

SESSION II

WASTE TREATMENT: VOLUME REDUCTION AND PREPARATION FOR STORAGE

Monday, August 2, 1976  
CHAIRMAN: R. W. Ramsey, Jr.

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OPENING REMARKS OF SESSION CHAIRMAN:

The processing of waste to achieve volume reduction and passivate or stabilize material for storage or disposal is an important frontier of research and development for waste management in general and for air cleaning in particular. The removal of radioactive material from effluents of air and water are major sources of waste material that must be managed. Therefore, processes to reduce the volume of these residues are receiving major attention in the ERDA Waste Management R & D Program. Several of the processes under development are described in papers at this Conference along with the many other significant contributions to this technology.

VOLUME REDUCTION OF CONTAMINATED FILTER WASTES

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Abstract

Reported are details of a pilot project to design and construct a compactor to reduce the handling of high efficiency particulate air (HEPA) filters used in air filtration systems at facilities where radioactive materials are processed. In such systems at Rocky Flats Plant, filters require frequent change and removal. Large quantities are used and will be increased for future operations. With the completion of the pilot model, it has been demonstrated that volume reductions of more than 80 percent can be achieved and cost savings will be realized also.

I. Introduction

A highly efficient air filtration system is essential in plant operations to safeguard personnel and the environment. The high efficiency particulate filters (HEPA) used in the system must be replaced frequently because of exposure from radioactive materials being processed in various areas.

Currently, some 3000 (2 by 2 by 1-foot) filters are handled per year and future operations will require use of about 10,000 filters. Replacement and handling procedures from procurement through retrievable storage will cost about \$415.00 for each HEPA filter. To reduce space consumption and handling problems of the volume of filters, a pilot compactor was designed and constructed to demonstrate its feasibility.

II. Description of Compactor

The constructed pilot model consisted of a hydraulically operated punch, rams, and an extruding die. The function of the model was to separate the filter components from the frame and to extrude them through the die. The HEPA filters were 8 by 8 by 6 inches.

In the model, a standard 5000 pounds per square inch (psi) pump is connected through a series of valves to four cylinders which can be operated and controlled independently (see Figure 1). A ram is attached to the piston rod of each cylinder. The main cylinder has a capacity of 25 tons of force and is used to extrude the filter media through the pelletizing die. Although different configurations of

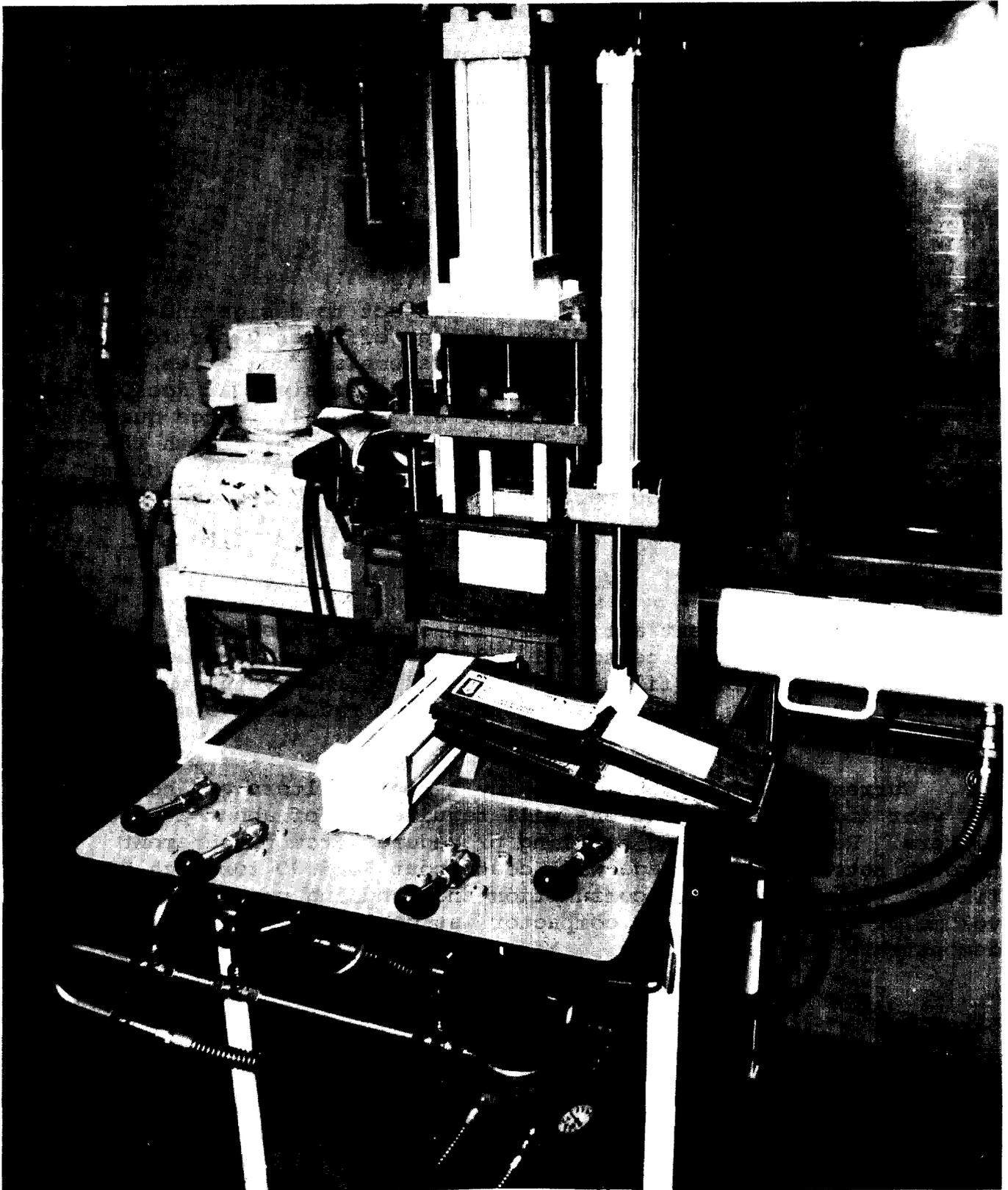


Figure 1. Filter-Media Compactor

dies were tested, one that produced pellets with a square cross section proved the most satisfactory (see Figure 2).

The overall dimension of the inside of the die is 4 inches and is divided into four equal sections. The leading edge of the divider comes to a knife edge where the filter media is sheared. Each of the four sections is 2 inches square at the knife edge. These openings are tapered down to 1.75 inches square, 1 inch into the 2-inch thick die. Because of poor flow characteristics of the filter media, the dividers and the taper provide sufficient resistance to the ram to compact the media being extruded. Attempts to produce cylindrical pellets failed because the die openings were too severely tapered for the filter media to be extruded. By moderating the taper, undoubtedly, pellets of different shapes could be produced.

The original concept involved punching the media out of the frame and shredding them before pelletizing. However, because the flow characteristics of filter media were poor, it was decided to use a shear die and eliminate the shredding operation. For the 8 by 8 by 6-inch filter, it took a force of about 2000 pounds to separate the media from the frame. About 20,000 pounds are required to compact and extrude the media through the die.

With the current system, the filter is soaked with water before compaction, otherwise, the extruded pellets tend to re-expand. Pellets resulting from soaked media expand by about 20 percent as they come out of the die. The lubricating properties of water appear to be minimal. The water serves to make the filter components pliable so that the compacted material retains its shape and size. The use of water as a rinse to partially wash off contamination will be considered in the future.

The pressure exerted on the wet media squeezes out most of the liquid and no free liquid exudes from the compacted pellet. In the current laboratory atmosphere, the exterior of the pellet is visibly dry within 24 hours. The frame of the filter can be crushed in preparation for combustion in the incinerator being planned for Rocky Flats (see Figure 3). An 83 percent volume reduction of the media and separator is obtained.

### III. Benefits of Compaction

The current system of packaging the 2 by 2 by 1-foot contaminated filters for disposal consists of crushing the filters in a press and packing them in 4 by 4 by 7-foot fiberglass reinforced polyester coated plywood boxes. Each box costs about \$320.00. Approximately 20 to 27 of the filters are presently packed in a box.

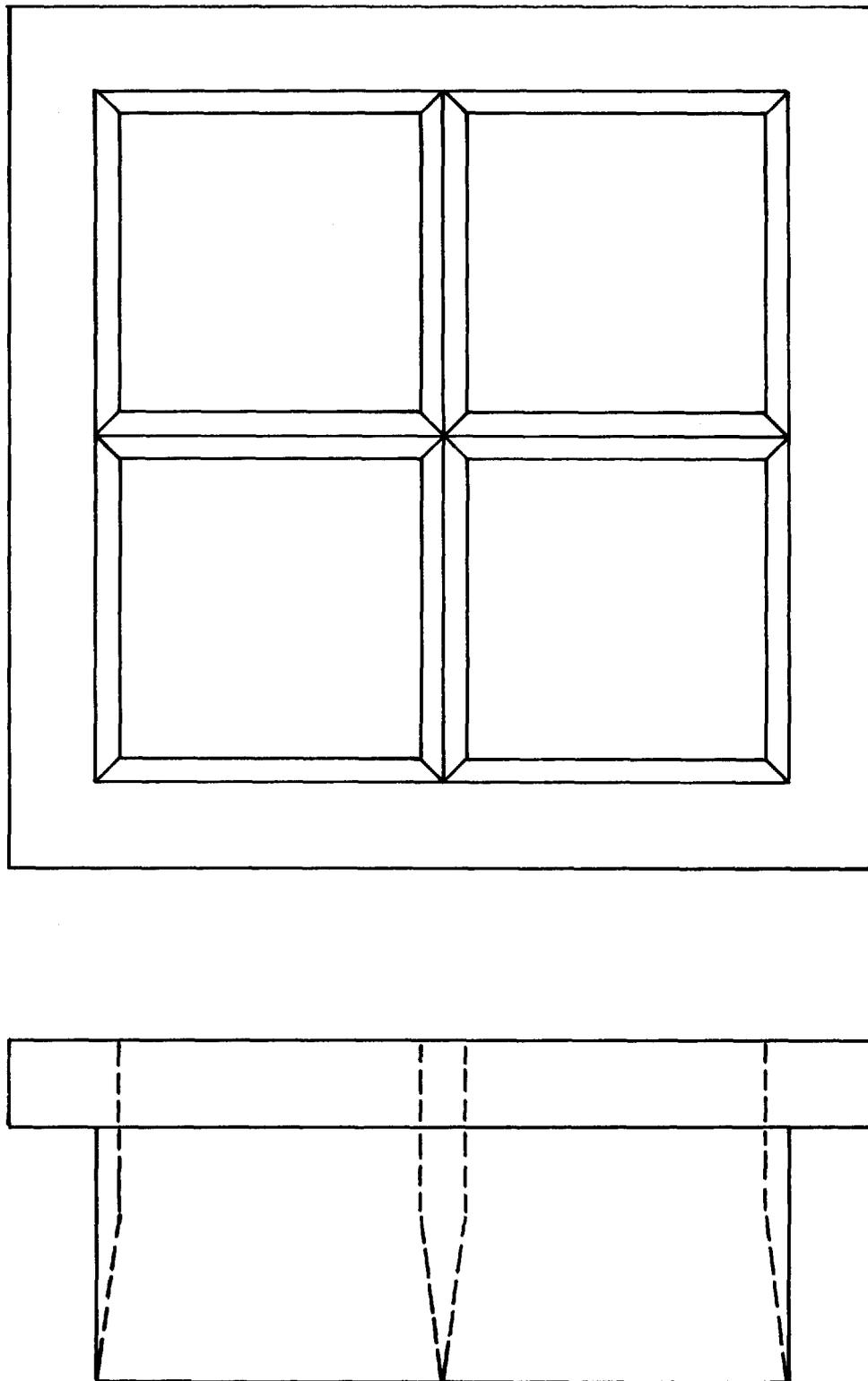


Figure 2. Pelletizing Die.



