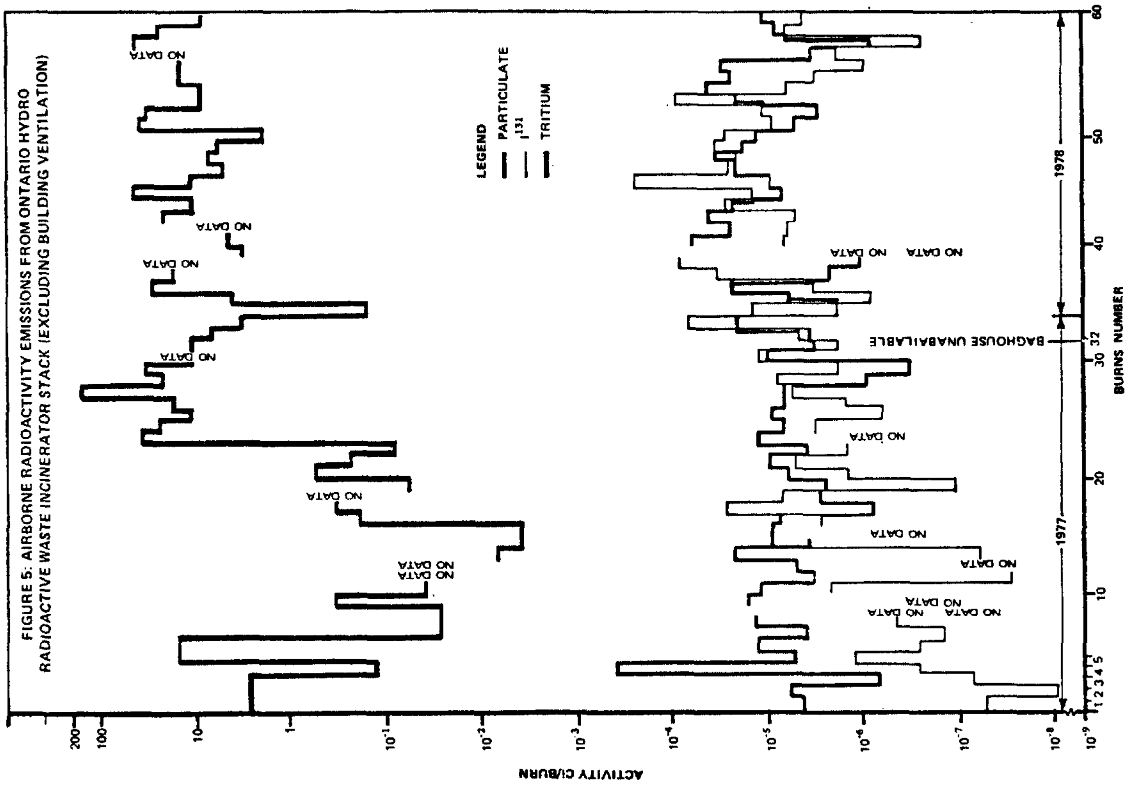

FIGURE 5: AIRBORNE RADIOACTIVITY EMISSIONS FROM ONTARIO HYDRO RADIOACTIVE WASTE INCINERATOR STACK (EXCLUDING BUILDING VENTILATION)

3.4 Other Airborne Emissions

The Environmental Protection Act of Canada(2) limits the emissions of HCl (most restrictive among other contaminants such as Cl_2, SO_2) by requiring that its half-hour average ground level concentration at the site boundary (first point of impingement) be no more than $100\,\mu g/m^3$. This is equivalent to a maximum emission rate of 10 g/s under Type D Atmospheric Stability.

The Ontario Ministry of Health further requires that the air quality in the working environment be lower than the Threshold Limit Value of $7000\,\mu g$ of HCl/m^3 for an 8 hour working day, and 5 day working week. Time averaging is not allowed in this case. Under the hypothetical situation that the wind blows in the same direction as the line between the radioactive waste incinerator stack and the building ventilation intake, this is equivalent to a maximum emission rate of 2.6 g/sec. Emission rate of HCl has been kept below this level by restrictive burning of PVC wastes.

4.0 ECONOMIC ANALYSIS

With the impressive average volume reduction factor of 23:1 after final storage of the ash in engineered trenches, there can be significant savings in the storage cost of Type 1 combustible solid wastes. Detail estimates are given in Table 4. The annual saving can be even higher if longer useful life of the incinerator is applied in the depreciation estimate, and if higher capacity factor is achieved.

5.0 CONCLUSION

Ontario Hydro's radioactive waste incinerator has been in operation since mid-1977. Operating experience has proven that incineration is a viable process to reduce the volume of the wastes stored, and thus the storage cost.

Due to the low activity levels of the wastes processed, airborne emissions of radioactivity have been well below 1% of the Derived Emission Limits. More extensive off-gas treatment system may be required if wastes with higher levels of radioactivity and PVC are processed; but airborne emissions are expected to remain controllable if tritium levels in the wastes are not excessive. Incineration of highly tritiated wastes is not recommendable due to the volatility of tritium upon incineration.

REFERENCE

1. Drolet, T.S., J.A. Sovka, "An Incinerator For Power-Reactor Low-Level Radioactive Waste", presented at the 14th ERDA Air Cleaning Conference, Sun Valley, Idaho, August 2-4, 1976.

2. The Environmental Protection Act of Canada, 1971, Regulation 15.

DISCUSSION

HILLIARD: Would you care to comment on the experience you've had with the bag filter portion of your treatment?

CHOI: The airborne particulate emissions are very low (about 0.02 mCi/burn or 0.1 mCi/week) because of the controlled-air incinceration process. At such low emission levels, the requirement for a baghouse is only marginal, and coating the filter bags for higher efficiency is not necessary. On the whole, the baghouse performance has been satisfactory.

FLUIDIZED-BED CALCINATION OF LWR FUEL-REPROCESSING HLLW: REQUIREMENTS AND POTENTIAL FOR OFF-GAS CLEANUP

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Abstract

Fluidized-bed solidification (calcination) was developed on a pilot scale for a variety of simulated LWR high-level liquid-waste (HLLW) and blended high-level and intermediate-level liquid-waste (ILLW) compositions. It has also been demonstrated with ICPP fuel-reprocessing wastes since 1963 in the Waste Calcining Facility (WCF) at gross feed rates of 5 to 12 m^3/day.

A fluidized-bed calciner produces a relatively large volume of off-gas. A calciner solidifying 6 m^3/day of liquid waste would generate about 13 standard m^3/min of off-gas containing 10 to 20 g of entrained solids per standard m^3 of off-gas. Use of an off-gas system similar to that of the WCF could provide an overall process decontamination factor for particulates of about 2×10^{10}.

A potential advantage of fluidized-bed calcination over other solidification methods is the ability to control ruthenium volatilization from the calciner at less than 0.01% by calcining at 500°C or above. Use of an off-gas system similar to that of the WCF would provide an overall process decontamination factor for volatile ruthenium of greater than 1.6×10^7.

I. Fluidized-Bed Calcination

Fluidized-bed calcination is one of the processes developed for calcination of liquid wastes from reprocessing of expended reactor fuels. A fluidized-bed calciner solidifies liquid wastes in a fluidized bed of hot, granular solids. The bed of granular solids is fluidized by forcing air upward through a distributor plate and through the bed of solids at a rate that suspends and causes a rapid mixing of the solids--i.e., makes them behave like a fluid. The bed density is decreased by roughly 20% upon fluidization. The rapid mixing that accompanies fluidization results in uniform compositions and uniform temperatures throughout the bed. The liquid being calcined is sprayed into the calciner in the form of droplets, which calcine very rapidly upon impact on the surface of the hot bed granules. The solids are converted mostly to oxides; the water, nitrates, and other volatiles are evaporated and/or decomposed. The calcined solids generated in a fluidized-bed calciner consist of both granular bed particles with diameters of 0.2 to 1.0 mm and fines with particle diameters that are submicron to about 0.2 mm.

The process heat needed to evaporate and/or decompose the volatiles can be supplied by either in-bed combustion or indirect heating. With in-bed combustion (IBC), fuel and oxygen are introduced directly into the bed; combustion takes place in the fluidized bed. In-bed combustion functions efficiently at temperatures of 500°C and above and calcining wastes containing nitrates (which aid combustion). Advantages of in-bed combustion are: (1) a relatively simple installation, (2) suitability for high-temperature operation, and (3) efficient heat transfer. With indirect heating, the process heat is supplied by a heat-exchanger placed in the fluidized bed. With small calciners, heat can also be supplied through the calciner wall (the small calciners have a higher wall surface to bed volume ratio). Advantages of indirect heating are: (1) its suitability for low-temperature operation, and (2) a lower volume of calciner effluent (no combustion gases).

The Waste Calcining Facility (WCF) has demonstrated solidification of radioactive zirconium-fluoride and aluminum-nitrate wastes in a fluidized bed with a cross-section of about one m^2. Gross feed rates have ranged from 5 to 12 m^3/day. Since 1963, the WCF has solidified approximately 13,000 m^3 of radioactive liquid waste forming 1600 m^3 of calcined solids.[1,2,3,4,5] Process heat was supplied first by indirect heating with an in-bed heat exchanger[1,2,3] and later by in-bed combustion.[4,5]

Flowsheets for calcination of radioactive liquid wastes from the reprocessing of commercial LWR fuels were developed on a pilot scale (10-cm and 30-cm-diameter calciners). Nonradioactive solutions simulating a variety of HLLW and HLLW-ILLW compositions were solidified.[6] Most of the tests were made with solutions simulating the gadolinium-poisoned HLWW-ILLW once anticipated from the Barnwell Nuclear Fuel Plant (BNFP).

The potential advantages of fluidized-bed calcination are: (1) the demonstrated large calcining capacity, and (2) the demonstrated ability to control the formation of volatile ruthenium species.[6,7] Disadvantages are: (1) the need to select and prepare the feed carefully--e.g., the sodium concentration must be kept below 1 M to prevent agglomeration of the bed caused by the formation of molten sodium compounds--and (2) the relatively large volume of off-gas requiring cleanup.

II. Characterization of Off-Gas

A. Physical Characteristics

The design requirements for a calciner off-gas system depend largely on the characteristics of the off-gas being

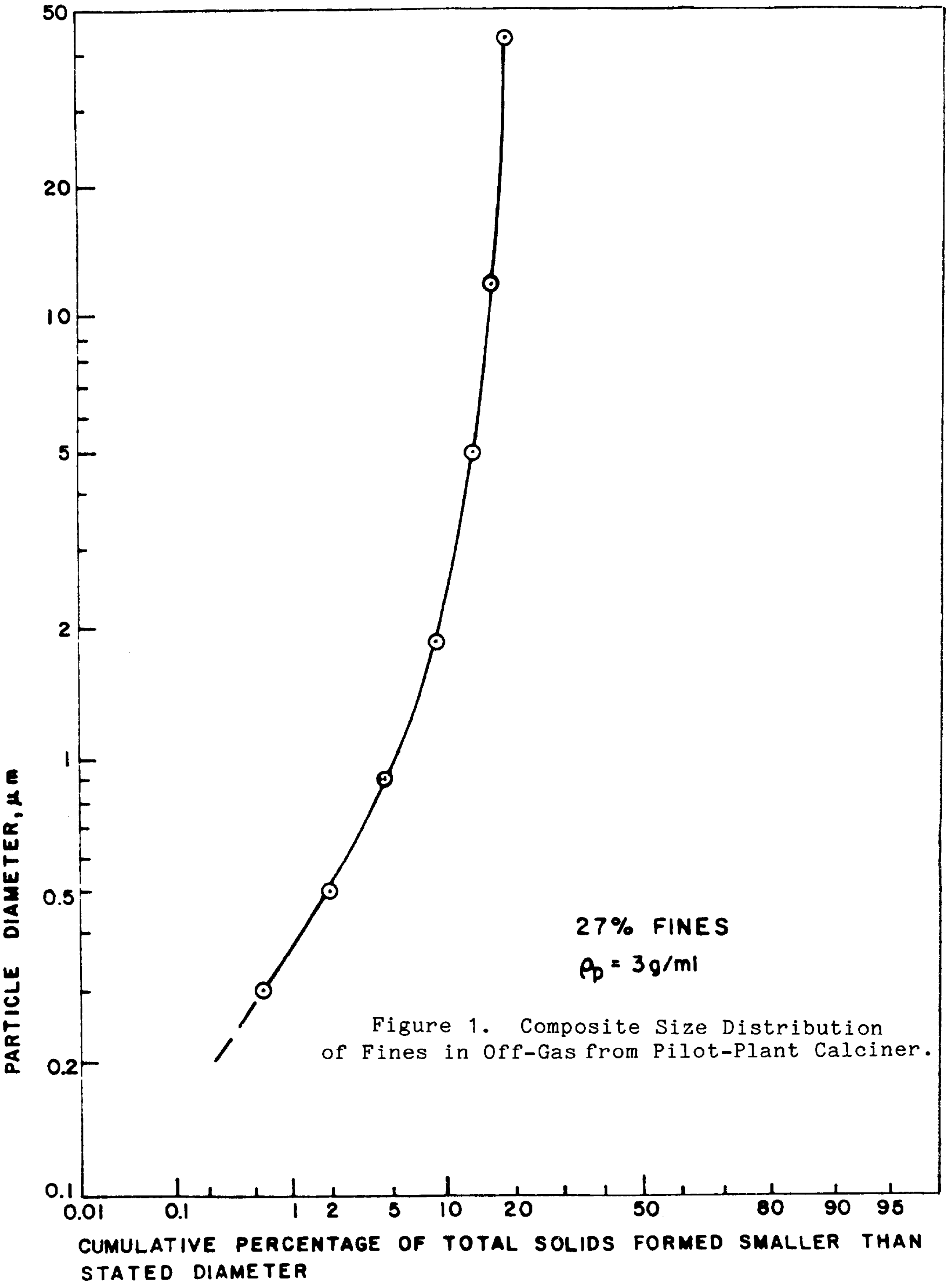

Figure 1. Composite Size Distribution of Fines in Off-Gas from Pilot-Plant Calciner.

cleaned. The off-gas described in Table I is postulated for a relatively large fluidized-bed calciner designed to provide 50% excess or catch-up capacity for a 5 MTU/day fuel-reprocessing plant using a gadolinium-poisoned flowsheet. It would solidify 6 m^3/day of waste to about 1100 kg/day of calcined solids. Heat would be supplied by in-bed combustion at 500°C.

Table I

Calciner Off-Gas Characteristics

Flow, standard condition, m^3/min	13
Flow at 500°C, m^3/min	38
Composition	
Air, %	50
Combustion gases (CO_2, CO, H_2,) %	8
Water vapor, %	42
NO_X, ppm	14,000
Solids, g/std m^3	10-20

The off-gas composition of Table I is a flowsheet composition based on operating conditions in the WCF and in the pilot plant calciners. Most of the air is fluidizing air. The NO_X concentration is a value measured in a pilot plant test[6] calcining simulated LWR HLLW-ILLW; it is about half the stoichiometric concentration of NO_X based on the nitrate input in the feed.

The solids concentration is based on pilot plant measurements of solids carryover from the calciner. Solids carryover from a plant calciner will depend on the calciner design: disengaging height, baffles, and calciner diameter. Figure 1 shows a size distribution of the fines in the off-gas of a pilot plant calciner. The size analysis is a composite of: (1) a cascade-impactor analysis of the fines penetrating the cyclone, (2) a screen analysis of the fines collected by the cyclone, and (3) a cascade-impactor analysis of the smaller-than-325-mesh fraction of the collected fines after redispersal with a sonic ejector. At the point they were sampled, the fines were probably agglomerating rapidly; the estimated particle concentration is in the 10^{12} to 10^{13} particles/m^3 range. Agglomeration during transport of the off-gas through a length of pipe into another cell and through a cyclone and a quench vessel would shift the tail of the curve upward--i.e., to larger particle sizes.

B. Volatile Components

Ruthenium volatility during solidification is a major concern. A potential advantage of fluidized-bed calcination over other solidification methods is that ruthenium volatilization from the calciner can be controlled by calcining at 500°C or above.[6,7,8]

Figure 2 shows the measured[6,7,8] percent of ruthenium in the feed that is volatilized with heating by in-bed combustion at 500°C or above, plotted as a function of (dual abcissa) acidity and nitrate concentration. At nitrate concentrations below 6.5 M and acidity below 4 N, the ruthenium volatility is mostly below 0.01%--0.001 to 0.01%. High nitric acid concentrations result in increased ruthenium volatility. No definite effect of other parameters--e.g., temperature and composition variations--could be observed. However, limits in the sensitivity of the analytical methods used would not permit the detection of volatiles below 0.001%.

The volatility of ruthenium when calcining low-acid feeds (0 to 3N) with indirect heating was investigated over the temperature range from 300°C to 570°C with short-term calcining tests. The test results are plotted in Figure 3. The ruthenium volatility decreased rapidly with increasing temperature between 300°C and 500°C dropping from 76-78% at 300°C to less than 0.01% at temperatures of 500°C and above. The ruthenium volatility appeared to level out at temperatures above 500°C; however, this may be an artifact resulting from vapor concentrations below the analytical detection limits. The cause of the factor-of-a hundred data spread at 390°C and 400°C is not known.

Feed denitration with formic acid was evaluated as a potential means of reducing ruthenium volatility when calcining at lower temperatures with indirect heating. As shown in Figure 3, feed denitration reduced ruthenium volatility by a factor of about 10^4 in short-term tests. However, long-term calcining tests with the denitrated feed (HLLW-ILLW) were unsuccessful because of bed agglomeration. The main problem with denitration was that it also deacidified the feed. The basic, sodium-bearing, HLLW-ILLW then agglomerated[6] when calcined.

When calcining fluoride wastes with in-bed combustion, ruthenium appears to behave as a semi-volatile species. The volatile ruthenium forms a particulate when cooled in a spray quench tower. The net result is that the fraction of the ruthenium from the feed that is in the fine particles carried in the off-gas is 10- to 40-times higher than that of the particulate fission products--e.g., strontium and cerium. This behavior was not observed in pilot plant tests with simulated LWR

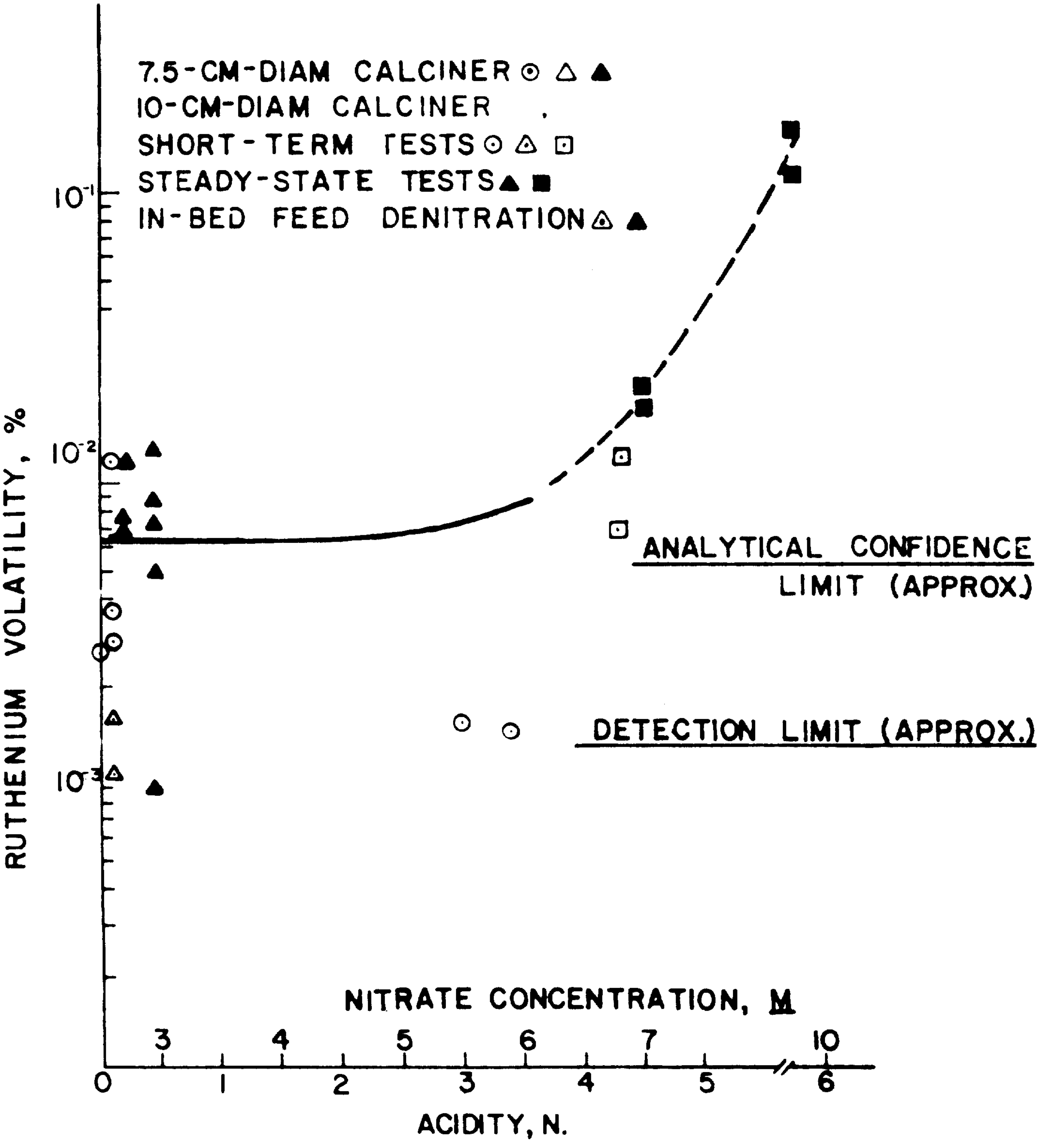

Figure 2. Ruthenium Volatility During In-Bed Combustion.

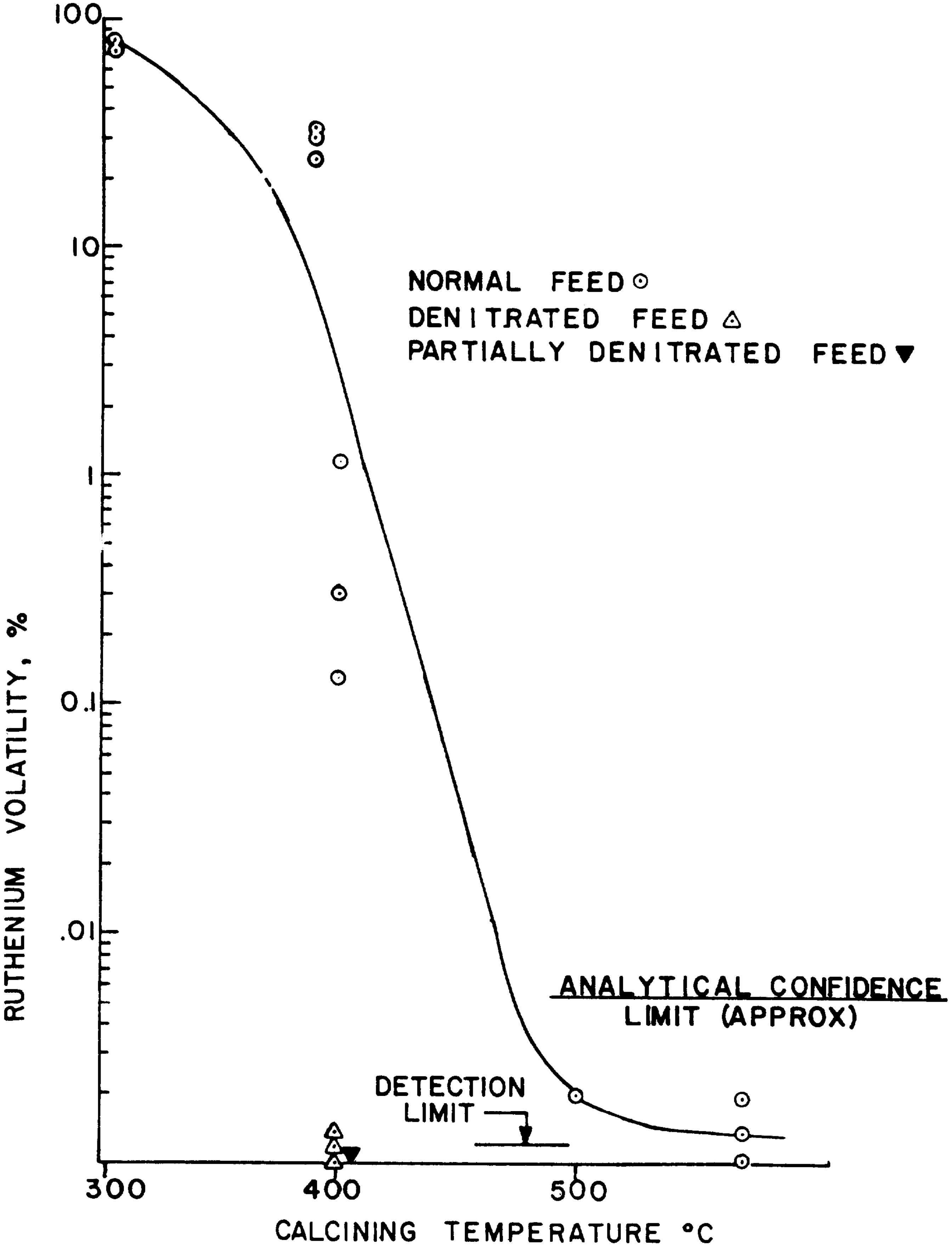

Figure 3. Ruthenium Volatility When Calcining Low-Acid, HLLW-ILLW with Indirect Heating.

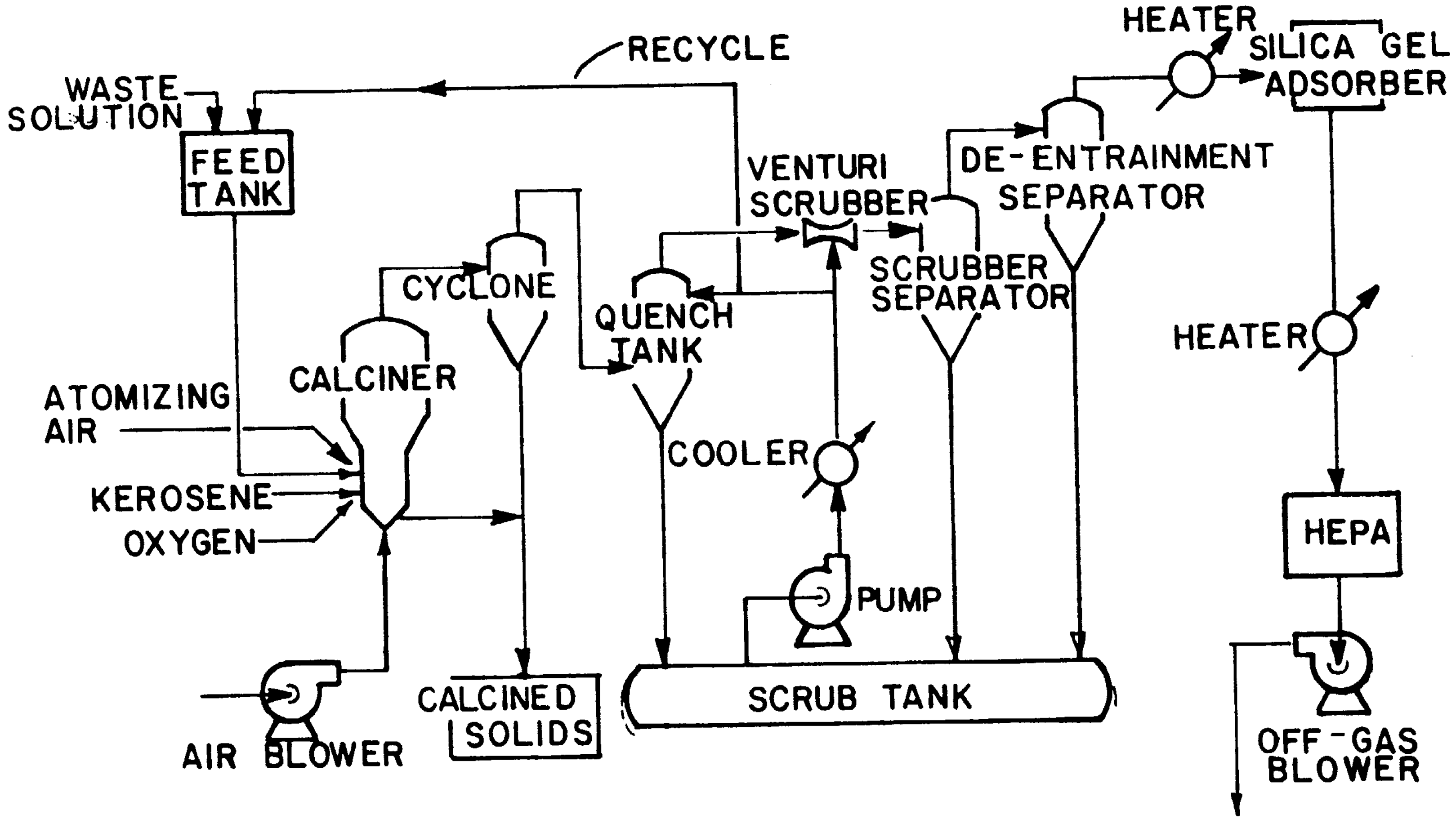

Figure 4. Schematic Flowsheet of a Commercial Calcining Facility.

HLLW-ILLW; however, it was not thoroughly checked. Christian[8] argues that this should not be expected with non-fluoride wastes.

There are also some indications of semi-volatile behavior of cesium during the WCF campaigns with in-bed combustion at 500°C. The fraction of cesium released from the calciner and penetrating through the off-gas system was a factor of about six higher than that of the particulate radionuclides. Cesium behavior was not evaluated in the pilot plant tests. The possibility of partial volatility of cesium should be considered in the design of an off-gas system for a fluidized-bed calciner operating at 500°C or above.

III. Off-Gas Systems

The WCF off-gas system[9] is of potential application to a calciner for LWR HLLW-ILLW. A schematic diagram is shown in Figure 4. Principal components are a cyclone, a venturi scrubber, a silica-gel ruthenium adsorber, and HEPA filters.

Figure 5 shows the predicted flow of solids through the off-gas system and the estimated airborne solids concentrations. The most sensitive components of the off-gas system are the HEPA filters which can deteriorate in service due to age and to contact with moisture. If filter performance is monitored, and deteriorating filters are replaced when necessary, a set of filters in series can probably provide essentially any required collection efficiency. The basis for the assumed filter-system DF of 10^6 is: (1) the filter system contains a pair of HEPA filters in series followed by a backup filter system containing another HEPA filter, and (2) two of the 3 HEPA filters are in good condition providing a DF of 10^3 each. The DF values for the other off-gas components are based on WCF[1,2,3,4,8,9] and/or pilot plant[6] data. The overall DF for particulates is 2×10^{10}. The DF's for any particulate fission product would be the same as shown in Figure 5. For example, the calciner feed would contain about 560,000 Ci/day of strontium of which about 30×10^{-6} Ci/day would be released with the off-gas.