In packaging the pellets for waste shipment, the possibility is being explored of placing them in unused space of plywood boxes which are already filled with other types of waste. Thus a savings would occur in the number of boxes shipped. Waste Management personnel are interested in the procedure and do not envision any major problems. At Rocky Flats, excess weight would not be a problem since the average weight of the crate shipped is about 4000 pounds and the maximum allowable is 5000 pounds.

Preliminary discussion with Nuclear Safety has not revealed any insurmountable criticality problems associated with the compacting and proposed packing of contaminated filter media.

At Rocky Flats, we currently discard about 3000 2 by 2 by 1-foot filters a year. (This requires approximately 120 waste boxes at a cost of about \$600.00 each, including shipping.) A potential savings of \$72,000.00 a year could be achieved at the present level of usage. This does not include the cost of retrievable or permanent storage (or both) which has been quoted as high as \$30.00 per cubic foot. Also, when the new plutonium recovery facility comes on stream, the volume of contaminated filter waste will increase.

#### IV. Future Plans

Design is in progress for a new scaled-up compactor to handle the 2 by 2 by 1-foot HEPA filters. Tests show that pressures of about 20,000 pounds of force are required to punch the media from the frame of the large filters.

After development and testing, it is planned to enclose the new unit and test it in actual use with contaminated filters. The system will be automated with the addition of flow control and sequencing valves so that it can be operated remotely. The compactor is expected to be in operation by 1979.

DISCUSSION

MOELLER: I had two questions. How much of the activity from the filter media is carried off by the water and, secondly, is this whole process conducted in an airtight room or with exhaust ventilation and so forth?

BUTTEDAHL: At the present time, we are operating this pilot model strictly with uncontaminated filters for development purposes. We haven't done any work with contaminated filters yet.

OLSON: What is being done to reclaim plutonium from the filter before it is crushed, if anything?

BUTTEDAHL: At this point we have come up with a relatively new thing. Our group has not been concerned about plutonium recovery but, hopefully, when we wet these filters (we will spray them and rinse them off) we expect some of the Pu contamination will rinse off with the dirt. The chemical operations group surveys each filter and recovers the Pu when economically feasible.

PITTMAN: You mentioned the current costs of shipping packages and the potential costs of the long range management of the packages. Have you made any cost estimates for doing what you are planning to do; namely, for the equipment, the operation, and the recovery, obviously, of some waste from the operation itself? In other words, have you been able, yet, to make a cost analysis?

BUTTEDAHL: No, we have just started engineering on the scaled-up model and at this point we don't have figures.

BURCHSTED: Is it necessary to reduce this to a cube in two directions or could you reduce it to just a leaf and simplify the process, i.e., a layer of materials that, in this case, would be 23- x 23-in.?

BUTTEDAHL: You mean, rather than pelletizing it, just flatten it?

BURCHSTED: Right.

BUTTEDAHL: Yes, that is possible. We went the way we did because we could get smaller pellets that would better fill the voids in waste boxes. You can always get a few more pellets in a waste box that is technically full.

GRADY: You said originally you had looked at the concept of taking the entire filter and putting it through a shredder and then compacting the resulting material. You indicated that you had problems with this. Could you elaborate on what these problems were and why you went through the separate concept of dividing it into two parts?

BUTTEDAHL: We never considered shredding the frame. We had always planned to incinerate the frame. We were only operating with

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the media, and the media just didn't flow properly on the design of the die that we had. So, rather than go with the shredding operation, we decided that if we could get it through this particular die we are using, we would eliminate the shredding operation. It is just one less operation.

GASKILL: Since the filter frames are usually made out of wood, have you given any consideration to cleaning up the effluent from incineration and if so, what?

BUTTEDAHL: Not at this point. We aren't far enough into the program to be concerned with that. Don Ziegler has a paper later this morning on incineration, and, hopefully, we can run them through such a device.

KAHN: Since you have liquid waste, what about dissolving the filter media? Have you looked into the possibility of dissolving the filter media rather than pelletizing?

BUTTEDAHL: No.

W. C. BROWN: I was wondering if this method of compaction was limited to filters without separators.

BUTTEDAHL: No, these are standard HEPA filters that have asbestos separators.

DEITZ: The authors mention soaking the filter with water before compaction. It is suggested that an alkali or CaO be added so as to harden the final pellets due to slow formation of a cement-like silicate. The hardened product should be easier to handle without abrading.

BUTTEDAHL: Good suggestion. It certainly will be considered.

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## MOLTEN SALT COMBUSTION OF RADIOACTIVE WASTES\*

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### Abstract

The Atomics International Molten Salt Combustion Process reduces the weight and volume of combustible  $\beta$ - $\gamma$  contaminated transuranic waste by utilizing air in a molten salt medium to combust organic materials, to trap particulates, and to react chemically with any acidic gases produced during combustion.

Typically, incomplete combustion products such as hydrocarbons and carbon monoxide are below detection limits (i.e., <30 ppm and <0.05%, respectively). Hydrogen chloride in the off-gas, when pure polyvinyl chloride is burned, is also below detection limits (<5 ppm). Particulate concentration in the off-gas (typically 0.2 mg/m<sup>3</sup>) is directly related to the sodium chloride vapor pressure of the melt; >80% of the particulate is sodium chloride. Essentially all metal oxides (combustion ash) are retained in the melt, e.g., >99.9% of the plutonium, >99.6% of the europium, and >99.9% of the ruthenium are retained in the melt.

Both bench-scale radioactive and pilot scale (50 kg/hr) non-radioactive combustion tests have been completed with essentially the same results. Design of three combustors for industrial applications are underway.

### I. Introduction

Atomics International has been investigating the use of molten carbonate salts for industrial applications for over two decades. These processes vary from utilization of the molten salt as a chemical scrubber<sup>(1,2)</sup> for acid gases to the use of the molten salt as a reaction media for in-situ combustion.<sup>(3,4)</sup> By feeding less than the stoichiometric requirements of air, molten carbonates are also being utilized to gasify coal,<sup>(5)</sup> organic wastes,<sup>(6)</sup> high sulfur oil, etc., to produce a source of clean combustible gas.

Since 1974, application of this combustion process to reduce the weight and volume of solid transuranic (TRU) fuel cycle wastes has been under development.<sup>(3,4)</sup> In this application, the molten salt medium is utilized to combust the organic materials, to trap inorganic (noncombustible) particulates, and to react chemically with acidic gases (such as HCl, or SO<sub>2</sub>,) produced during combustion. Subsequently (in a company funded program), this process has also been applied to other nuclear fuel cycle wastes such as  $\beta$ - $\gamma$  contaminated solid wastes.

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Following the combustion step, there are two options available: Option 1 direct fused casting of the spent salt into disposal containers or Option 2 processing the spent salt to recover the salt and transuranics. Option 1 has been studied on a bench-scale with both uncontaminated waste tests (Figure 1) and radioactive waste tests (Figure 2) and on a pilot-scale (Figure 3) with uncontaminated waste tests (50 kg/hr feed - 1000 kg casts of fused salt). Salt and transuranic recovery (Option 2) has been studied only on a bench-scale (0.5 kg/hr feed) with uncontaminated and contaminated melt-ash mixtures. Salt recovery tests have been performed on a pilot scale in related combustion applications. Following a brief process description, results of various development tests are presented particularly as they relate to control of air pollution during volume reduction of these wastes.

## II. Process Description

In the Molten Salt Combustion Process, the shredded waste is fed, with air, to the molten salt combustor. Initially, the molten salt consists of sodium carbonate, an inexpensive natural mineral, and about 10 wt % sodium sulfate. Rapid and complete combustion of the organic material (>99.999%) occurs in the melt producing steam and carbon dioxide. As the combustion products rise through the melt and are scrubbed by it, the melt reacts chemically with any acidic pollutants such as hydrogen chloride, sulfur oxides, and phosphorus oxides to form sodium chloride, sulfate and phosphate. The noncombustible inorganic matter, such as oxides of aluminum, silicon, iron, and transuranics, is trapped in the melt. The molten salt completely oxidizes the waste; no incomplete combustion products such as hydrogen, hydrocarbons, or carbon monoxides are observed as long as excess air is fed with the combustible waste.

Inorganic combustion products can build up to different levels before the physical and chemical properties of the melt are altered significantly. Ash, such as aluminum or iron oxides, can build up to 20 wt %. If the melt becomes viscous due to too high a buildup of insoluble materials, the hydraulics become impaired and the melt must be changed, more salt must be added, or the temperature must be increased. Soluble products, such as sodium chloride, can build up to about 85 wt %. About 5 wt % sodium carbonate and sulfate must remain in the melt to assure complete combustion and removal of acidic gases from the off-gas.

To control the amount of noncombustible substances in the melt, a portion of the molten salt is periodically drained from the combustor. The product salt-ash mixture can be cast directly into a metal canister for retrievable storage (Option 1; Figure 4). Alternatively, it is possible to process the salt-ash mixture to separate ash for disposal, to recover the salt for recycle, and to recover fissile materials (Option 2; Figure 5). Either option results in the rapid, complete, and nonpolluting destruction of the combustible waste. No liquid wastes are produced. With typical TRU solid waste, a volume reduction factor of 47 is obtained if the salt is not processed for recycling (Option 1) and a volume reduction of 57 is obtained if the salt is recycled and the insoluble ash sent to waste disposal (Option 2).