The predicted flow of volatile ruthenium vapors (with 1-yr-cooled waste) through the off-gas system is shown in Figure 6. The component DF's are conservative values as might be used in a safety analysis:

(1) The calciner DF of 10^4 is based on ruthenium volatility of 0.01%, which is roughly an upper limit value for the data in Figure 2. The actual volatility may be lower; however, refined experimental methods will be required to demonstrate a lower volatility value

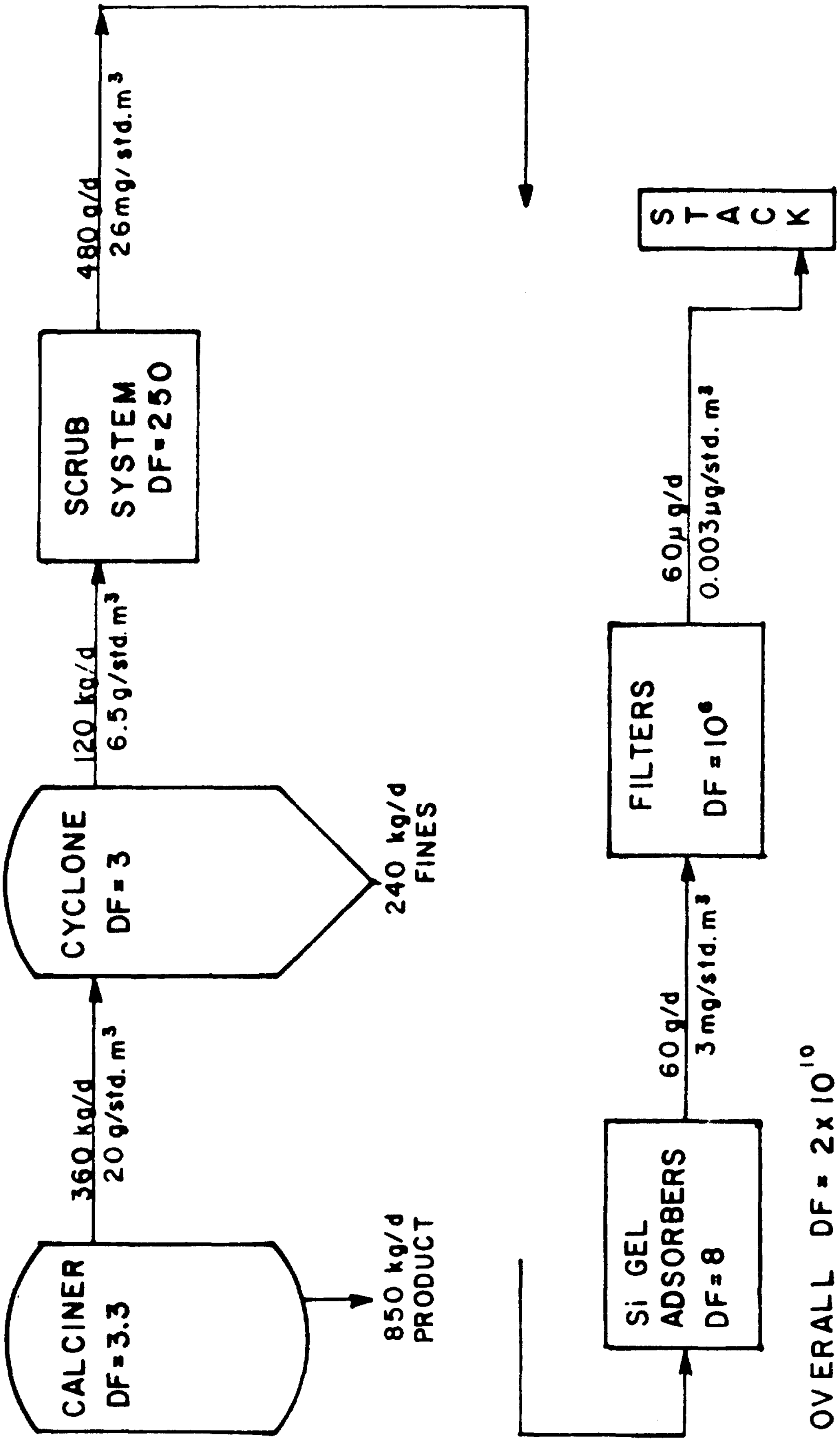

Figure 5. Flow of Solids through Candidate Off-gas Cleanup System.

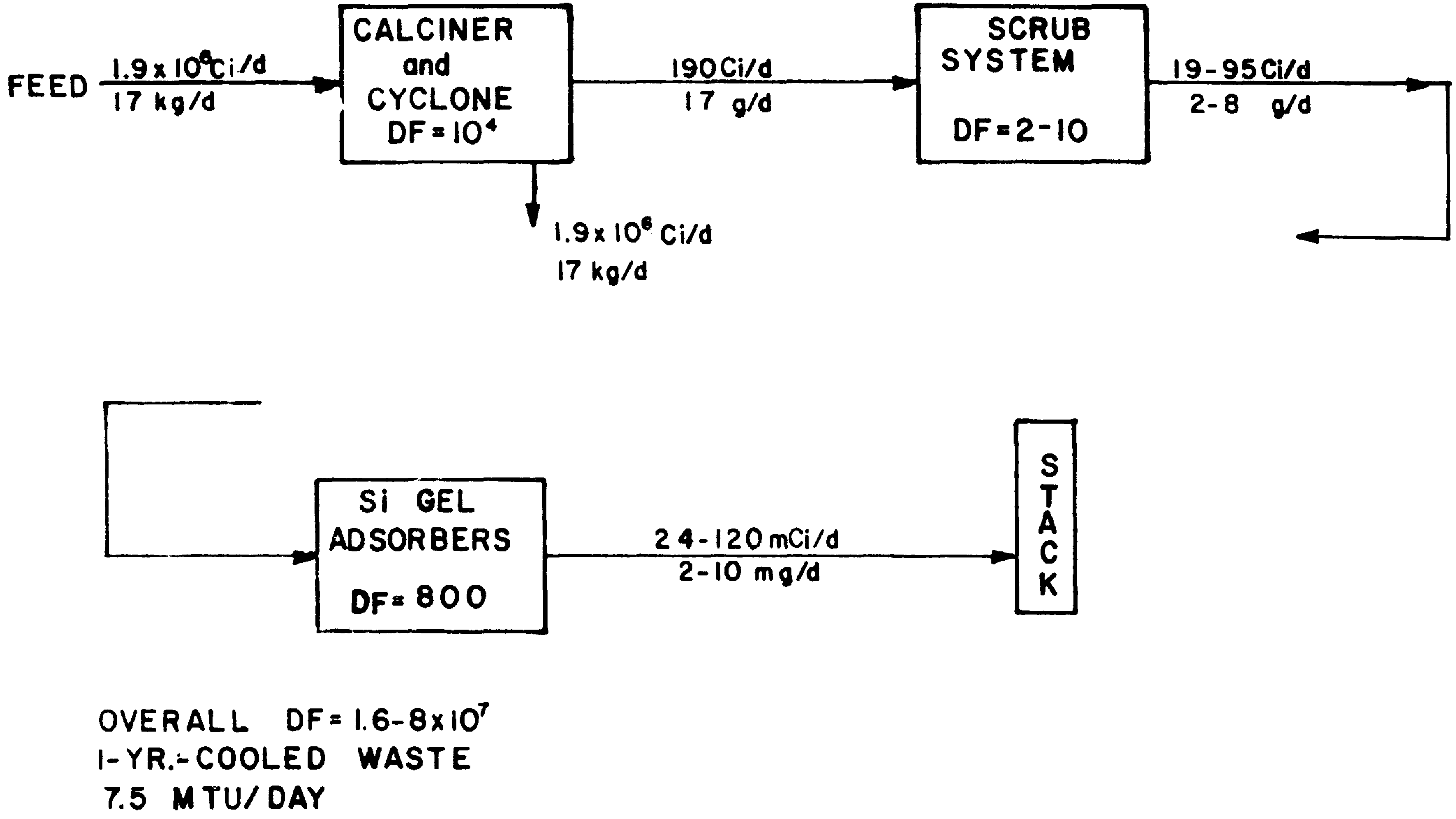

Figure 6. Flow of Volatile Ruthenium through Candidate Off-Gas System.

(2) The scrubbing system DF of 2 was measured[6] in a pilot plant scrubbing system which uses a venturi scrubber without a quench tower. Christian and Rhodes[8] estimate a DF of 10 for a scrubbing system with a quench tower and scrubber.

(3) The adsorber DF of 800 is based on observed[1,2,3,8] performance of the WCF adsorber during operation with indirect heating

The overall DF for volatile ruthenium is 1.6×10^7 to 8×10^7. The release of volatile ruthenium would be 120 mCi/day or less (with 1-yr-cooled waste). A second stage of ruthenium adsorbers would provide additional ruthenium adsorption if required.

In conclusion, an off-gas system similar to the one used in the WCF would probably be satisfactory for a large fluidized-bed calciner for LWR HLLW-ILLW. Alternative designs may offer improvements.

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VOLATILIZATION FROM BOROSILICATE GLASS MELTS OF SIMULATED SAVANNAH RIVER PLANT WASTE*

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Abstract

Laboratory scale studies determined the rates at which the semivolatile components sodium, boron, lithium, cesium, and ruthenium volatilized from borosilicate glass melts that contained simulated Savannah River Plant waste sludge. Sodium and boric oxides volatilize as the thermally stable compound sodium metaborate, and accounted for ∿90% of the semivolatiles that evolved. The amounts of semivolatiles that evolved increased linearly with the logarithm of the sodium content of the glass-forming mixture. Cesium volatility was slightly suppressed when titanium dioxide was added to the melt, but was unaffected when cesium was added to the melt as a cesium-loaded zeolite rather than as a cesium carbonate solution. Volatility of ruthenium was not suppressed when the glass melt was blanketed with a nonoxidizing atmosphere.

Trace quantities of mercury were removed from vapor streams by adsorption onto a silver-exchanged zeolite. A bed containing silver in the ionic state removed more than 99.9% of the mercury and had a high chemisorption capacity. Beds of lead-, copper-, and copper sulfide-exchanged zeolite-X and also an unexchanged zeolite-X were tested. None of these latter beds had high removal efficiency and high chemisorption capacity.

I. Introduction

One process being studied for long term management of Savannah River Plant (SRP) high-level waste sludge is incorporation into a borosilicate glass matrix by spray calcination and electric melting. Several components of the melt will volatilize during the high temperature vitrification process. Savannah River Laboratory (SRL) has therefore initiated studies to determine the types and quantities of species that vaporize during fixation of SRP waste into glass. These studies provide basic data that are required to design an off-gas clean-up system for a vitrification process. This paper discusses laboratory-scale studies of the vaporization of sodium, lithium, boron, cesium, and ruthenium from glass melts. The chemical form in which these semivolatiles vaporize, the rates of vaporization, and some of the factors that influence volatility are discussed. All results were obtained with glasses that contained simulated nonradioactive sludges.

Based on previous studies at SRL, all of the mercury in SRP waste is expected to volatilize during vitrification. A process was developed to remove trace quantities of mercury from gaseous streams by adsorption onto a bed of silver-exchanged zeolite. This process is discussed in the second part of this paper.

II. Experimental Procedure

Sodium, Lithium, Boron, and Cesium Compounds

The apparatus used to measure the volatility of Na, Li, B, and Cs is shown schematically in Figure 1. The crucible, collection tube, lid assembly, and hypodermic tubing were all fabricated from platinum. The transfer line from the collection tube to the scrubber was made of stainless steel, and the scrubber was made of glass. Volatility was determined by mixing the required proportions of glass frit/simulated sludge in the platinum crucible, which was then placed in the furnace. Normal melting conditions consisted of holding a 2-g sample at 1150°C for three hours. Nitrogen gas (750 mL/min) was introduced through the hypodermic tubing and across the melt. A vacuum was applied to the scrubber to insure that all volatilized species were removed from the crucible.

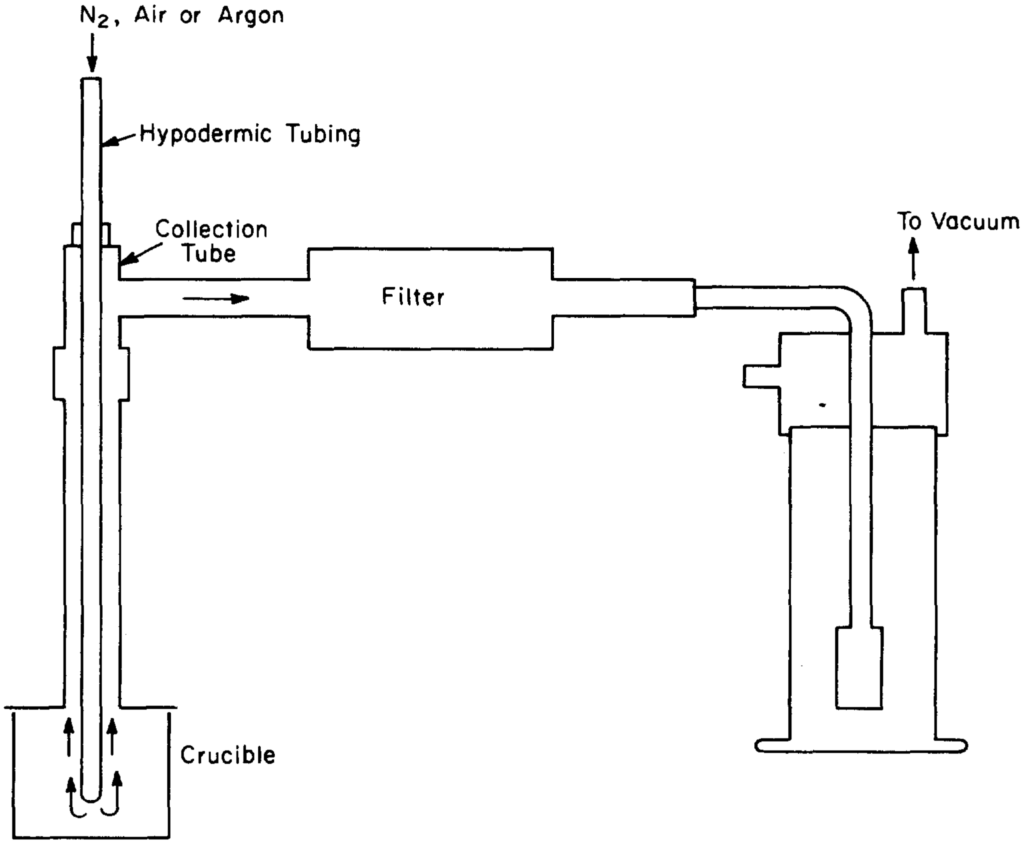

FIGURE 1
VOLATILITY APPARATUS

Compounds of Li, B, Na, and Cs condensed at the top of the collection tube, on the hypodermic tubing, in the transfer lines, and on the surface of the filter. Less than 1% of the semivolatiles penetrated through the filter; these were collected in the scrubber. The condensed gases were washed from the various parts of the apparatus and analyzed for Li, B, Na, and Cs by atomic absorption spectrophotometry (AA). A solution of 0.1M HNO_3 was used both for washing out the apparatus and as a scrubber solution.

Ruthenium Compounds

The apparatus and procedure described above were used to measure ruthenium volatility, except that a 6-g sample size was used and the in-line filter was removed. To minimize plating-out of ruthenium on the walls of the platinum collection tube, the inside of the tube was polished just prior to running each sample. This procedure prevented buildup of ruthenium in the transfer line. The collection tube was washed out after each sample was run, and residual ruthenium was removed from the walls. The washings containing the residual ruthenium were combined with the scrubber solution prior to analysis. This technique did not distinguish between particulate and volatile ruthenium, nor did it measure the extent to which ruthenium plates out.

The ruthenium was analyzed by a modification of the spectrophotometric technique developed by Woodhead.(1) This technique measures the absorbance at the isosbestic point (415 nm) of a RuO_4^{2-}/RuO_4^- mixture. Ruthenium was converted to the mixture by the action of $K_2S_2O_8$ in the presence of boiling KOH. The method detected ruthenium concentrations as low as 0.3 ppm in 100 mL of solution, which covered the range of ruthenium concentrations in the scrubber solutions.

III. Glass Compositions

Table I lists the two borosilicate glass-forming frits used in these studies. The high Fe, high Al, and average simulated calcined

Table I. Frit compositions.

Component	Concentration, wt %	
	Frit 21	Frit 18
SiO_2	52.5	52.5
Na_2O	18.5	22.2
B_2O_3	10.0	10.0
TiO_2	10.0	10.0
CaO	5.0	5.0
Li_2O	4.0	—

sludges were prepared by mixing quantities of the dried metal oxides in the proportions required to give the compositions shown in Table II. The compositions are based on actual analyses of SRP waste sludge(2,3) and represent sludges from waste tanks with typically high Fe concentrations, Al concentrations, and an overall average for all tanks sampled.

Table II. Composition of simulated calcined sludges.

Metal Oxide	Metal Oxide in Sludge, wt %		
	High Fe	High Al	Average
Fe_2O_3	61.4	6.0	43.5
Al_2O_3	5.6	86.3	25.8
MnO_2	4.1	4.9	11.7
U_3O_8	14.2	1.5	11.0
CaO	4.2	0.4	3.0
NiO	10.5	0.9	5.0

The cesium content of SRP waste glass was calculated to be 0.06 wt % (as Cs_2O). Because this small amount of material could not be added in solid form to the 2-g samples, cesium was added by either adsorption of the cesium onto zeolite or by adding aliquots of a cesium carbonate solution to the glass-forming mixture. In cases where cesium was added from solution, the sample was dried to remove excess water before placing the loaded crucible into the furnace. Pre-drying prevented entrainment of particulates in the steam that would result from placing the wet mixture in the furnace heated to 1150°C.

Ruthenium was incorporated into the glass-forming mixture by adding the volume of a 3 g/L solution of $Ru(NO)(NO_3)_3$ required to give 0.05 or 0.15 wt % Ru in the final glass. The $Ru(NO)(NO_3)_3$ solution was prepared by dissolving $Ru(NO)(OH)_3$ in 4M HNO_3. After addition of the $Ru(NO)(NO_3)_3$ solution, the glass-forming mixture was dried at 115°C to drive off excess water to prevent entrainment of ruthenium.

IV. Specific Element Volatility

Sodium, Boron, and Lithium Volatilities

Volatilities of Na, Li, and B are discussed together because these species vaporized from the melt as alkali borates. The thermally stable compound sodium metaborate ($Na_2O \cdot B_2O_3$) accounted for ~90% of the semivolatiles that vaporized. Trace quantities of $LiBO_2$, $LiNaBO_2$, Na_2BO_2, and B_2O_3 were also detected in the vapor above the melt by Knudsen cell - mass spectrometer measurements. In the condensed phase, the species that volatilized were determined from the molar ratios of Na/B and (Li + Na)/B in the condensate. A ratio of one would indicate the metaborate, a ratio of two would indicate the diborate, and a mixture of the two compounds would be indicated by a ratio between one and two. The ratio of Na/B should be less than one when the melt contains lithium, because only part of the boron is associated with sodium; the remaining boron forms a lithium borate. The ratio of (Li + Na)/B would equal one, however, if $Li_2O \cdot B_2O_3$ and $Na_2O \cdot B_2O_3$ are the compounds that volatilize. A melt that contains sodium (but no lithium) should give a Na/B ratio of 1 if $Na_2O \cdot B_2O_3$ is the vaporizing species. When Frit 21, which contained both sodium and lithium, was used to prepare glasses (Table III), the molar ratio of Na/B was 0.89, and that of (Na + Li)/B was 1.02. Off-gasses from glasses prepared from Frit 18, a frit that contains no lithium, gave a Na/B ratio of 1.05 (Table IV). These three ratios are

Table III. Volatility of Na, Li and B from Frit 21 glass melts.

Code	Na_2O in Glass, mole %	Volatility, mg/cm^2			Molar Ratios	
		Na_2O	Li_2O	B_2O_3	Na_2O/B_2O_3	$(Na_2O + Li_2O)/B_2O_3$
21-Avg-25		0.4	0.04	0.4	1	1.0
-35		0.4	0.05	0.5	1	1.1
-45	13.6	0.9	0.14	1.2	0.84	0.97
21-Fe-25	17.1	1.4	0.20	1.5	0.99	1.1
-35	15.7	1.4	0.20	2.0	0.82	0.93
-45	14.2	0.7	0.13	1.0	0.83	0.98
21-Al-25	16.1	1.3	0.16	2.0	0.74	0.84
-35	14.5	0.7	0.13	1.0	0.84	1.0
-45	12.6	0.5	0.08	0.5	1	1.2
				Avg	0.89	1.02

Table IV. Volatility of Na and B from Frit 18 glass melts.

Code	Na_2O in glass, mole %	Volatility, mg/cm^2		Molar Ratio,
		Na_2O	B_2O_3	Na_2O/B_2O_3
18-Avg-25	21.2	2.6	3.0	0.97
-35	19.4	1.9	1.9	1.1
-45	17.1	1.5	1.6	1.1
18-Fe-25	21.6	1.8	1.9	1.1
-35	19.9	2.2	2.3	1.1
-45	17.7	1.0	1.4	0.86
18-Al-25	20.4	0.7	0.7	1.1
-35	18.2	1.5	1.9	0.93
-45	15.8	1.2	1.2	1.2
			Avg	1.05
Frit 18	22.7	4.0	4.5	
Frit 21	17.8	1.7		

consistent with a mechanism of alkali and boron volatilization as the compounds $Na_2O{\cdot}B_2O_3$ and $Li_2O{\cdot}B_2O_3$. Solomin(4) and Walmsley,(5) in their work on borosilicate glass volatility, also concluded that alkalis volatilize from borosilicate melts as thermally stable alkali borates.

The quantity of $Na_2O{\cdot}B_2O_3$ evolved increased exponentially when the mole % of sodium in the glass melt was increased (Figure 2). Measurements were made over a range of 12 to 23 mole % Na_2O in the glass. Volatility varied from 1.5 mg/cm^2 (at 12 mole % Na_2O) to 8.5 mg/cm^2 (at 23 mole % Na_2O). The linear relationship between the logarithm of weight loss and Na_2O content of the melt is similar to that obtained by Kolykov(6) when he studied the system Na_2O-B_2O_3-SiO_2. Barlow(7) also concluded that sodium volatilizes from a borosilicate glass melt as either sodium metaborate or sodium diborate, and that volatility increases as the logarithm of sodium concentration.

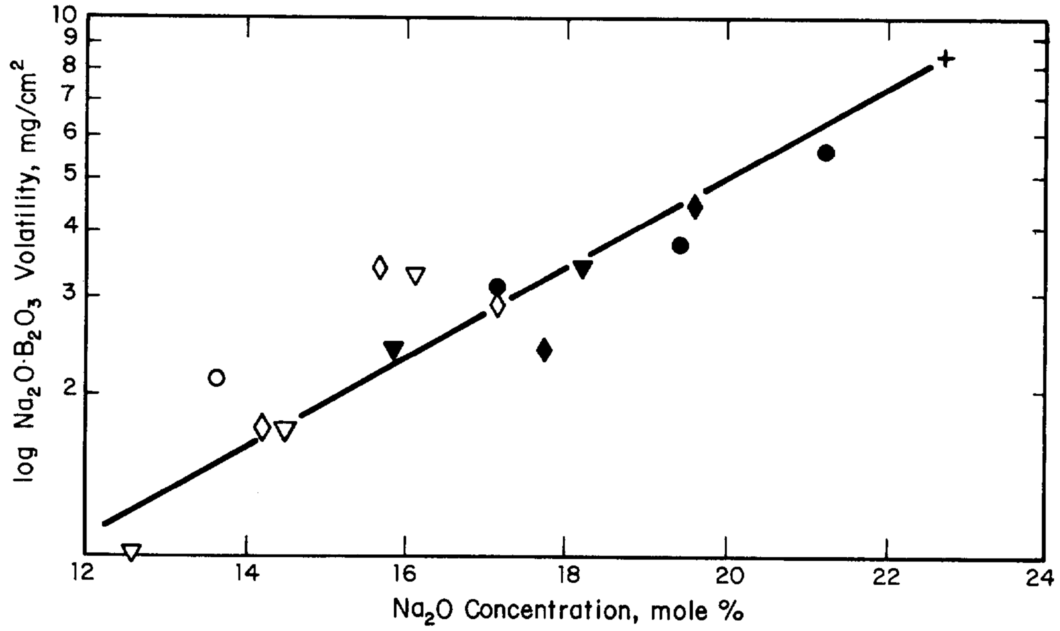

FIGURE 2
EFFECT OF Na_2O CONCENTRATION ON $Na_2O{\cdot}B_2O_3$ VOLATILITY

Lithium metaborate volatility was about 1/10 that of sodium borate. Changes in melt composition or in melting conditions had no appreciable effect on lithium volatility.

The type sludge, the type frit, and the concentration of other glass components affected volatility only to the extent that changes in these variables affected changes in the mole % of Na_2O in the glass melt.

Cesium

Cesium, which volatilized from the melt as either elemental cesium or as some oxide of cesium, is the most volatile of the three alkali metals studied. An average of 0.11 mg/cm^2 of cesium (as Cs_2O) volatilized from samples that contained a range of 0.03 to 0.09 wt %

cesium. Because previous workers(8) have reported that addition of TiO_2, B_2O_3, or MoO_3 to glass melts reduces cesium volatility, one part of the current work compared cesium volatilization from glass melts prepared from frits that contained 0, 5, and 10 wt % of TiO_2. Also, a comparison between cesium volatility from melts which contained cesium as a cesium-loaded zeolite and as a cesium carbonate solution was made.

Tables IV through VII summarize the effect on cesium volatility of the wt % TiO_2 added, the form of cesium addition, and the concentration of cesium in the melt. The high volatilities in these tests reflect the high surface-area-to-weight ratios for the small samples used and should not be interpreted as a direct measure of the amount of cesium expected to volatilize from a full-scale melter. If these levels of volatility are scaled up to a 2.2 ton/day melter, they

Table V. Effect of addition of TiO_2 on cesium volatility.

Cesium Added as	Cs_2O in Glass, wt %	TiO_2 in Frit, wt %	Volatility, mg/cm^2
Zeolite	0.03	0	0.08
Zeolite	0.03	10	0.06
Carbonate	0.03	0	0.08
Carbonate	0.03	10	0.06

Table VI. Effect of form of addition on cesium volatility.

Cesium Added as	Cs_2O in Glass, wt %	TiO_2 in Frit, wt %	Volatility, mg/cm^2
Zeolite	0.03	0	0.08
Carbonate	0.03	0	0.08
Zeolite	0.03	10	0.06
Carbonate	0.03	10	0.06
Zeolite	0.09	10	0.10
Carbonate	0.09	10	0.15

Table VII. Effect of Cs_2O concentration on cesium volatility.

Cs_2O in Glass, wt %	TiO_2 in Frit, wt %	Volatility, mg/cm^2
0.03	0	0.08
0.03	10	0.06
0.06	5	0.11
0.06	5	0.13
0.09	0	0.21
0.09	10	0.15

represent volatilization of 0.05% of the cesium in the melter charge. Battelle Northwest Laboratories (BNWL), by comparison, measured ~0.3% volatility when they vitrified simulated light-water-reactor (LWR) waste that contained 0.2 wt % of Cs_2O.(9) A melting temperature of 1050°C for 6 hours was used in the BNWL study.

The slight suppression of cesium volatility by titanium dioxide can be seen by comparing samples in Table V. The volatility is decreased so slightly that it would not significantly reduce problems of cesium vaporization during glass melting. The failure of titanium dioxide to significantly reduce cesium volatilization can be explained by the work of Rastogi, et al.,(10,11) who found that reductions in cesium volatility were obtained only at temperatures below 1000°C and for vitrification times ≤ 1 hour. They found, for example, that the compound $Cs_2O \cdot 4TiO_2$ does not volatilize at 400°C, but that 31% of this compound volatilizes at 1200°C. Other work by Rudolph, et al.(8) and by Kupfer and Schulz(12) report that titanium dioxide effectively suppresses cesium volatilization, but in the 1000 to 1050°C temperature range. Another probable cause of the failure of titanium dioxide suppress cesium volatility significantly is the large amounts of boric oxide present in the melt compositions used for SRP glasses. Rudolph, et al.(8) found that boric oxide, though not as effective as titanium dioxide, does reduce the volatility of cesium. The effect of titanium dioxide, then, is probably reduced when the melt contains boric oxide as a constituent.

Incorporation of cesium into the glass as cesium-loaded zeolite (0.02 g Cs/g zeolite), rather than as a cesium carbonate solution, did not increase cesium volatility from the glass melt. The insensitivity of cesium volatility to the form of cesium addition is shown in Table VI. Kelley, in his work on radionuclide vaporization from SRP waste,(13) also found that volatility of cesium was unchanged when cesium-loaded zeolite was substituted for direct addition of cesium carbonate.

Total cesium volatility increased when the total amount of cesium in the melt was increased (Table VII). The increase in volatility was proportional to the increased cesium concentration, suggesting that cesium vaporizes by diffusion from the melt surface.

The Knudsen cell studies conducted as a part of the experiments in this report did detect elemental cesium above the melt at a temperature of 1200°C. No cesium borates were detected.

Ruthenium

The high alumina, high iron, and composite sludges (Table II) along with Frit 21 were used to study ruthenium volatility. The two gases used to blanket the melt, air and argon, showed the effect of the oxygen on ruthenium volatilization. Each sludge-atmosphere combination was run in duplicate, and the result was interpreted by the analysis of variance method. For these experiments, nitrate-free simulated sludge was used. Neither the composition of the sludge nor the atmosphere over the melt affected the volatilization of ruthenium. Table VIII shows the per cent of ruthenium volatilized for the various combinations of sludges and atmospheres above the melt. The failure

Table VIII. Effect of sludge type and atmosphere over melt on ruthenium volatility.

Sludge Type	Cover Gas	Ru Volatilized, %
High Al	Argon	5.5
	Air	6.3
High Fe	Argon	2.8
	Air	7.4
Composite	Argon	7.5
	Air	5.3

of oxygen to increase ruthenium volatility, indicates that volatilization of ruthenium depends on the bulk rather than surface conditions of the melt. This result also indicates that atmospheric oxygen is not the only oxidant for ruthenium. This is consistent with previous work(13) that identified manganese dioxide as one component of SRP sludges that oxidizes ruthenium. All three sludges contained an excess of manganese dioxide relative to the ruthenium content.

The effect of nitrate concentration on ruthenium volatility depended on the level of ruthenium in the melt. Figure 3 summarizes

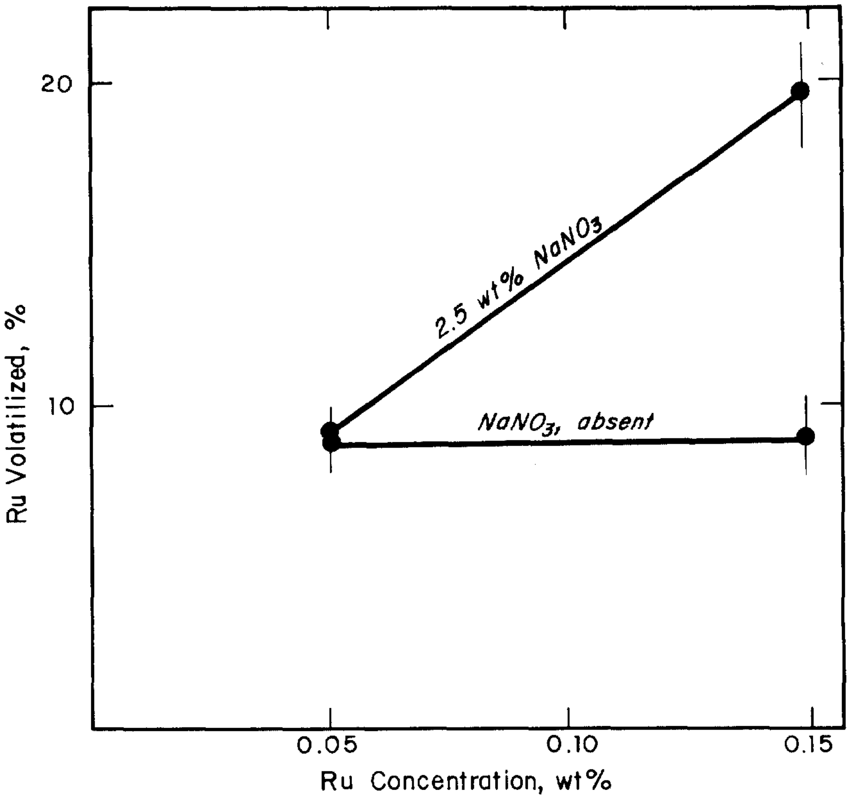

FIGURE 3
EFFECT OF SODIUM NITRATE CONCENTRATION ON RUTHENIUM

the volatility dependence on the level of ruthenium and the concentration of nitrate in the waste. Neither increasing the nitrate concentration at a low ruthenium concentration nor increasing the ruthenium concentration in nitrate-free melts caused increased ruthenium volatilization. However, a sharp increase in volatility was obtained when both the nitrate and ruthenium contents were increased. The nature of the nitrate/ruthenium concentration interaction has not been defined. These results do show, however, that acceptable nitrate levels for SRP waste sludges may depend on the amount of ruthenium present in composite (blended) SRP sludge.