III. Bench Scale Combustion Tests With Nonradioactive WasteA. Test Description

A diagram of the bench scale combustion apparatus<sup>(3)</sup> is given in Figure 6. The combustor consisted of a 6" dia alumina tube inside a thick-walled Type 321SS vessel in a clam-shell tube furnace. The waste was placed in the feed-hopper and then fed (by a screw feeder) into the combustion air stream which conveyed the waste down the central alumina tube into the molten salt bed. Combustion took place in the bed. The combustion products passed up through the melt and out of the combustor, past ports where off-gas and particulate samples were taken. The off-gas was monitored continuously for carbon dioxide, carbon monoxide, nitrogen oxide, and hydrocarbon content, and periodically (by gas chromatography) for oxygen, nitrogen, and trace components that might be present. Isokinetic particulate samples were also taken and analyzed. Downstream of the particulate filter, aqueous hydroxide scrubbers were used to verify that no acidic gaseous components escaped from the melt.

The simulated radioactive waste consisted of 50 wt % paper, 32 wt % polyethylene, 8 wt % polyvinyl chloride, and 10 wt % rubber (mixed surgeon gloves and black rubber) and was reduced to <3 mm size in a Wiley mill before feeding. This mixture had essentially the same heating value, ash content, ash composition, and chloride content as typical TRU waste. This material was fed with a 1/2" or 5/8" dia x 6" variable speed screw feeder.

Two different ash-melt mixtures were used in these combustion tests (16 wt % ash-16 wt % NaCl-10 wt % Na<sub>2</sub>SO<sub>4</sub>-58 wt % Na<sub>2</sub>CO<sub>3</sub> and 20 wt % ash-20 wt % NaCl-10 wt % Na<sub>2</sub>SO<sub>4</sub>-50 wt % Na<sub>2</sub>CO<sub>3</sub>). The two mixtures are the concentration extremes anticipated in actual rad-waste combustion.

B. Off-Gas Analysis

Typically in combustion tests nitrogen oxide emissions were ~20 ppm, and carbon monoxide and hydrocarbon emissions were less than the detection limits of the instruments, i.e., <0.05% and <10 ppm, respectively. As shown in Table I no HCl could be detected in the off-gas (i.e., <5 ppm).

Particulates in the off-gas were greater than 80 wt % sodium chloride and varied with temperature (Figure 7). It was found that the particulate loading depended on the sodium chloride vapor pressure at the combustion conditions (Figure 7) and was essentially independent of the carbon dioxide content of the off-gas. At about 800°C the particulate loading is ~0.2 mg/m<sup>3</sup> (0.1 gr/scf) which is the allowable particulate loading for new combustion sources.

C. Retention of Specific Elements in the Melt

In several combustion tests the waste was contaminated with known amounts of (non-radioactive) specific elements such as cesium, strontium, europium, ruthenium, and iodine, by adding an aqueous solution (nitrate, chloride, or sodium) containing these elements to the waste. The particulates, off-gas scrubbers, and melt were then

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analyzed for these elements to determine the melt retention of specific elements. In general, none of the cations ( $Ce^+$ ,  $Sr^{++}$ ,  $Eu^{+++}$ ,  $Ru^{+++}$ , were detected downstream of the melt, indicating that essentially all (>99.5%) of these cations were retained in the melt (see Table II)).

Iodine was detected downstream of the melt and the amount was related to the sodium iodide vapor pressure above the melt (as might be expected). Under combustion conditions about 99% of the iodine was retained in the melt.

### IV. Bench Scale Combustion of TRU Wastes

A bench-scale combustor (see Figure 2), was incorporated in a glove-box in Atomics International's Plutonium Facility to study combustion of transuranic (TRU) contaminated wastes.<sup>(4)</sup> A diagram of this combustor is shown in Figure 8. Except for safety features (water trap, heat exchangers, prefilters, and HEPA filters) this combustor was essentially the same as described previously, except it was smaller i.e., a 4" dia alumina combustor tube was used instead of a 6" tube.

Typical combustion conditions used in the plutonium ( $PuCl_4$ ,  $Pu(NO_3)_4$  and  $Pu(SO_4)_2$ ) contaminated combustion tests of the paper-plastic-rubber waste (described previously) and the off-gas composition are given in Table III. The disposition of plutonium in the system after the tests is given in Table IV. These results show that waste combustion is complete in the molten salt and that essentially all (>99.9%) of the plutonium is retained in the melt. A similar test with uranium indicated that uranium and plutonium behave identically during combustion, i.e., >99.9% of the uranium was also retained in the melt.

### V. Pilot Scale Combustion Tests

Large scale combustion tests of typical paper-plastic-rubber wastes were performed in Atomics International's Molten Salt Test Facility (MSTF) shown in Figure 3.<sup>(4)</sup> A schematic diagram of this combustor is shown in Figure 9. This system consists of a 4' dia steel vessel lined with alumina blocks (Monofrax A)<sup>(7,8)</sup>, an industrial sized hammermill, rotary valve feeder, venturi scrubber, and HEPA filters. Approximately 1000 kg of salt are contained in the MSTF during combustion. The multipurpose system can be operated at reduced pressure (for radioactive containment) or positive pressure (for coal gasification) and is designed to readily by-pass or modify various components in the system. In these tests, all components were used and the system was operated at reduced pressure.

Typical combustion parameters observed in these tests are given in Tables V and VI. Again, combustion was complete and particulate loading was  $\sim 0.2$  mg/m<sup>3</sup> during 800°C combustion temperature. No HCl could be detected in the off-gas even when pure polyvinyl chloride was burned. In some of these tests magazines were used to increase the ash content of the waste. The magazines had colored dyes containing nitrogen which accounted for the high nitric oxide content of the off-gas (up to 500 ppm) observed for part of the test.<sup>(9)</sup>

VI. Salt and Plutonium Recovery

In some applications, it may be desirable to recycle the salt and transuranics from the melt-ash mixture. A scheme for accomplishing this has been developed and tested on a bench scale; large scale salt recovery tests are underway in other molten salt applications.

Salt recovery is accomplished using technology developed to recover minerals from dry lake beds. Briefly the salt is recovered by dissolving the salt in water and selectively crystalizing sodium carbonate-sulfate mixtures for recycle and sodium chloride for disposal. Although crystal purity has not been optimized to date, typical results are given in Table VII. Typically, the sodium carbonate crystals contain about 8% sodium chloride and the chloride crystals contain about 6% sodium carbonate and sulfate. Since these contaminants in the various crystal fractions do not detract from the process, studies to improve the crystal purity have not been made. Weight and volume reductions found for the two process options (with and without salt recycle) are given in Table VIII. Without salt recycle (Option 1) a volume reduction of 47 was found; with salt recycle (Option 2) a volume reduction of 57 was obtained.

Although the specific plutonium recovery procedure has not been selected, initial tests indicate that essentially all of the plutonium can be recovered. Plutonium remains with the insoluble ash when the salt is dissolved; only about one percent of the plutonium is dissolved in concentrated salt solutions. (This dissolved plutonium crystalizes with the sodium carbonate and is recycled to the combustor; it is not lost from the system). The plutonium remaining with the ash fraction is leached with acid (HCl or HNO<sub>3</sub>). About 99% of the plutonium in the ash is dissolved in a single acid leach and about 99.6% is dissolved in two acid leaches. The plutonium is readily recovered from these solutions by existing ion-exchange or solvent extraction technology.

VII. Development Status

Development of molten salt combustion technology has progressed to the point where large systems are being designed. Conceptual design of a combustion unit for hazardous organic chemicals has been completed by AI and Title I design is underway; this design and required safeguards are very similar to a TRU waste combustion unit. Furthermore, AI is presently designing a 1000 kg/hr molten salt coal gasification unit, with many features similar to the TRU waste combustor. Design of a 50 kg/hr radwaste combustion system for INEL began July 1, 1976; this unit should be operational in early 1978.

VIII. References

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Table I Typical offgas analyses found in nonradioactive bench-scale combustion tests.

<u>Component</u>		<u>Typical Amount in Offgas</u>
Hydrocarbons	(HC)	<10 ppm*
Hydrogen Chloride	(HCl)	<5 ppm*
Nitrogen Oxides	(NO <sub>x</sub> )	15-30 ppm**
Carbon Monoxide	(CO)	<0.05%
Oxygen	(O <sub>2</sub> )	4-12
Carbon Dioxide	(CO <sub>2</sub> )	6-15%
Nitrogen	(N <sub>2</sub> )	balance

\*Detection limit

\*\*Varied with nitrogen content of feed material and was essentially all nitric oxide (NO)

Table II Retention of specific elements in the melt.

<u>Element</u>	<u>Compound</u>	<u>Disposition in Combustion System (wt %)*</u>		
		<u>Scrubber</u>	<u>Particulates</u>	<u>Melt</u>
Ce	CeNO <sub>3</sub>	(ND) 0.01	<0.5	>99.5
Sr	Sr(NO <sub>3</sub> ) <sub>2</sub>	(ND) 0.01	<0.2	>99.7
Ru	HRuCl <sub>4</sub>	(ND) 0.01	(ND) <0.05	>99.9
Eu	Eu(NO <sub>3</sub> ) <sub>3</sub>	(ND) 0.01	(ND) <0.1	>99.8
I	NaI	0.01	~1	~99

\* (ND) = Not detected; in most tests no Ce, Sr, Ru, or Eu was detected in the particulates; values reported are maximum amounts found in any of the tests downstream of the scrubber or the maximum amounts that could have been present based on the analytical detection limit

Table III Test parameters for plutonium waste combustion tests.

<u>Test No.</u>	<u>Pu Concentration in Waste Feed (wt %)</u>	<u>Feed Rate (g/hr)</u>	<u>Average Combustion Temperature (°C)</u>	<u>Off-Gas Analysis</u>			
				<u>CO<sub>2</sub> (%)</u>	<u>CO (%)</u>	<u>HC (ppm)</u>	<u>O<sub>2</sub> (%)</u>
1	9 x 10 <sup>-3</sup>	190	895	7	0.1	5	12.0
2	1.1 x 10 <sup>-1</sup>	180	892	6.3	0.1	5	12.0
3	9 x 10 <sup>-3</sup>	170	880	6.0	0.02	5	13.0

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Table IV Disposition of plutonium in bench-scale radwaste combustion tests.