V. Solid Sorbents for Mercury Vapor

It is estimated that 2.3 lbs/hr of mercury will be vaporized from the calciner/melter during vitrification of SRP waste. The calciner/melter off-gas system will include a quench column and a condenser that is cooled to 5°C to reduce the mercury vapor concentration to $\sim 3 \times 10^{-9}$ g/cm^3. Laboratory data show that the final traces of mercury can be removed by adsorption onto silver-exchanged zeolite. A bed of Ag^+ exchanged zeolite irreversibly chemisorbed 0.190 g Hg/g of bed at an adsorption efficiency of >99.9%.* Over the temperature range of 20 to 400°C, the efficiency of the silver zeolite bed remained >99.9%; at 500°C, efficiency dropped to 92%.

Preparation of Zeolite and Analytical Method

The Na, Ag^+, Ag^0, Pb^{2+} and the CuS forms of zeolite were available from previous studies.(14) The Cu^{2+} zeolite was prepared by exchanging Cu^{2+} from a saturated cupric acetate solution with *Linde Type 13X®* molecular sieve for 10 days at 80°C. After exchange, the Cu^{2+} zeolite was thoroughly washed to remove any residual cupric acetate solution and then dried.

Mercury vapor concentrations were measured with a mercury analyzer previously used in a study of the dispersion of buried elemental mercury.(15) The analyzer is shown schematically in Fig. 4 and is more fully described in Reference 15. In these experiments, the accessory mercury vapor source is replaced by the adsorption bed being tested. A septum, through which known amounts of air saturated with mercury vapor can be injected, is placed just upstream from the bed.

Capacities of adsorption beds were measured by passing mercury vapor through the bed at a face velocity of ∿3 m/min and measuring the weight of the bed until no further weight gain was recorded. After constant weight was attained, argon was passed through the bed and the weight loss recorded. The weight lost to the argon stream was assumed to be physically adsorbed mercury, while the remaining weight gain by the bed was assumed to be chemisorbed mercury. During desorption of physisorbed mercury, the bed was placed in line with the specific mercury analyzer, and the evolution of mercury was measured.

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* Efficiency is defined as the % of mercury in the vapor stream that is trapped by the adsorbent bed.

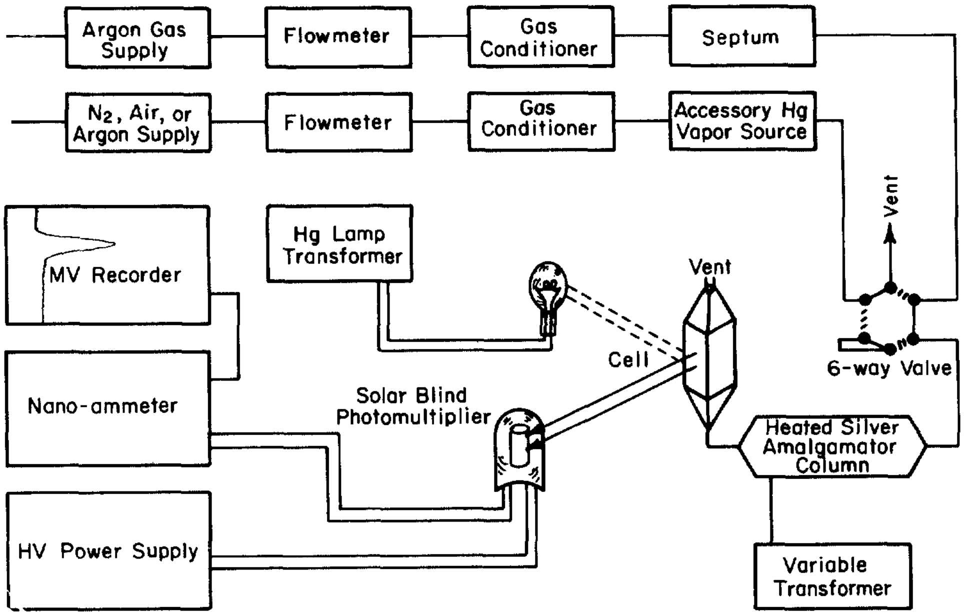

FIGURE 4
SCHEMATIC DIAGRAM OF MERCURY ANALYZER

Screening Tests

The adsorption efficiency of the beds was first measured at room temperature (∿20°C). The results in Table IX show that only Ag^+, Ag^0, and CuS exchanged beds have a high adsorption efficiency for mercury. Table IX also shows that apparent residence times* influence mercury adsorption efficiency. The importance of residence time is shown by comparing the efficiencies of the Ag^+ exchanged bed at various residence times. The efficiency of >99.9% at 0.04 seconds apparent residence time decreased to 80% at 0.0006 sec. In these experiments, the lower detection limit for mercury was 0.1%, so that an efficiency of at least 99.9% may be assigned for the cases where no mercury was detected in the vapor. This assumption gives a lower limit of $\sim 10^3$ for the mercury decontamination factor for cases in which no detectable mercury vapor was found exiting the adsorption bed.

Effect of Temperature on Efficiency

The effect of bed temperature on adsorption efficiency for Ag^+, Ag^0, and CuS exchanged zeolite beds was measured over a temperature range of 20 to 500°C (Table X). Beds were first heated to the desired temperature, and then the mercury vapor was passed through the adsorbent. Of the three beds, the Ag^+ form was least affected by temperature, showing an adsorption efficiency of >99.9% up to 400°C. The Ag^0 bed had >99.9% efficiency up to 200°C, while the CuS bed had this level of efficeincy only up to 50°C. These results are consistent with work reported by Barrer and Whiteman,(16) who found that sorption of mercury onto metal-exchanged zeolites was inversely proportional to temperature.

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* Apparent residence time is defined as the bed volume divided by the volume flow rate of the vapor stream.

TABLE IX. Efficiency of mercury adsorption beds.

Sorbent[a]	Apparent Residence Time, sec	Hg Vapor Adsorbed, %
None	0.04	0
Shredded Rubber	0.04	0
Na-X	0.04	0
Pb-X	0.04	15
Cu-X	0.04	0
CuS-X	0.04	>99.9[b]
Ag^0-X	0.04	>99.9[b]
Ag^+-X	0.04	>99.9[b]
Ag^+-X	0.0002	98
Ag^+-X	0.001	95
Ag^+-X	0.0006	80

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[a] X = A near-faujasite type of zeolite.

[b] No mercury was detected in the gas exiting the bed; percent adsorption taken by using minimum detection level of 0.1%.

Table X. Effect of temperature on efficiency of mercury adsorption beds.

Bed Temperature, °C	Adsorption Efficiency, % Hg Adsorbed		
	CuS-X	Ag^+-X	Ag^0-X
20 to 25	>99.9	>99.9	>99.9
50	>99.9	>99.9	>99.9
100	97	>99.9	>99.9
200	79	>99.9	>99.9
300	59	>99.9	92
400	39	>99.9	88
500	-	92	-

Adsorption Capacity

The capacity of a zeolite adsorption bed depends on the bed depth, the face velocity of the gas stream entering the bed, and the nature of the sorbent. The capacities of Ag^+, Ag^0 and CuS beds were measured for a bed depth of 1.5 cm and a superficial face velocity of ∿3m/min.

The only bed with an appreciable adsorption capacity was the Ag^+ exchanged zeolite which chemisorbed 0.190 g of Hg/g of bed and physisorbed another 0.0264 g Hg/g of bed before a constant weight was achieved. The irreversible chemisorption of mercury is attributed to the reaction,

$$2Ag^+ + Hg \rightarrow 2Ag + Hg^{2+}.$$

Barrer and Whiteman(16) studied adsorption of mercury onto several zeolites. At low mercury concentrations, the exchange between silver and mercury reached 63% of the value calculated for complete exchange. At mercury concentrations higher than those expected to be encountered in the calciner/melter off-gas system adsorption beds, the reactions,

$$Hg^{2+} + Hg \rightarrow Hg_2{}^{2+}$$

$$Ag + Hg \rightarrow Ag(Hg) \text{ amalgam}$$

and

$$Hg_2{}^{2+} + XHg \rightarrow Hg^{2+}_{(X+2)}$$

can also occur.

The adsorption capacities of Ag^0 and CuS exchanged zeolite beds are quite low under the conditions of these experiments (Table XI). No detectable weight gain was recorded for either bed. Therefore, the smallest measurable weight gain (0.1 mg) was used to calculate the upper limits on capacities shown in Table XI. Even though the capacities are very low, Ag^0 and CuS exchanged zeolite beds efficiently removed mercury vapor at low concentrations. However, Ag^+ zeolite beds are recommended for plant processing because less frequent replacement is required.

Table XI. Capacities of mercury adsorbent beds.

Sorbent	Bed Length, cm	Bed Weight, g	Mercury Adsorbed, g Hg/g Bed Total	Mercury Adsorbed, g Hg/g Bed Chemisorbed
Ag^+-X	1.5	0.1525	0.2164	0.190
CuS-X	1.5	0.1495	$<7 \times 10^{-4}$	-
Ag^0-X	1.5	0.1505	$<7 \times 10^{-4}$	-

VI. Acknowledgement

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DISCUSSION

DEMPSEY: How does your program relate to the similar work underway at Pacific Northwest Laboratory? Do you see any insurmountable obstacles in control of off-gases from the vitrification process?

WILDS: First, the two programs have several common areas. For example, PNL is currently conducting large scale tests with simulated SRP waste. We expect to obtain data on sodium borate volatility and particle sizes of volatile species from that work.

Second, the answer is no. I believe that with our current research and development programs, we are well on our way to defining an adequate off-gas clean-up system.

GIRTON: What are your Hg concentrations in the off-gas?

WILDS: The concentration of mercury will depend on the particular waste being processed since, as I previously mentioned, the composition of SRP waste is quite variable. However, the initial concentration of mercury from an average waste composition is expected to be $\sim 4 \times 10^{-4}$ g/l. This concentration will be reduced to 3×10^{-6} g/l prior to entering the mercury adsorber bed. The temperatures of the off-gas stream are 300°C initially and $\sim 20^{\circ}$C entering the adsorber.

McFEE: Have you speculated as to the mechanism of sodium metaborate volatility? Is it simply vaporization of sodium metaborate, or is there another mechanism going on?

WILDS: We haven't done a lot of work trying to determine the exact mechanism, but I believe it is sodium metaborate that vaporizes. We're using a premelted frit so we're not simply putting the material in as sodium carbonate and boric acid. The frit we put into our glasses has already been melted so, presumably, we have sodium and boron already in a network and I think it's simply volatilizing as a compound.

McFEE: Have you tried to check the vapor pressure of sodium metaborate against your results?

WILDS: We have done a little of this in our Newton cell measurements. It's in a very early stage of development.

McFEE: I'm aware that the orthoboric acid is nonvolatile but in the presence of water vapor becomes volatile. Are you seeing the same effect?

WILDS: I really don't know. The only indication we've had is when we had a melt with boric acid present, or some sodium tetraborate present, we would get volatilization as boric acid and not as the sodium metaborate. We have tested that. I think I should be very careful in stating that when we get sodium metaborate, we get it from the premelted fret. When we use batch chemicals, we do not get sodium metaborate. We do get crystals of boric acid and, presumably, some boric oxide coming off as well. We have made limited measurements of sodium metaborate vapor pressures. These studies indicate that the mechanism of sodium borate volatility is simple vaporization. References 4, 6, and 7 of this paper confirm that sodium metaborate vaporizes without decomposition up to temperatures of 1400°C.

DISPOSAL OF HEPA FILTERS
BY FLUIDIZED BED INCINERATION

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Introduction

High efficiency particulate air filters (HEPA) are used in virtually all nuclear facilities, the majority in main production building exhaust plenums and others on smaller unit operations. These filters must be periodically changed, due to radioactive contamination or flow restriction by trapped particulates. Used, and/or radioactively contaminated HEPA filters constitute a high volume, low density waste stream that must be disposed of by a safe and efficient method. Presented in Table I, are approximations of the HEPA filter usage in some of the nuclear facilities which gives some idea of the magnitude of this waste stream.

Table I. HEPA Filter Use At DOE Facilities
Calender Year 1977 Partial Listing

	Filter Size	
Facility	Plenums 2 ft x 2 ft x 1 ft	Unit Operation Other Smaller Size
Hanford	500	-
Livermore	200	-
Lovelace	250	-
LASL	500	1500
Mound	100	350
Oak Ridge	150	525
Sandia	85	15
Savannah River	-	325
Rocky Flats	2600	1300
Total	4385	4015

One factor that must be considered in the development of a method for HEPA filter disposal is the waste acceptance criteria now being established for the waste isolation repository. It is highly unlikely that unit HEPA filters will be acceptable under proposed criteria on flammability, gas generation, and leachability.

Discussion

The HEPA filter, packaged as a unprocessed unit, occupies a comparative large volume, estimated at about 85% empty volume. The general composition of a HEPA filter, given in Table II, illustrates this point.

Table II. HEPA Filter Composition
Size: 2 ft x 2 ft x 1 ft

Component	Weight (lbs.)	Volume (ft^3)	Density (lbs./ft^3)
Frame	25.1	0.5	50.1
Media	16.1	3.5	4.6
Unit Filter	41.2	4.0	10.3

Frame: 3/4 inches plywood or particle board - phenolic resin bonded.
Media: Fiberglass and fiberous asbestos with corrugated asbestos paper separators.