Plutonium Found in Various Components (wt %)

Test No.	HEPA Filters	Pre-Filter	Condensate	Water Trap	Combustor Offgas Line	Melt*
1	<10 <sup>-4</sup>	0.07	<10 <sup>-4</sup>	--	--	(99.9)
2	<10 <sup>-4</sup>	0.01	<10 <sup>-4</sup>	--	--	(99.9)
3	<10 <sup>-4</sup>	0.02	<10 <sup>-4</sup>	0.01	0.009	(99.9)

\*By difference, melt analysis indicated that 99.0 ±1.3% of the plutonium was in the melt

Table V Particulate loading for combustion of simulated TRU waste in the MSTF pilot plant.

Sample No.	Feed Material	Feed Rate (kg/hr)	Average Melt Temp. (°C)	Particulate Loading (g/m <sup>3</sup> )		
				Before Venturi	After Venturi	After HEPA Filter*
1	PVC	16	975	0.31	0.014	(ND; <10 <sup>-6</sup> )
2	Radwaste** +40% PVC	50	1020	0.62	0.043	(ND; <10 <sup>-6</sup> )
3	Radwaste** +40% PVC	50	845	0.11	0.016	(ND; <10 <sup>-6</sup> )
4	Radwaste** +45% PVC	43	790	0.10	0.014	(ND; <10 <sup>-6</sup> )

\*(ND) = not detected

\*\*Radwaste consisted of 33 wt % high ash paper, 20 wt % Kimwipes, 32 wt % polyethylene, 8 wt % PVC, and 7 wt % rubber

Table VI Typical offgas analysis for simulated TRU waste combustion in the molten salt test facility.

Component	Amount in Offgas*
N <sub>2</sub>	76-78%
O <sub>2</sub>	5-12%
CO <sub>2</sub>	10-15%
HC	(ND) (< 5 ppm)
SO <sub>2</sub>	(ND) (< 2 ppm)
CO	(ND) (< 0.1%)
HC	(ND) (< 0.1%)
NO <sub>x</sub>	30-500 ppm**

\*(ND) = not detected

\*\*Depended on nitrogen content of feed material

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Table VII Comparison of salt compositions from flowsheet and experimental results.\*

<u>Process Product</u>	<u>Flowsheet Calculations (kg)</u>	<u>Experimental Results (kg)</u>
Ash Disposal	16 Ash	18 Ash + Na <sub>2</sub> O
Furnace Recycle	40 Na <sub>2</sub> CO <sub>3</sub> 8 Na <sub>2</sub> SO <sub>4</sub>	40 Na <sub>2</sub> CO <sub>3</sub> 8 Na <sub>2</sub> SO <sub>4</sub> 4.3 NaCl 1.6 Ash
NaCl Disposal	16 NaCl	16 NaCl 1 Na <sub>2</sub> CO <sub>3</sub> -Na <sub>2</sub> SO <sub>4</sub>
Recycle Solution	15 NaCl 14 Na <sub>2</sub> CO <sub>3</sub> 1 Na <sub>2</sub> SO <sub>4</sub>	15.2 NaCl 13.6 Na <sub>2</sub> CO <sub>3</sub> 0.7 Na <sub>2</sub> SO <sub>4</sub> 0.4 Ash

\*Assumes 200 Kg of typical waste with 8 wt % ash and 4.9 wt % chloride content.

Table VIII Weight and Volume Reductions for Various Processing Options.\*

	<u>Weight Reduction</u>		<u>Volume Reduction</u>	
	<u>Kg</u>	<u>Factor</u>	<u>m<sup>3</sup></u>	<u>Factor</u>
Original Waste	200		1.79	
Option 1 (No Processing)	80	2.5	0.036**	47
Option 2 (Theoretical Maximum w/Disposal of Chloride + Ash)	32	6.2	0.029**	62
Option 2 Experimental	35	5.7	0.031 <sup>†</sup>	57

\*The reduction factors are process estimates; they do not take into account the waste generated by normal operation of the facility and the air cleaning train. Some of these wastes would probably also be processed through the salt.

\*\*Assumes 200 Kg of waste containing 8 wt % ash and a bulk density of 112 Kg/m<sup>3</sup>.

<sup>†</sup>Fused cast salt product (Option 1) has a density of (2200 Kg/m<sup>3</sup>) while the product filtered and crystallized from aqueous solution (Option 2) has a density of 1120 Kg/m<sup>3</sup>.

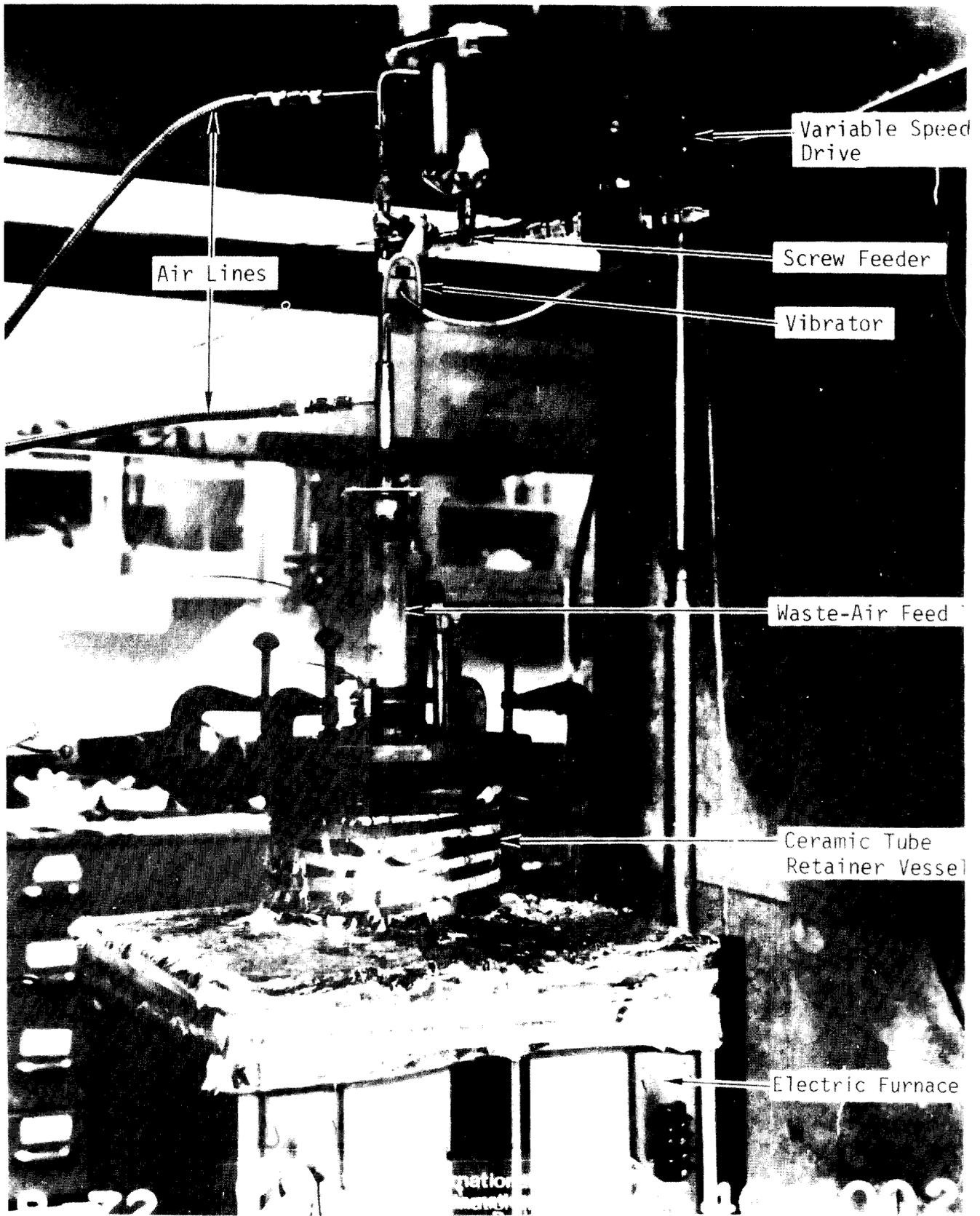


Figure 1. Continuous solid feeding components of bench-scale combustor.

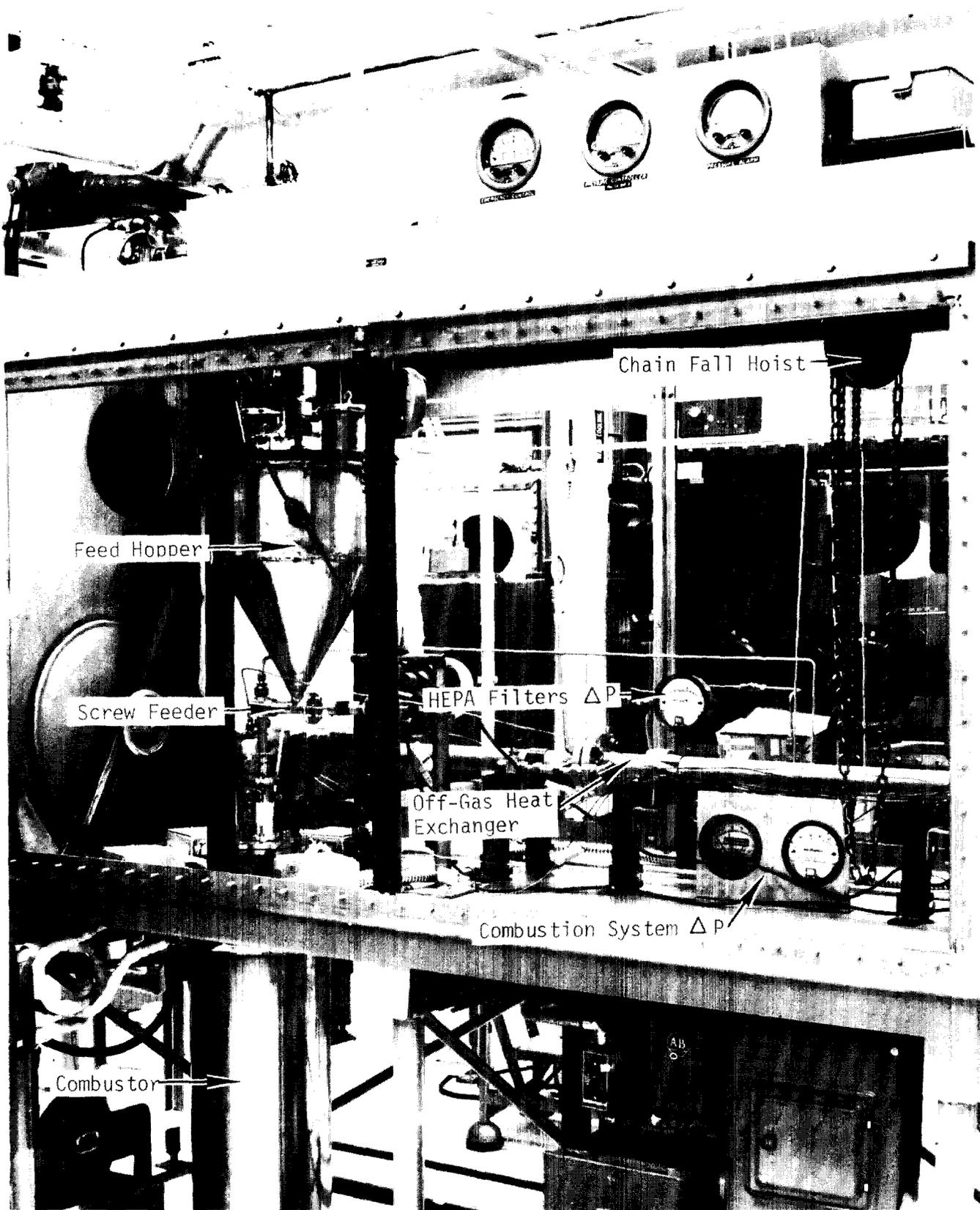


Figure 2. Bench scale radwaste combustion system.