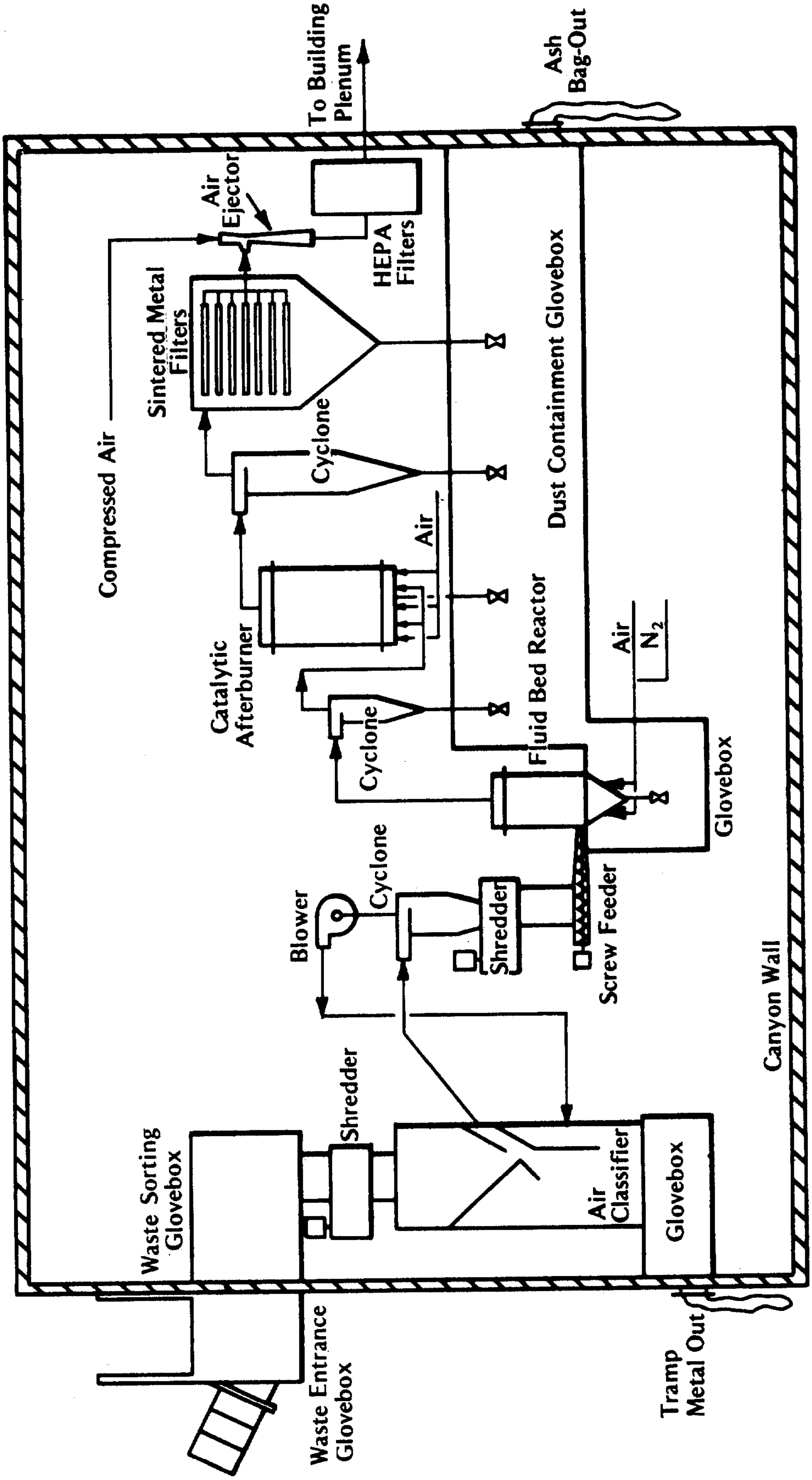
Present methods of HEPA filter disposal vary according to the level of contained radioactivity. The large 24 inch by 24 inch by 12 inch filters from building exhaust plenums usually fall into the low level TRU Waste category. A simple arbor press is used to break the filter into an elongated diamond configuration, the pressed filter is wrapped with a wire tie, and plastic bagged before packing in a crate for shipment. The compression allows only a few more filters to be packed per crate. Filters containing significant levels of radionuclides are generally the smaller size used on unit operations and gloveboxes. The present disposal method used at Rocky Flats is to cut the media out of the frame with a reciprocating saw, send the media to reprocessing, and incinerate the frame. A method being developed is to punch the media from the frame with a hydraulically operated ram and an extruding die. This process will provide a separation of the frame from the media and result in a significant volume reduction of the media.

The applicability of these disposal methods for future use must be accessed in light of the proposed criteria for the permanent waste storage repository. A study on the content of filters that had been in use for direct filtration of unit operations indicated the presence of absorbed H_2O, HF, and HNO_3.(1) These components could also react with particulate matter trapped in the media. It is evident that outgassing, or gas generation from HEPA filters is a distinct possibility. Another matter of concern is leachability. The same study also included the measurement of weight loss due to water leaching. In addition to the consituents leached, the leach solution was found to be acidic. This could cause problems when contacting other stored materials.

Incineration Process

The incineration of the entire filter would offer advantages over other present methods of disposal. It would be a one step operation, material trapped in the media would be destroyed, and the residue would be in an ideal form for further reprocessing. The fluidized bed incinerator used for test burns of HEPA filters is shown in Figure 1. The small nails used in the filter frame cause no problem either to the shredder or the screw, which feeds into the incinerator. Shredding of used filters does generate some dusting, but the low speed cutters hold this to a minimum. As the dust is about 95% non-combustible asbestos and glass fibers, no dust explosive hazard is presented.

As mentioned earlier, only the wooden frame comprising about 61% of the filter weight is combustible. This results in a large amount of residue, or ash, from the incineration. Reduction, by incineration, was approximately 4.4 to 1 in volume and 2 to 1 by weight. The residue, collected from the cyclone separators



FLUIDIZED BED INCINERATION PILOT UNIT
FIGURE 1

and sintered metal filters, is a fine powdery material. Without further treatment this material may be unacceptable for storage in the waste repository. Proposed criteria does not allow material present as respirable fines.

Immobilization of HEPA Filter Ash

Various methods of waste immobilization have been tested at the Rocky Flats Plant over the past few years. For our use, and because it appears to best meet repository acceptance criteria, vitrification was selected as the most promising immobilization method. The composition of HEPA filter media, shown in Table III, appears to be an ideal feed for a vitrification process. Two vitrification alternatives were tested, 1) punching out the media, feeding it into the vitrification process, and incinerating the frame, and 2) incinerating the entire filter and vitrifying the incinerator residue.

Table III. Composition of
HEPA Filter Media

	Weight Percent		
Component	Fiber Glass Filler	Crocidolile Filler	Crysolite Separators
SiO_2	60	51.1	46.7
MgO	13	2.3	50.7
Al_2O_3	21	-	0.2
CaO	6	-	-
FeO	-	35.8	0.8
Na_2O	-	6.9	-
H_2O	-	3.9	-
Fe_2O_3	-	-	1.6
Weight Represented	23.5	1.5	75

The first alternative was tried in a series of crucible tests. Heating HEPA filter media at 1100°C, with no fluxing aids added, did not produce a glass. By the addition of 20% boric oxide and 10% sodium oxide, a glass with a workable viscosity range could be obtained only after holding the melt at 1150°C for one hour. In all the tests, the media was first pulverized using a laboratory ball mill; unground media was impossible to vitrify under any of the test conditions. The necessity of the ball milling step, and the 1150°C operating temperature, diminished the desirability of reacting HEPA filter media separately.

Incineration of HEPA filters can be handled by "campaigning" the filters or by incinerating them with a mix of general solid waste. The first batch of filters incinerated were "campaigned", producing a residue from filters alone. This ash was used for another series of crucible vitrification tests. The present Rocky Flats bench scale vitrification system uses an Inconel 690 reactor vessel, and it is desirable to hold the process temperature around the 1050°C operating level. For this reason, these crucible tests were limited to a 1050°C maximum temperature.

The initial test was made with 20% boric oxide and 10% sodium oxide added to the filter residue as fluxing aids. This mixture, at 1050°C, would not produce a pourable melt. However, mixtures of 50% HEPA filter ash with 50% general solid waste ash was found to produce a good viscosity range glass at 1050°C when 20% boric oxide and 10% sodium oxide was added. The incineration of mixtures of HEPA filters and general waste appears to offer a residue amenable to vitrification in the Rocky Flats Plant vitrification process.

A major advantage of vitrification is the volume reduction obtained by immobilizing waste in a glass matrix. The residue from incineration of solid waste has about the same density as HEPA filter residue, roughly 0.5 on the average. By the addition of 20% boric oxide and 10% sodium oxide, glass with a density of 2.5 can be produced. The volume of additives will be about 30% of this, leaving a volume reduction factor of 3.75 for going from ash into a glass waste form.

Conclusions

1. Present methods of handling HEPA filters produces a waste probably unacceptable at a permanent repository.

2. HEPA filters can be successfully incinerated using a fluidized bed incinerator.

3. Separation of the frame from the media and incinerating only the frame is an unnecessary operation.

4. The residue from incineration of HEPA filters can be processed into a glass acceptable under proposed repository criteria.

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DISCUSSION

MURROW: Most of the nuclear power plant regulatory guides require a metal frame. Can you separate the frames from the media and do something with the two components separately?

JOHNSON: At our plant, we have worked on a combination punch and compressor to merely punch the medium out of the frame. So, if you have to use a metal frame, you could go that route. Thenyou'd have the metal left over as contaminated material that you might be able to decontaminate by electropolishing or other methods. In our plant we use all wooden frames.

CHOI: Do you see any advantage in using fluidized bed incinerators for the HEPA filter?

JOHNSON: For HEPA filters alone, maybe not. But since we have one operating and we use it for all types of waste, we generally just combine the filter waste with the rest of the waste.

CHOI: So there's no real advantage or disadvantage in using other types of incinerators for the HEPA filter.

JOHNSON: Probably not. Although, our residue comes out as extremely fine particles that are ideal for mixing with the flux to make a glass.

CHOI: The point that you made at the end of the session was that industry really needs a type of HEPA filter that can be processed and, indeed, we find that this is the best solution for Ontario Hydro. We have to change over 1,000 HEPA filters a year at just two stations and we will have more stations in the future. At $30 per cubic foot, that's a lot of money. That's why Ontario Hydro is seeking types of filters that are processable. In other words, we will try to avoid metal parts as much as possible in the HEPA filter.

BURCHSTED: That was one of the points I was also going to make. People here are probably using metal frame filters instead of wood and that presents a different situation when considering incineration. The other point is that most of the people here are using either aluminum separators or a separatorless construction so this magnesium oxide you talked about probably would not be a problem for most other organizations. I think you're the biggest user of asbestos separators today.

JOHNSON: Yes, we are by far. We used over half of those I mentioned.

BURCHSTED: Yes, the absence of asbestos separators does simplify the problem for other people considerably.

JOHNSON: Yes, it does. Thin aluminum would give us no problem in our shredding operations or in vitrification.

DEMPSEY: Does the small size of the particles inherent in the glass making process pose any special problems?

JOHNSON: Right now we are working on our vitrification unit. We are using a modified moving bed filter. Yes, it is a problem. The effluent from glass making pots does produce offgases that are very difficult to handle. And we do get vaporized sodium chloride as one of our main compounds. Off-gas filtration has been a problem in all vitrification processes.

VOLUME REDUCTION OF LOW-LEVEL, COMBUSTIBLE, TRANSURANIC WASTE AT MOUND FACILITY

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Abstract

Low-level combustible waste (<100 nCi per g of waste) generated during plutonium-238 processing is collected and stored in 55-gallon (200-liter) drums. The composition of this waste is approximately 32 wt % paper, 46% plastic, 16% rubber and cloth, and 6% metal. Treatment of this waste is initiated by burning in the Mound Cyclone Incinerator, which consists of a burning chamber, deluge tank, venturi scrubber and blower.

During the two years of operating the Cyclone Incinerator, experiments have been performed on particle distribution throughout the system using various mixtures of feed material. Measurements were taken at the incinerator outlet, after the spray tank, and after the venturi scrubber. An average emission of 0.23 g of particles per kg of feed at the venturi outlet was determined.

The distribution of chlorine from the combustion of polyvinyl chloride was studied. Analyses of the off-gas and scrubber solution show that approximately 87 wt % of the chlorine was captured by the scrubber solution and approximately 0.6 wt % remained in the off gas after the venturi scrubber. Measurements of the amount of NO_x present in the off-gas were also made during the chloride studies. An average of approximately 200 ppm NO_x was produced during each incineration run.

Immobilization of the incinerator ash is being studied with regard to long-term behavior of the product. The immobilization matrix which looks most promising is ash mixed with Portland 1A cement in a 65/35 wt % ash-to-cement ratio. This matrix exhibits good mechanical properties while maintaining a maximum volume reduction.

Cyclone Incineration

The Mound Cyclone Incinerator project, funded by the Division of Waste Management of the U. S. Department of Energy, has as its goal the development of processes that will reduce combustible, low-level radioactively contaminated waste to a compact, inert material suitable for long-term storage or burial. At present, combustible waste, contaminated to <100 nCi of plutonium-238 per gram of waste,

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*Mound Facility is operated by Monsanto Research Corporation for the U. S. Department of Energy under Contract No. EY-76-C-04-0053.

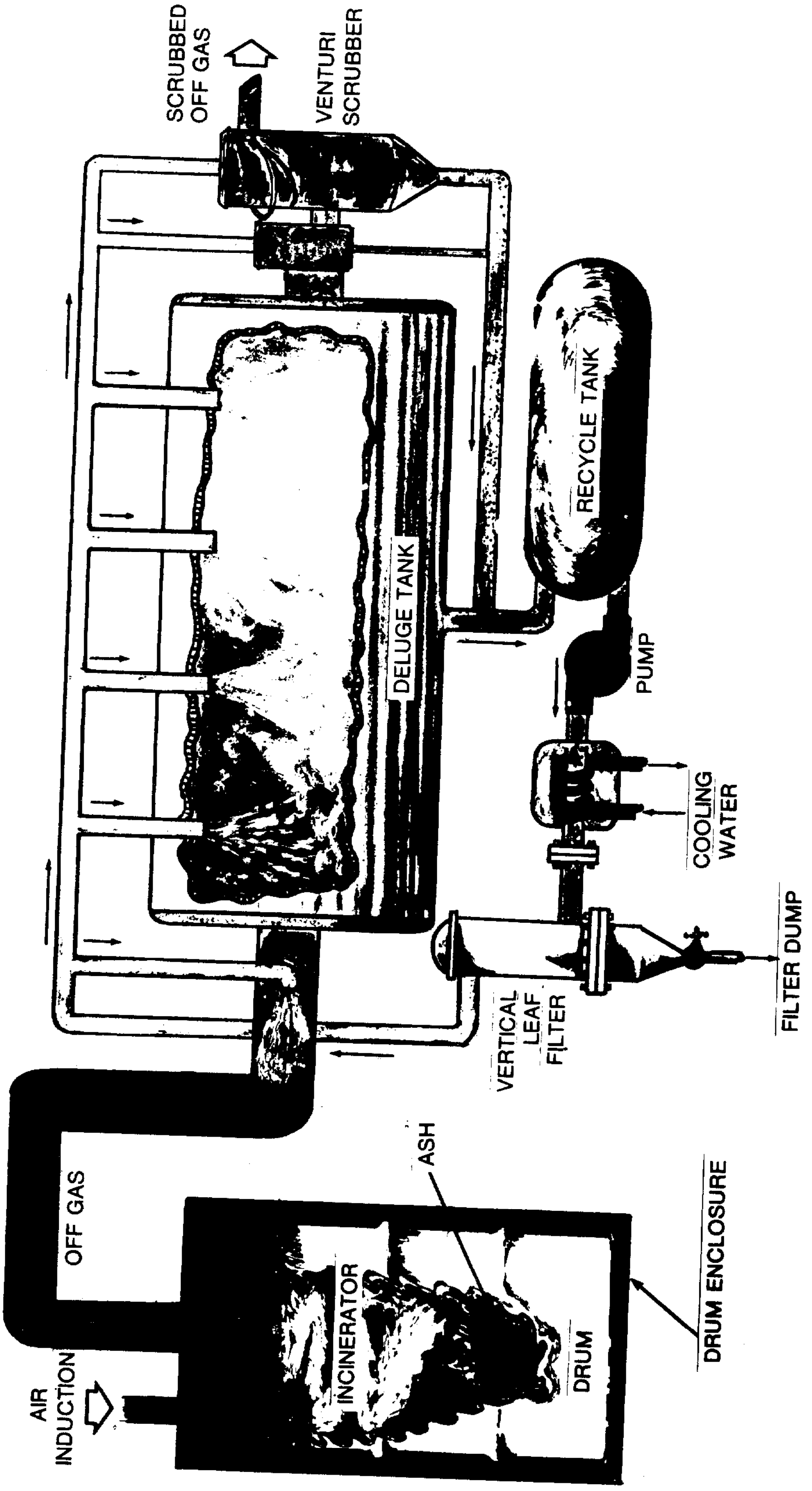

Figure 1 — Mound Cyclone Incinerator

is being incinerated on a routine basis. To date, a quantity of contaminated waste in excess of 5,000 kg has been incinerated. This waste was generated in the course of plutonium processing at Mound. The ash resulting from incineration receives further treatment to achieve immobilization during long-term storage.

Details of the Cyclone Incinerator are shown in Figure 1. The Cyclone Incinerator normally uses a 55-gallon (200-liter) drum as the burning chamber. The advantages of using the drum in which the waste has been shipped or stored are that 1) radioactive waste handling is reduced to removing the lid from the drum; and that 2) the drum, which is subjected to destructive thermal shock during combustion, is expendable, providing an inexpensive, easily replaceable burning chamber.

Previously, combustion air was introduced to the primary burning chamber through a single adjustable inlet (see Figure 2). Vertical movement of the inlet was provided to follow the burning interface as it progressed down the drum. Movement about the vertical axis was made possible to experimentally determine the optimum angle of air introduction. This angle is vital to the creation of the cyclone effect -- the heart of the cyclone incinerator. The cyclone effect produces a spiraling airflow down the inside burning chamber surface which cools the metal while preheating the air. When the airstream reaches the fuel surface, it not only supplies oxygen for combustion, but also agitates the top layers of fuel, resulting in a thorough mixing of oxygen and fuel in the combustion zone. The air sweeps across the fuel surface to the center of the chamber and rises to exit through the centrally located exhaust at the top of the chamber. The products of initial combustion, which include particles of unburned fuel and combustible gases (see Tables I and II), are retained in a high-temperature environment by the cyclone effect in the primary burning chamber. Combustion is continued in a secondary burning chamber which incorporates a baffle to prolong particle retention time in the hot zone.

Table I Characteristics of the off-gas stream.

	mg/m^3
Combustion Chamber Outlet	504.9
Deluge Tank Outlet	236.6
Venturi Scrubber Outlet	18.4
Primary HEPA Filter Outlet	Nil
	°C
Temperature, Average at Outlet	1090
Temperature, Maximum at Outlet	1320

More recently, an experimental lid assembly has replaced the upper burn chamber. The air inlets are placed 90° apart around the cylinder to provide a smoother air flow and are directed toward the side of the cylinder both to cool the metal and to initiate the swirling action that was previously found to be so important to burning in a drum.

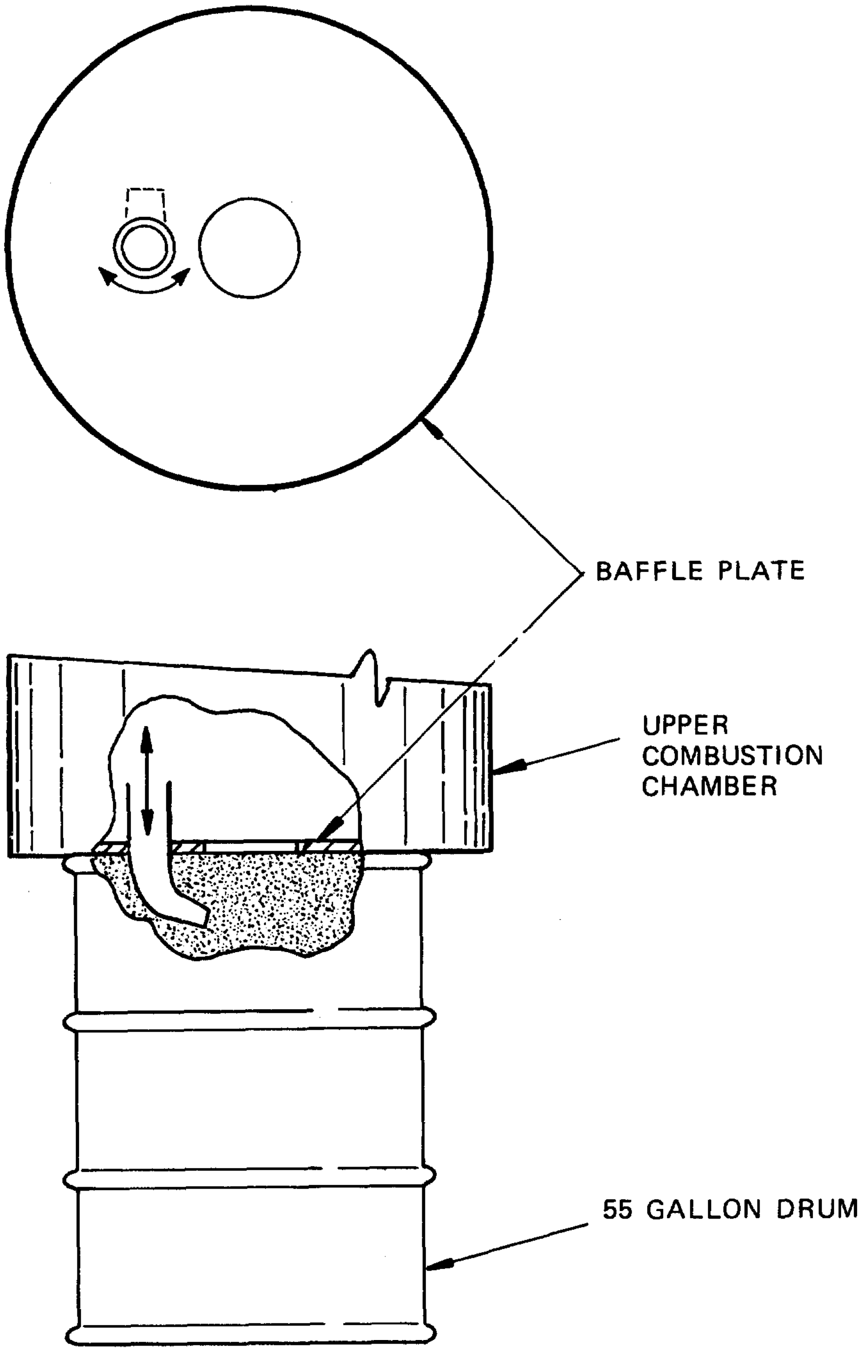

Figure 2 – Adjustable air inlet.

Table II Analysis of cyclone incinerator off-gas.

Component	Treated Off-Gas
Carbon Dioxide	9.0 wt %
Oxides of Nitrogen	10-600 ppm
Oxygen	13.5 wt %
Sulfur Dioxide	Not Detectable

The lid was installed to improve combustion characteristics such as burning rate, amount of combustible material in the ash, and particle carry-over to the off-gas system. Experiments conducted with the new lid assembly show improvements in the burning rate and in the amount of combustible material in the ash. Particle carry-over measurements are inconclusive so far.

Treatment of the incinerator off-gas begins with a deluge tank which cools the off-gas, neutralizes the acid agases, and removes a high percentage of the particles entrained in the off-gas. Further particle removal is accomplished by a high-energy venturi scrubber. The liquid used in the deluge tank and venturi scrubber is a sodium carbonate or sodium hydroxide solution which is recirculated through a heat exchanger for cooling and a vertical leaf filter for suspended solids removal.

The exhaust gas, cooled to about 65°C, passes through a HEPA filter before being discharged by a blower to the building exhaust. The blowers provide the airflow for the combined incinerator/off-gas system and maintain the system at a negative pressure relative to the room, thus simplifying contamination control and operational safety.

Volume and Weight Reduction

One of the ultimate goals of waste reduction is to achieve a maximum volume reduction, although the performance of waste reduction processes cannot be accurately measured by using volume reduction alone. Waste densities vary considerably and directly affect reduction measurements. Not only does tightly packed waste contain less volume than the same amount of loosely packed waste, it also requires longer combustion times. Therefore, both weight and volume reduction measurements are necessary to fully evaluate the performance of a waste reduction system. To determine the volume/weight reduction of the Cyclone Incinerator a series of 45 drums of waste was incinerated. The results are summarized in Table III.

The "incinerator ash" includes the remains in the combustion chamber but excludes metals present in the feed material. The "solids in the scrubber solution" consist of fly ash and precipitated salts formed during neutralization; they are collected in the vertical leaf filter. The sodium carbonate scrubber solution is controlled to a pH of approximately 9 by the addition of fresh carbonate solution. When the dissolved solids (NaCl, Na_2SO_4, and $NaHCO_3$) reach a maximum of 210 g per liter (solubility limitation), the scrubber solution is replenished. The "solid from waste treatment" is sludge generated during the chemical treatment that removes radionuclides from the spent scrubber solution. This treated scrubber solution is combined with other waste streams, and discharged to the environment.

Table III Volume/weight reduction for the cyclone incinerator.

Input Wt(kg)	Input Vol(m^3)	Material	Output Wt(kg)	Output Vol(m^3)
1574	9.172	Incinerator Ash	86.9	0.153
		Solids in Scrubber Solution	76.6	0.086
		Solid from Waste Treatment	3.3	0.004
		Total	166.8	0.243
		% Reduction	89.4	97.4

Using feed material containing approximately 18 wt % chloride and 2 wt % sulfur, the spent scrubber solution has been found to contain 14.9 wt % NaCl, 4.3 wt % Na_2SO_4 and 1.4 wt % $NaHCO_3$. Considering these primary and secondary waste streams, a total of 1574 kg of waste was reduced to 166.8 kg, giving a reduction factor of 9.4 to 1. The volume reduction accomplished was 97.5% (volume reduction factor of 37.8 to 1).

Mode of Operation

The cyclone system can be operated in a batch or continuous mode using solid or liquid feed. The batch method is ideally suited for wastes from storage or those requiring transportation, because it allows in-situ burning in the original drums. This is the normal mode of operation for waste currently being processed at Mound.

Continuous feeding is preferred when sufficient amounts of waste are generated in one place and packaging in drums would be a needless operation. Advantages of continuous feeding are that 1) total pollutants per quantity of feed burned are fewer, because most pollutants come from the cyclone incinerator during startup and shutdown and that 2) the metals in the incinerator will last longer because of fewer thermal cycles. The disadvantage of continuous feeding is increased capital and operating costs for an additional step, since the feed must be sorted and shredded in order to be fed to the incinerator.

The first attempt at continuously feeding the Cyclone Incinerator was made by dropping shredded feed into an air inlet line with a rotary valve fed from a bin. Jamming of the rotary valve was the major fault of the system. The second attempt will be with a screw feeder and a revised bin. Feed rates up to 50 kg/hr were achieved with the rotary valve system.

Experiments have shown that the cyclone system can also reduce volumes of combustible liquids. For example kerosene, kerosene/tributyl phosphate and vacuum pump oils have been burned.

For burning combustible liquids, a commercial oil burner, designed to burn all types of fuel oils, was chosen as the primary combustion unit. The steel drum combustion chamber was modified somewhat with the addition of a castable refractory liner and the installation of the oil burner at the base of the drum. Interchanging the burn chambers is a practical way of providing multiple fuel burning capabilities with minimum effort. The induced air current is as useful as in the solid-batch incineration; it prolongs retention time in the high-temperature zone so that all necessary secondary combustion can be completed. No changes were considered to be necessary in the off-gas handling system.

Several safety devices have been installed to protect against a possible local concentration of flammable vapors. A propane pilot flame with automatic ignition was installed to initiate liquid burning. In the event that an oil flame would extinguish through blowout, feed cut off, etc., an ultraviolet sensor automatically reignites this pilot flame.

Tests using liquid feed have shown that mixtures of tributyl phosphate (TBP) and kerosene burn readily, at least in the percentages used. It was found that igniting kerosene alone, prior to feeding the mixture, resulted in a superior initial burning of the mixture. The feed rate, after ignition, was 15 liters per hour. At this feed rate, the scrubber cooling system approached capacity. Increased cooling capacity would, therefore, be necessary for a higher feed rate. The primary conclusion of this experiment was that the incinerator system can handle the mixture of 30% TBP-70% kerosene common to the nuclear industry.

Off-Gas Composition

We have extensively monitored the exhaust from the Cyclone Incinerator to determine the effectiveness of the scrubbers in removing acid gases generated in the combustion of materials commonly used in nuclear operations. The data in Table IV were collected during the incineration of waste containing 18 wt % chloride and 2 wt % sulfur. Because no externally fueled burner is utilized for solid waste combustion in the Cyclone Incinerator, the composition of the waste determines the peak temperatures of combustion which range from 1100 to 1300°C.

Table IV Typical off-gas analysis for cyclone incinerator.

Component	Treated Off-Gas
Carbon Dioxide	9.0 wt %
Oxides of Nitrogen	10-600 ppm
Nitrogen	66.2 wt %
Hydrogen Chloride	1-13 ppm
Oxygen	13.5 wt %
Sulfur Dioxide	Not detectable
Water	11.0 wt %

A series of chloride mass balance runs was made to define more clearly the disposition of chlorides generated during the combustion of polyvinyl chloride (PVC) in the cyclone incinerator. Known amounts of PVC were burned. Before the first run and after each succeeding run, the scrubber solution was sampled for chloride. A collection train monitored the off-gas prior to the HEPA filter. Chemical analysis indicated that 87 wt % of the chlorides in the PVC went into the scrubber solution and a statistical average of 0.6 wt % showed up in the off-gas. The remaining 12 wt % is unaccounted for, but most likely some remained with the ash and some was attached to solids removed from the scrubber solution by the liquid filter.

We have also monitored the off-gas during liquid incineration. A solution of potassium hydroxide was cycled through the deluge tank and venturi scrubber to remove phosphates from the flue gas stream. The scrubber system effectively removed phosphates from the off-gas. Measurement of phosphates in the flue gas indicated a range of from 0.3 to 2.1 ppm at an average phosphate concentration of 1.3 ppm.

Extensive particle monitoring was performed at appropriate points in the incineration system during combustion of simulated wastes to assess the effect of adjustments to the system, to determine the effectiveness of the off-gas system components and to estimate the HEPA filter life expectancy. The HEPA filter, unlike the off-gas system components, is not self-cleaning and must be replaced when loaded. A low loading rate is desirable from operating cost and volume reduction aspects.

Radioactive contamination of actual waste has made particle sampling more difficult, but at points where comparisons have been made, the size and distribution of particles are nearly identical for all types of feed.

Immobilization

Controlled experiments were conducted on the selected pressed-pellet matrix chosen for the immobilization process of incinerator ash residue. The experiments were designed to provide data for evaluation and selection of the best pellet matrix for incinerator ash and Portland Type 1A cement.

Certain process parameters previously determined and evaluated during screening studies with the pressed ash-cement matrix were fixed throughout the entire experimental sequence. The parameters in the process which were held constant are:

1. Pressing pressure of 25,000 psi for 1-min duration.
2. Three-gram matrix weight.
3. One-half inch pressing die, which, with a 3-g charge, produces a relatively standard 1/2-in. diameter by 1/2-in. high pellet (L/D ratio approximately 1).
4. Dry Cure Cycle - two days (48 hr) in open atmosphere.
5. Wet Cure Cycle - four-day (96 hr) cure in distilled water followed by a two-day cure in open atmosphere.

Five groups of waste matrices samples were evaluated during the controlled experiments. Pellets were pressed with 60%, 65%, 70%, 80% and 0% ash residue (100% Portland 1A cement). The pure cement pellets were pressed for control comparison conditions. The water-to-cement ratio was varied in each sample group to determine the water-to-cement ratio which would produce acceptable pressed pellets. Normally, six water-to-cement ratios were evaluated ranging from a too dry condition (fracturing pellet matrix after pressing) to a wet condition (excess water ejected from die during pressing operation).

The control condition matrix (100% Portland 1A cement) containing 0% incinerator ash at acceptable water-to-cement ratios produced nearly identical pressed pellets. The dry-cure method produced pressed pellets of uniform compressive strength, density, and final weight. Based on the final weight of the pellets, the calculated percentage of water remaining in the matrix is approximately 2% for the dry-cure method. Similarly the wet-cure method produced pressed pellets also of uniform but higher compressive strength, density, and final pellet weight. However, the wet-cure method retained approximately 10% water in the matrix form.

The data shown in Table V for the 60%, 65%, 70% and 80% ash-cement pressed matrices are given only for the two best water-to-cement ratios even though four acceptable and tested water-to-cement ratios were attained. The data clearly indicate that the wet-cure method produces ash-cement matrix having higher compressive strength than pellets which were dry cured. In general, the compressive strength increased as the percent of ash in the matrix decreased. This result was expected since the cement (binder) contributes significantly to the pellet compressive strength.

As the percent of incinerator ash was increased, the water-to-cement ratio also increased. This was also expected as observed in past screening studies conducted on the ash-cement pressed matrices. Although a small portion of water must be required for cement interaction and blending, the ash requires significant amounts of water to wet the ash because of its hydrophilic characteristic. Although this condition exists, the final pellet weights after curing are close in final weight value as the 0% ash matrix final weight. The 60/40 ash-cement matrix after wet-cure processing, however, gained weight; the reason for this is presently being investigated.