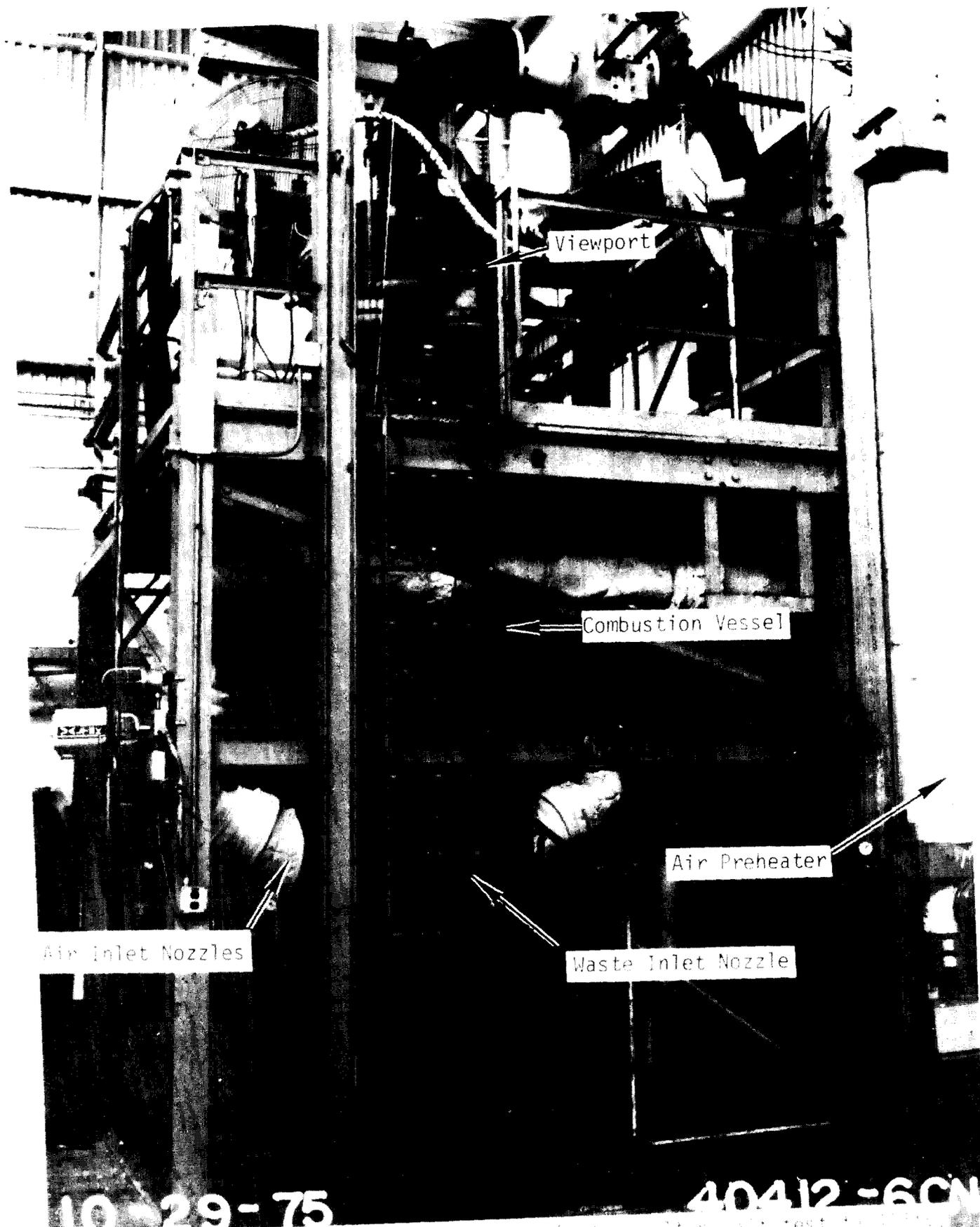
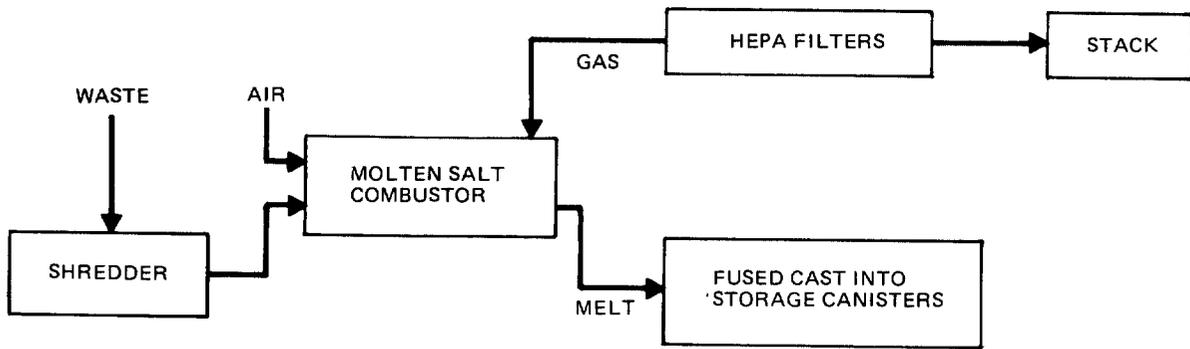
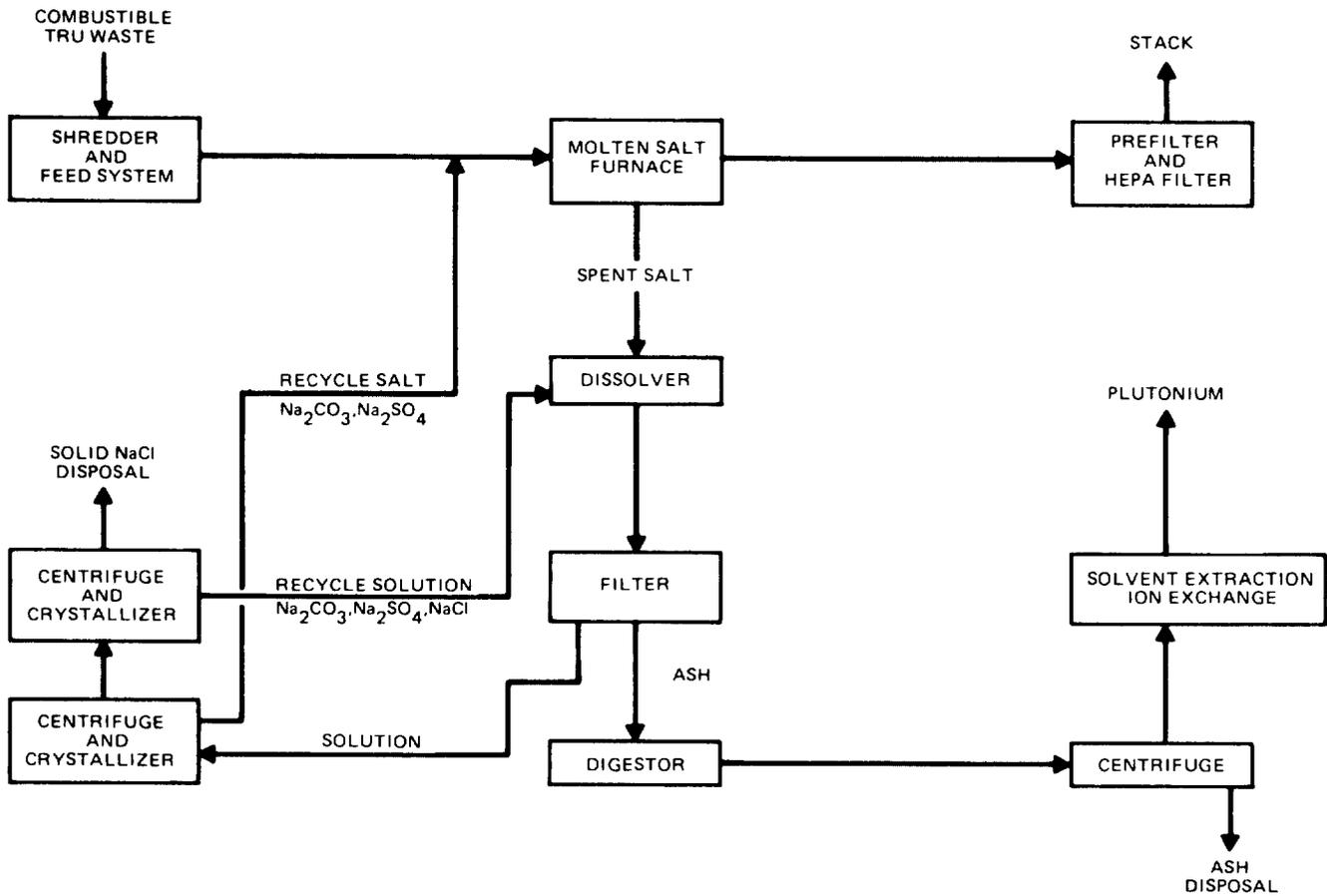


Figure 3. Pilot-scale combustor in the metal air test facility.



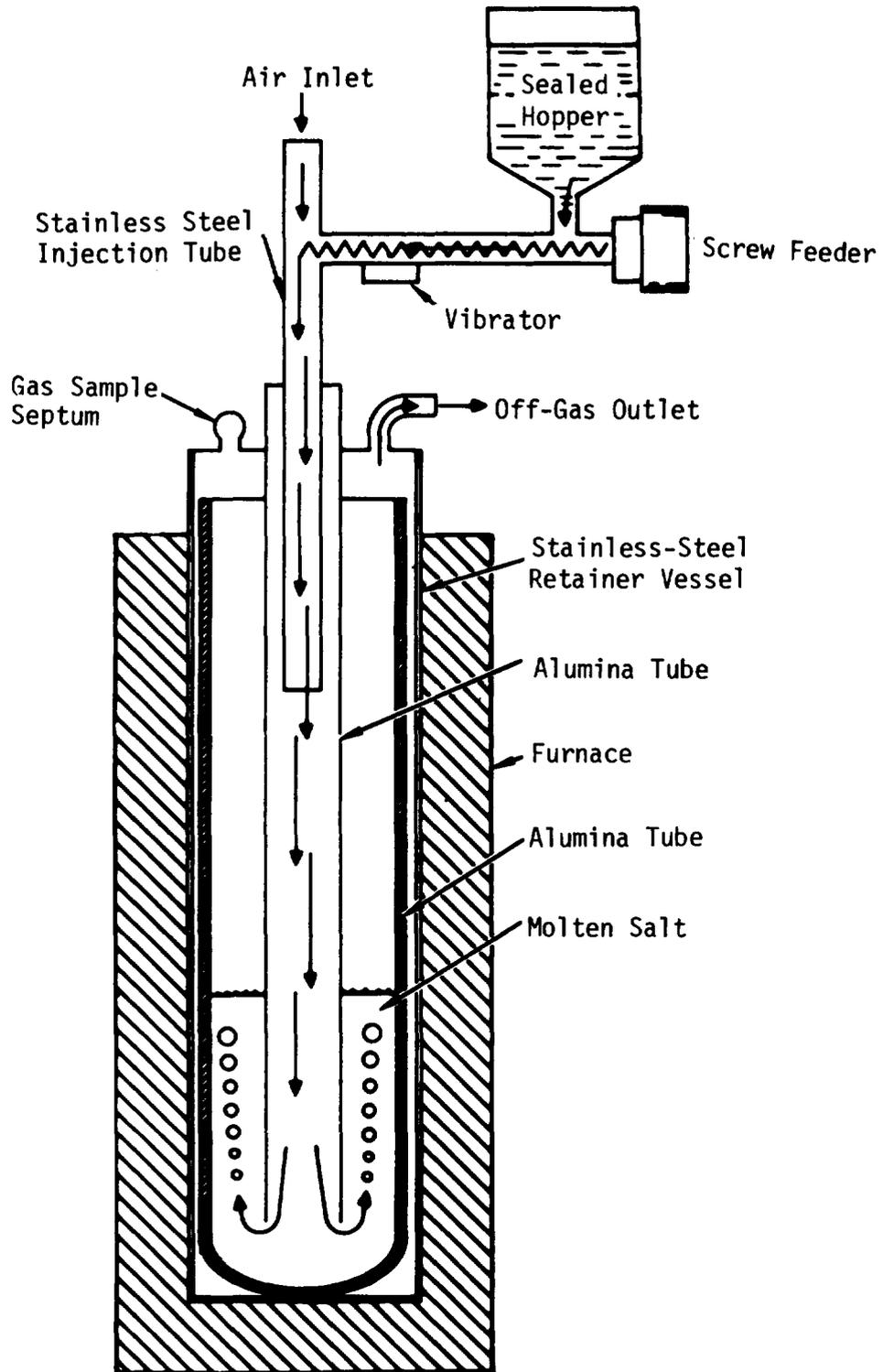
9063-4009

Figure 4. Flow diagram of molten salt combustion process without salt recovery (Option 1)



9063-4009

Figure 5. Alternate molten salt combustion process flow diagram with plutonium and salt recovery (Option 2)



42400-1016

Figure 6. Bench-scale molten salt combustion unit.

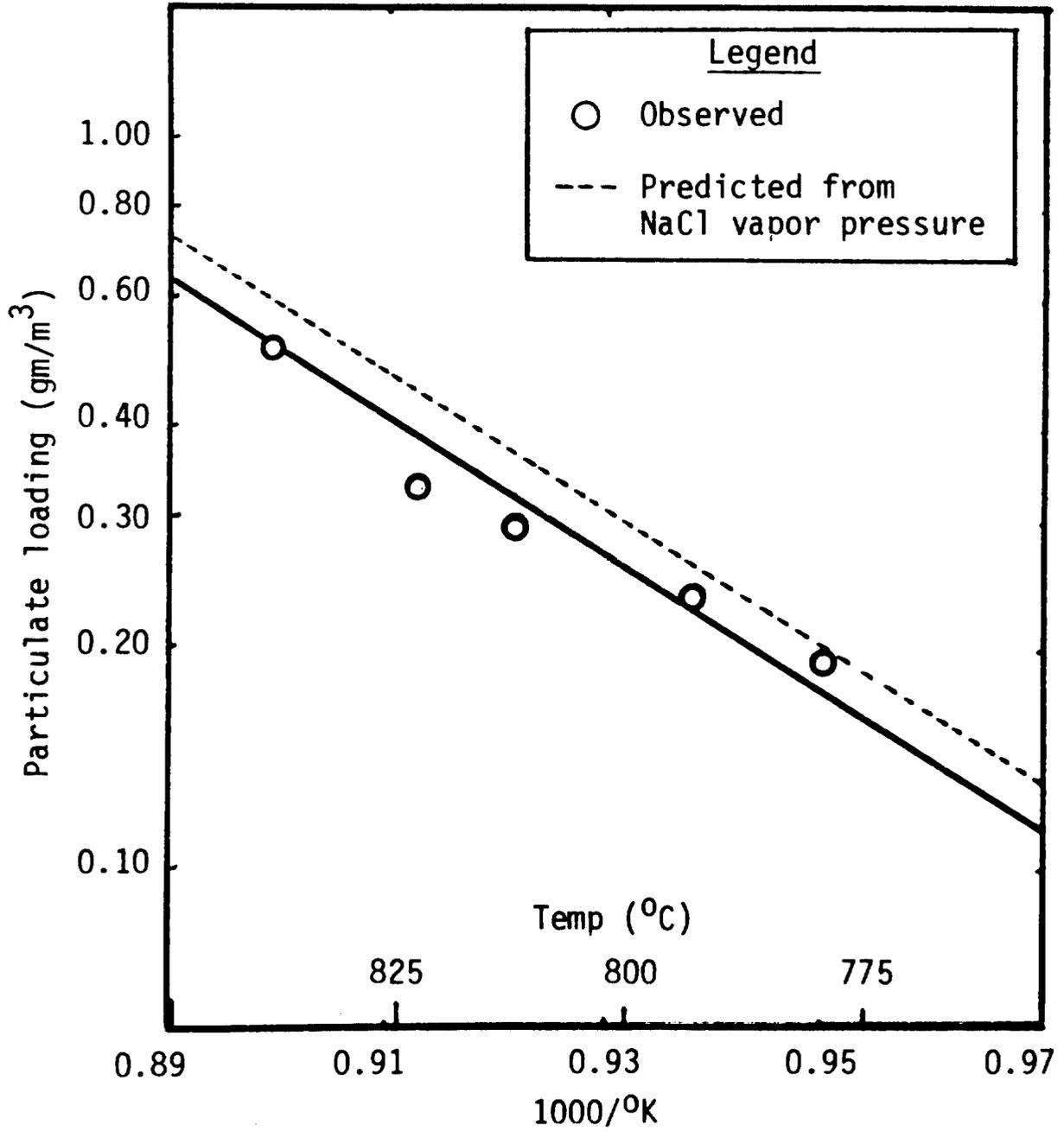


Figure 7. Relationship between observed particulate loading of the off-gas and sodium chloride vapor pressure.

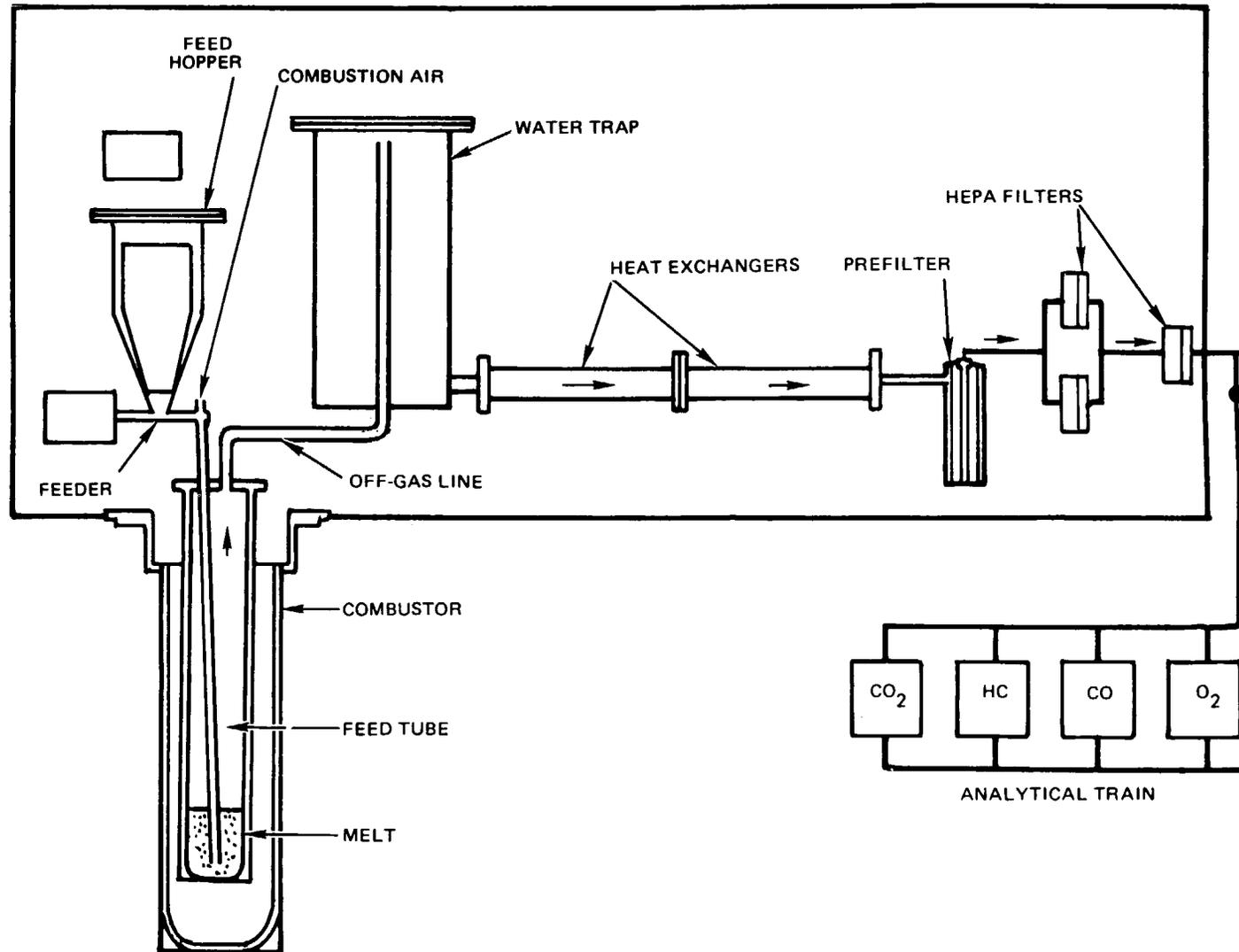


Figure 8. Bench-scale radwaste combustor flow diagram.