The density of the various ash-cement pressed pellets increased as the percent of ash decreased. The density ranged from 83-88% of the 0% ash-cement pressed matrix; however, the density values calculated for the ash-cement various matrices were taken, and the radiographs clearly show that no void, crack, or fissure exists in any of the ash-cement pressed pellet matrices.

Mechanical strength and corresponding percent weight loss of the various pressed pellets were also determined. The pressed pellets were placed in stainless steel containers which were clamped into a Model BT Wrist Action Shaker. The shaker was set at the maximum 10° shake angle to vibrate the samples in a circular motion inside the fixed container. The shaking action was continued for 50 hr, and the weight loss was determined. The resulting weight losses are also shown in Table V. All the samples experienced a slight rounding of the edge that contacted the stainless steel container; one slight abrasion occurred on the walls of the samples. Figures 3 and 4 are photographs of the 100% cement pressed pellet before and after the shake test. Radiographs of the pellets taken before and after the shake test showed that the pellets were still homogeneous and contained no voids, cracks, or fissures. Although the percent weight loss is higher for the 60%, 70% and 80% ash-cement pressed matrices as compared to the 100% cement pressed matrices, this result would be expected based on the lower compressive strength values.

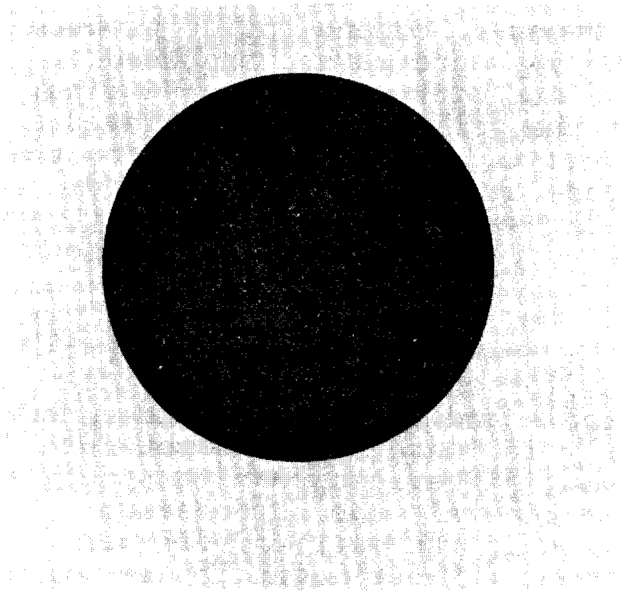

Figure 3 Pellet before shake test.

Figure 4 Pellet after shake test.

Volume Reduction Efficiency

Prior to the initiation of the controlled experimentation on the ash-cement matrix process, a new batch of incinerator ash was prepared with the cyclone incinerator. The composition of the incinerator feed was Type I, which consisted of 32 wt % paper, 9 wt % PVC, 29 wt % polyethylene, 8 wt % polypropylene, 13 wt % rubber, 3 wt % cloth, and 6 wt % metal. A total of 11.2 kg (24.6 lb) of the uncompacted combustible composition (2.2 ft^3) was burned in a 55-gal drum. The resulting ash, containing approximately 20% carbon, was then sintered for 1 hr at 800°C to reduce the carbon content to approximately 0.04% carbon. After grinding and sizing, the sintered ash weighed 340 g and contained a volume of 570 cm^3.

Based on the pelletization process for a pressed ash-cement matrix ratio of 70/30, approximately 162 pressed pellets could be produced. These pellets would weigh approximately 494 g if dry cured and approximately 534 g if wet cured. The resulting volume of the immobilized matrix would be approximately 252 cm^3 for the dry-cure product and approximately 256 cm^3 for the wet-cure method. This analysis is based on the preliminary data obtained during the experimentation controlled processes (Table V).

Table V Pressed Ash-Cement Pellet Matrix
Controlled Experimental Process

Ash Type	Percent Ash	Percent Cement	Water/ Cement	Cure		Average Loss During Cure (wt %)	Density (gm/cm^3)	Compressive Strength (psi)	Shaking Loss (wt %)
				Dry	Wet				
	0	100	0.10	x		5.9	2.29	3635	
	0	100	0.125	x		6.1	2.30	3661	
	0	100	0.15	x		6.5	2.32	3668	0.50
	0	100	0.175	x		6.7	2.33	3670	
	0	100	0.10		x	2.1	2.43	4580	
	0	100	0.125		x	2.0	2.45	4330	
	0	100	0.15		x	1.5	2.47	4192	0.84
	0	100	0.175		x	1.2	2.49	4293	
I	60	40	0.45	x		6.2	2.00	3470	4.45
I	60	40	0.45		x	(4.1)	2.30	3600	3.21
I	60	40	0.50	x		8.9	2.00	3470	0.62
I	60	40	0.50		x	(3.5)	2.29	3620	4.33
I	65	35	0.60	x		11.8	1.90	3484	
I	65	35	0.60		x	5.5	2.21	3583	
II	65	35	0.60	x		7.9	2.51	3605	
II	65	35	0.60		x	5.2	2.56	3911	
III	65	35	0.25	x		2.7	2.47	3618	
S-UK*	65	35	0.60	x		7.4	2.08	3619	
S-UK*	65	35	0.60		x	3.3	2.18	3733	
I	70	30	0.70	x		11.0	1.96	2480	1.78
I	70	30	0.70		x	4.9	2.01	3640	3.70
I	70	30	0.75	x		11.1	1.96	3470	2.27
I	70	30	0.75		x	3.2	2.11	3625	3.63
I	80	20	1.10	x		7.1	1.92	2480	3.72
I	80	20	1.10		x	3.3	2.08	3600	3.84
I	80	20	1.15	x		7.9	1.92	2480	1.85
I	80	20	1.15		x	2.9	2.08	3570	4.45
I	80	20	0.70	x		9.0	2.03	∿2507	
I	80	20	0.70		x	2.7	2.15	∿3640	
I	80	20	0.85	x		9.0	2.04	∿2500	
I	80	20	0.85		x	5.6	2.10	∿3670	

*S-UK denotes pellets containing 3 wt % Na_2SiO_3 that were made with "unknown type" ash

The data indicate the overall process efficiency starting with uncompacted combustible Type I composition through incineration and immobilization is approximately 95% in weight reduction and approximately 99% in volume reduction.

The selected fixation process, which is a cement/ash pressed pellet matrix, was chosen on the basis of the waste matrix meeting known WIPP acceptance criteria and, also, with respect to simplicity of the process in terms of processing, process equipment, and operating costs. Figure 5 shows a flowsheet for the pelletization process of incinerator ash residue.

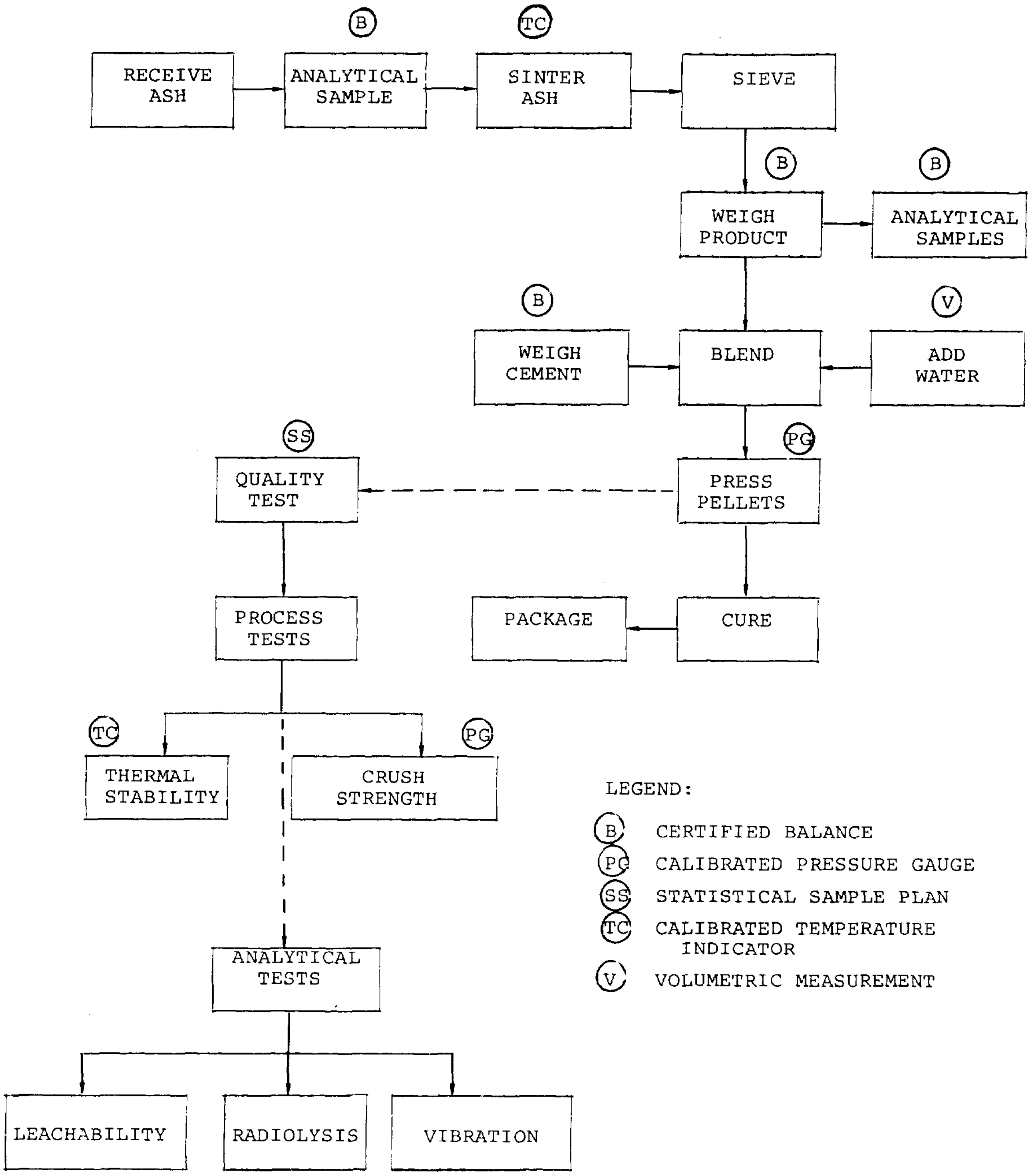

Figure 5 – Proposed Pelletization Flow Sheet.

DISCUSSION

BURCHSTED: I'd like to make an observation and ask two questions. First, I assume that the Venturi effluent efficiency of 95% for submicron particles is based on mass, and that the number efficiency would be closer to 5 or 10%.

BOND: That is correct. We have not measured numbers of particles in the submicron range.

BURCHSTED: Now, as to the HEPA filter, what was the air temperature?

BOND: That was the same as the scrubber outlet which was about 60°C.

BURCHSTED: Have you tried incineration of HEPA filters?

BOND: We have tried it. We, also, have only wooden frames that burn beautifully, but the asbestos, naturally, does not. It does, however, disintegrate. The reduction ratio is not as good as with more combustible waste. The filter must be broken up to fit inside a 55 gallon drum.

BURCHSTED: The comments I made before about aluminum separators would apply here, too?

BOND: Yes.

MURROW: The 60°C offgas, after going through the scrubber, would be pretty well saturated with water. Do you have any trouble with water condensation in the HEPA filter?

BOND: Yes, at one time we had a small amount of trouble. Subsequently, we added a heating element in the offgas line between the Venturi scrubber and HEPA filter which heats the offgas sufficiently to keep the water vaporized. The temperatures quoted in the talk were taken prior to the addition of the heater.

MURROW: Is your temperature high enough to avoid carbonaceous effluent from the materials you're burning, such as oils or plastics or rubber?

BOND: We have not detected any material of this sort coming from the combustion chamber. The design of the combustion chamber provides a cyclone action to both the incoming and exiting air which allows sufficient time for complete combustion of carbonaceous material.

MURTHY: Could you tell us what you do with the scrubber liquor that you get from both scrubbers?

BOND: Yes, at Mound facility the scrub liquor from the deluge tank and Venturi scrubber is combined in the recycle tank. The spent solution, at Mound, is processed in the plant waste disposal system. After processing, it is clean enough to be dumped into the river. We are working on a treatment method that will, when developed, provide an accessory to the cyclone system for use in applications where waste disposal facilities are not available, but we have not tested it yet. In fact, we haven't bought it yet.

ALVARES: What is used to measure aerosol at various incinerator stages? What reservations do you have about your efficiency results?

BOND: Leeds & Northrup Cascade impactors are used. We have no reservations. These data were taken over many incinerator runs with a wide variety of feeds. The results are consistently within a narrow range.

DEMPSEY: What are the binders in the pressed pellets that you spoke about? Do you press them without any binder at all? What binder do you use in the ideal pellets that you spoke about? What is the difference between "concrete pellets" and "pressed pellets"--if the latter also have concrete in them?

BOND: We use a small amount of water as a binder which is taken up by the cement and forms almost a concrete type of pellet. The second pellets were cast concrete. We mixed ash and cement with sufficient water to form concrete and these were then cast in molds. The others have just enough water to act as a binder and they are pressed in a die so that the water content is quite a bit lower.

DEMPSEY: Does the cement actually hydrate in the second case? Is it just a stoichimetric amount of water but not enough to be free water?

BOND: I'm not sure, but I believe that is the case.

COLLINS: Have you tried this on typical wastes from light water reactors; sludges and slurries? What about waste contaminated with iodine?

BOND: There were three types of waste that we have done experiments with, primarily paper, wood, leather, and rubber. We have tried a small amount of sludge mixed with the regular feed. The results were good, i.e., satisfactory burning. We hope to look into this problem more deeply in the future. Iodine contaminants are a recognized problem. One current project of ours is directed toward iodine removal, but we have not yet reached the experimentation stage. The liquids we have burned have been tributyl phosphate and kerosene mixtures primarily. Also vacuum pump oils.

CHOI: We have drums of oil, as in your case. How would it be burned in situ in the drums? For example if the drum is filled with oil?

BOND: The liquid can be pumped from any tank or drum and fed through our liquid burner. We have successfully burned mixtures of tributyl phosphate and kerosene, kerosene and vacuum pump oils. We expect to try liquids such as Hyprez and others commonly found in the nuclear industry.

CHOI: So, it would be different from what you have shown on the slides.

BOND: Yes, it's a different set-up completely.

CLOSING REMARKS OF SESSION CHAIRMAN:

We are done with the day, and I have no words of wisdom. Some of you who are not involved with this technology may wonder why we keep hearing of all these different types of incinerators. Why doesn't everyone use or purchase one particular unit and get on with it? The DOE is now supporting development of five. There were seven different types before. The intention is to keep narrowing the number down and we have narrowed it down a little. Now, we're coming to the end of Phase 2; namely, the pilot process where we have conducted tracer tests. Now, the narrowing down process really becomes in earnest as we prepare to process massive amounts of waste. Two years from now, I think there will be still another story with regard to this technology. However, each of the units you've heard about is finding its own little niche in small-scale, on-site-type applications even though they may not be suitable for a very large incineration center requirement.

SESSION III

TRITIUM, ^{14}CARBON, OZONE

Tuesday, August 8, 1978
CHAIRMAN: D. Pence

TRITIUM EFFLUENT REMOVAL SYSTEM
P. H. Lamberger, G. E. Gibbs

MODIFICATION AND TESTING OF THE SANDIA LABORATORIES, LIVERMORE TRITIUM DECONTAMINATION SYSTEMS
P. D. Gildea, H. G. Birnbaum, W.R. Wall

TRITIUM REMOVAL USING VANADIUM HYDRIDE
F. B. Hill, Y. W. Wong, Y. N. Chan

STUDY ON THE TRITIUM REMOVAL FROM THE SODIUM IN LMFBR
K. Hata, Y. Nishizawa, Y. Osawa

MONITORING AND REMOVAL OF GASEOUS CARBON-14 SPECIES
M. J. Kabat

ON THE CATALYTIC REMOVAL OF OZONE PRODUCED IN RADIOACTIVE MEDIA
R.-D. Penzhorn, K. Günther, P. Schuster