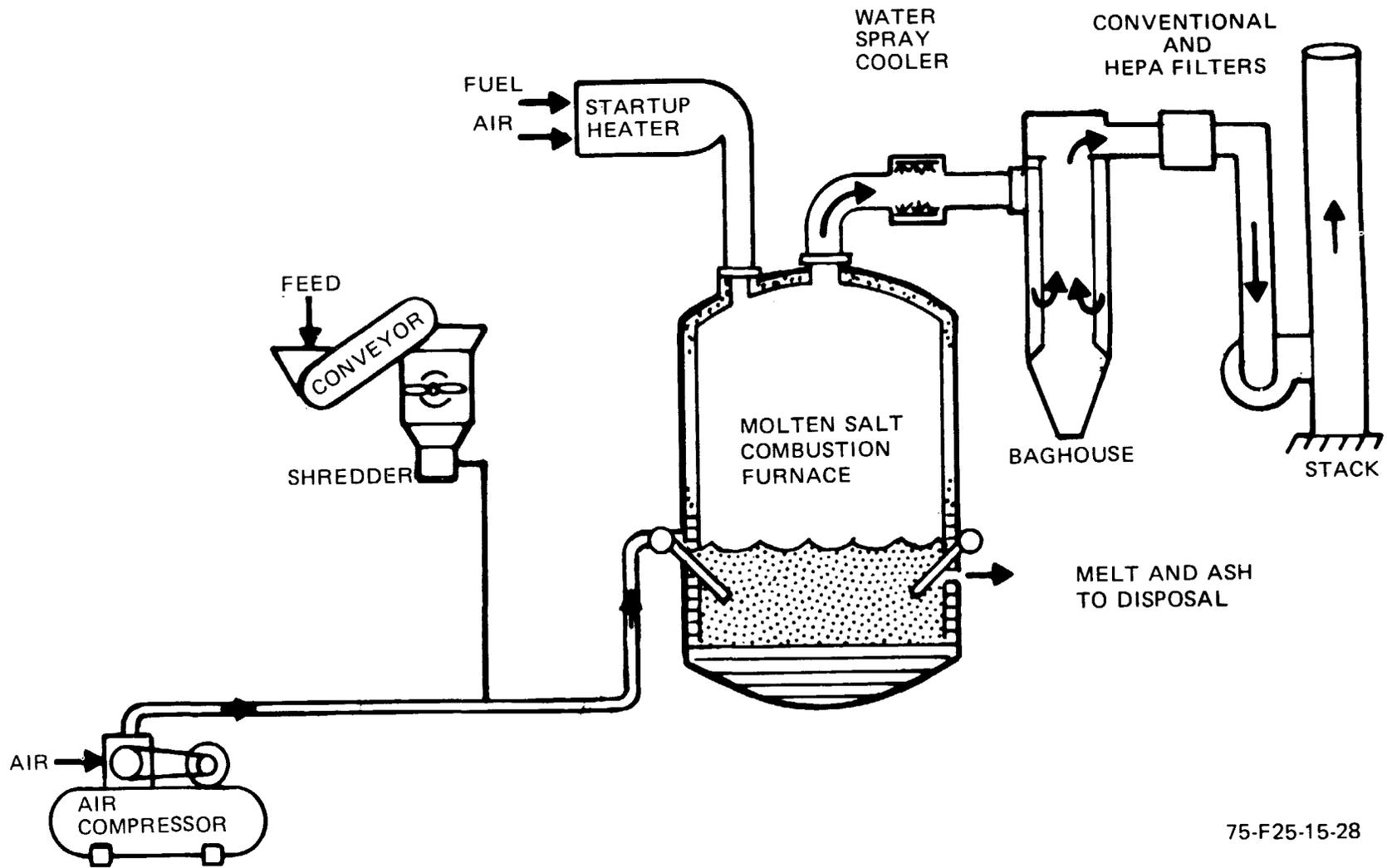


Figure 9. Schematic of a molten salt test facility.

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DISCUSSION

RAMSEY: I think this group might be interested in your comments on the feedbacks of the cycling of wastes through this system. Specifically, you have HEPA filters on the outlet. Would these HEPA filters be suitable as components to feed to the system?

GRANTHAM: Yes. The HEPA filters contain asbestos, silica and combustible materials. These can be shredded and fed directly to the molten salt. The silica will dissolve and some of the asbestos will also dissolve. The net result will be an increase in the ash content of the salt so that the HEPA filters themselves can be fed right back into the system.

B. P. BROWN: I was wondering if you can recover fissionable material such as plutonium?

GRANTHAM: Yes. We developed a technique to recover plutonium from the molten salt. This has been tested on a bench scale unit. We can recover about 99.5 per cent of the plutonium from the salt. The plutonium is quite soluble in dilute acid. It is not a refractory plutonium.

SCHURR: My question is in regard to your shredder or pre-treatment hammer mill. Are you going to be looking at potential maintenance of this item? This looks to me like a real critical weak point because most shredders or hammer mills will be high maintenance items with the need for changing blades or hammers.

GRANTHAM: We certainly agree with your concern. Our experience with the hammer mill has required little maintenance on materials we have fed during the past three years. Right now, we are using a hammer mill primarily because it was available, not because we think it is the best system. We are investigating knife shredders as well.

MCDOWELL: Have you noticed the formation of a slag on top of the molten salt from any of the material that you incinerate?

GRANTHAM: Perhaps we would if we let the molten salt settle, but the molten salt is being agitated by air that is injected with the combustible material. The ash is very evenly distributed in the molten salt when we drain the molten salt from the combustor. We have noticed no settling in the vessel during combustion.

CLAIRBORNE: You mentioned the retention of the transuranics but you only mentioned plutonium. How about americium and curium?

GRANTHAM: We haven't looked at americium and curium. We have looked at plutonium and uranium and both of these are retained in the molten salt.

BRODERSEN: I would like to know how long a time you expect your alumina to last in your big furnace. There will probably be some corrosion.

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GRANTHAM: The alumina is protected by the formation of a sodium aluminate film and the corrosion rate after this film is formed is in the neighborhood of a few mills per year. The alumina lining in our large scale molten salt vessel is six inches. This will last for years.

FREEMAN: What is your estimated capital cost for this 50 kg per hour unit?

GRANTHAM: We are designing a unit for INEL now and the cost, including engineering design and testing to support the design, equipment, installation, training, and start-up, is one million dollars. I don't have the exact breakdown.

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### CONTROLLED-AIR INCINERATION OF TRANSURANIC-CONTAMINATED SOLID WASTE

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#### Abstract

A controlled-air incinerator and an associated high-energy aqueous off-gas cleaning system are being installed at the Los Alamos Scientific Laboratory (LASL) Transuranic Waste Treatment Development Facility (TDF) for evaluation as a low-level transuranic-contaminated (TRU) solid waste volume reduction process. Program objectives are: 1) assembly and operation of a production scale (45 kg/hr operation of "off-the-shelf" components representative of current incineration and pollution control technology; 2) process development and modification to meet radioactive health and safety standards, and 3) evaluation of the process to define the advantages and limitations of conventional technology. The results of the program will be the design specifications and operating procedures necessary for successful incineration of TRU waste. Testing, with nonradioactive waste, will begin in October 1976. This discussion covers commercially available incinerator and off-gas cleaning components, the modifications required for radioactive service, process components performance expectations, and a description of the LASL experimental program.

#### I. Introduction

The Energy Research and Development Administration (ERDA) has directed LASL to establish a study program for the evaluation and development of production-level TRU solid waste treatment processes. This laboratory and other ERDA-contractor installation routinely handle large quantities of radioactive contaminated materials. The bulk of the waste generated by various operations at these sites is low-level activity and, as such, is currently either stored retrievably ( $>10\text{nCi/g}$ ) or buried ( $<10\text{nCi/g}$ ) at controlled disposal areas. However, estimates of future solid waste volumes strongly indicate the need for improved solid waste disposal techniques. Volume reduction, for example, combined with guaranteed control of long-lived isotopes, is a prime consideration for all facilities routinely handling large quantities of transuranic materials. Occupancy of the LASL TDF began in May 1976. This facility will be used to evaluate alternate production-scale (45-90 kgs/hr) processes for reducing the volume of combustible waste contaminated with transuranic isotopes. Candidate processes will be designed to accept waste generated by typical ERDA-site operations.

\*Work performed under the auspices of the USERDA, Contract W-7405-ENG. 36 and funded specifically through the Division of Nuclear Fuel Cycle and Production.

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Controlled-air incineration was the first process to be evaluated in the TDF. Although incineration is a well established method of volume reduction in industry, previous attempts to treat radioactive solid waste by this technique have met with only limited success. Problems encountered included equipment sealing, corrosion, and off-gas cleanup. As these are technical problems rather than basic process faults, a development program based on conventional incineration is warranted.

The specific incinerator design selected for the TDF was constrained by the need to implement a contaminated waste treatment study program without undue delay. Recognizing that several promising alternate processes exist or are under development, each system was evaluated in terms of the time required to allow proper engineering of a production-scale (45 kg/hr) plant. Of those systems meeting this criterion, the controlled-air concept was selected on the basis of operational flexibility, ease of combustion rate control, minimum particulate emission due to low turbulence in the primary combustion chamber, combustion efficiency, and availability of commercial equipment.

Proven technology guidelines were likewise followed in the selection of the off-gas cleanup system. The presence of transuranic-contaminated particulates, as well as inorganic acids, primarily HCl, in the incinerator off-gas requires a high-efficiency cleanup system. Thus a high-energy aqueous scrub system, with a variable-orifice venturi and packed-column scrubber as the primary components, was specified.

This paper discusses the incinerator and off-gas cleaning system only. The LASL Waste Management Research and Development Program and TDF, and design features of the feed preparation system are detailed in the references noted.

### II. Process Objectives

Processes selected for TDF installation will be oriented toward handling low-level wastes resulting from transuranic operations typical of ERDA-contractor sites. These wastes vary widely between individual facilities but may be categorized on the basis of origin, i.e. laboratory, line or process, and construction. Table I indicates the range of waste compositions expected in these categories, based on a 1973 LASL survey.

Table I. Typical waste composition.

<u>Material</u>	<u>Laboratory</u>	<u>Process</u>	<u>Construction</u>
Paper & Rags	10-60 wt. %	10-40 wt. %	5-20 wt. %
Plastics	5-60	30-40	5-30
Rubber	5-30	10-45	5-20
Lumber	-----	-----	5-30
Dirt & Concrete	-----	-----	5-60
Metallics & Glass	5-50	30-40	10-50

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Laboratory wastes are defined to include wastes from support areas in the immediate vicinity of, as well as, specific-laboratory refuse. Process wastes typically result from glovebox production operations; construction wastes originate with the disassembly of de-commissioned facilities. The bulk of routine, low alpha-activity waste is expected to originate in the laboratory areas.

Depending on the waste reduction process selected, a design feed can be defined by inclusion of those constituents treatable by that process. Waste materials not effectively reduced by, or incompatible with, the candidate process would be sorted out for disposal by other means. For conventional incineration, the "Design Basis" feed was defined as shown in Table II. Heat and material balances required for equipment sizing were based on this waste composition. The controlled-air incinerator can handle 100% of any of the given waste components at a 45 kg/hr feed rate. The off-gas cleaning system is designed to scrub the mineral acids and particulates generated while burning up to 100% of any component including PVC.

Table II. Design basis incineration feed.

<u>Component</u>	<u>Weight %</u>
Paper & Rags	35
Plastics	
Polyethylene	23
PVC	12
Rubber	<u>30</u>
	100

Following preliminary runs with nonradioactive waste, the first TRU wastes processed in the TDF experimental program will have activity concentrations around 10 nCi/g. Higher concentrations will be used as the program progresses. A production facility would be expected to process wastes containing concentrations equal to, or less than, the levels recoverable by current technology (normally 0.5 g/kg).

One criterion for candidate processes is a large volume reduction ratio (ratio of contaminated waste input volume to total contaminated waste output volume). Witness that the cost benefits of a treatment process (packaging, handling, transportation, and storage charges) would be reduced by a high volume reduction ratio, as would be the amount of land required for storage/disposal of waste. Another prime criterion is that related technologies have qualified the system for production-level operations. A survey of six ERDA sites determined that processing rates in the 45 to 90\* kgs/hr range were needed to meet current needs. Projected future needs increased the

\*The basis for hourly capacity is a 10 month, 5 day/wk, 24 hr/day operation of a production incinerator (217 days/yr). Two months was assumed as adequate maintenance and modification time.

probable upper limit to 230 kg/hr. The nominal throughput rate of the initial TDF process was set at 45 kg/hr following review of scale-up factors, commercially available equipment sizes, and program testing and development goals.

### III. Process Description

Wastes to be processed at the facility are sealed in plastic bags contained in sealed 0.3 X 0.3 X 0.6-m (1 X 1 X 2 ft) cardboard boxes and are transported to the site in 0.14-m<sup>3</sup> (30-gal) DOT drums. The drums are loaded individually into the introductory box of the feed preparation line. Packages are assayed for transuranic isotope content (4) and x-rayed (5) for incompatible materials; if necessary, packages are opened to remove non-combustible material. From the sorting glove box, (6) packages are transported to the storage glove box, which provides adequate material storage for approximately eight hours of operation. The storage box is connected to the ram feeder, which charges waste, batch-wise, to the dual-chamber incinerator.

#### Incinerator

The incinerator is a conventional dual-chamber design, manufactured by Environmental Control Products, Inc. (ECP) (see Figure 1). Similar models are currently in use for disposal of municipal, industrial, and pathological solid wastes. Underfire air is used in the lower (ignition) chamber to incinerate the solid wastes under sub-stoichiometric conditions. This "controlled-air" operation reduces the magnitude of temperature fluctuations and the emissions rates from those normally associated with "free-air" incineration. Unburned volatile components, as well as entrained particulates, exit the lower chamber via an interconnecting port. Excess air and supplemental heat are supplied in this turbulent region to promote complete combustion. The secondary chamber provides additional residence time for completion of combustion reactions. Normal operating temperatures, 650°C to 870°C in the lower chamber and 870°C to 1100°C in the upper chamber, are maintained by two low-intensity, natural-gas fired burner. Air introduction rates and nominal chamber temperatures are varied dependent on waste composition.

The incinerator chamber shells and other primary structural components are carbon steel. The two combustion chambers and the exhaust duct immediately downstream of the upper chamber are lined with 13-cm of high-density plastic refractory, 5-cm of mineral wool block, and 0.6-cm of mastic stack coating. The 2000°C-tolerance plastic refractory is more easily repaired and more resistant to thermal shock than castable-type refractories. The mastic provides diffusion barrier protection for the carbon steel shells, preventing corrosive attack by combustion product acid vapors such as HCl and SO<sub>3</sub>. This quantity of refractory is greater than normally specified for industrial incinerators, but is required to reduce the heat load on the secondary-containment ventilation system.

The incinerator represents conventional industrial technology. The following design modifications were incorporated in the purchase

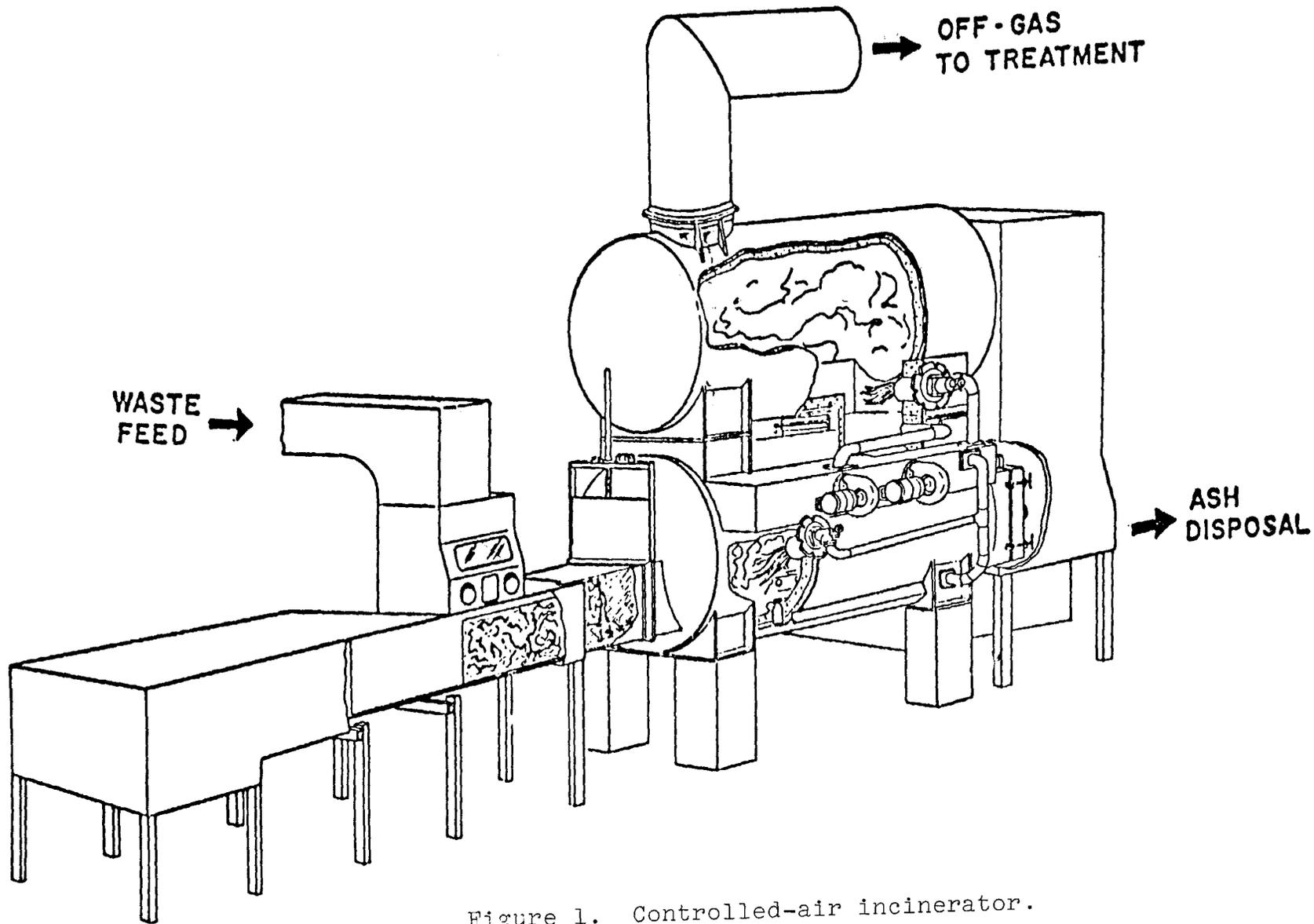


Figure 1. Controlled-air incinerator.

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specification to meet the needs of the development program and radioactive service requirements.

1. Oversize doors were provided in each chamber to ensure ample access for remote removal of ash and partially burned charges.
2. Sight ports with protective blast gates were installed in each chamber to permit observation during operation.
3. Gas sampling ports were provided between the two chambers and at the exit from the upper chamber.
4. Dimensions of the ash dropout door were increased to the floor width to provide improved ash removal efficiency when the ram feeder is in use.

Auxiliary equipment purchased with the incinerator includes a ram feeder assembly, complete with safety interlocks and flashback suppression system, an ash drop-out port, and a modular vacuum ash-removal system.

The incinerator system has been modified to ensure containment of radioactive materials and to permit maintenance of mechanical process equipment. Modifications include: a combustion gas supply glovebox, an ash removal glovebox, full enclosure of the ram feeding system, and secondary seals for all flanges.

Particulate loadings of 1.25 and 1.46 g/std m<sup>3</sup> at 12% CO<sub>2</sub> were demonstrated in EPA certification tests in a similar unit burning 225 kgs/hr of Public Health Service standard waste. (8) This loading is well below the Federal standard of 4.5 g/std m<sup>3</sup> at 12% CO<sub>2</sub>. Public Health Service standard waste is essentially a mixture of cellulose with very little plastics or rubber. Particulate loadings for the LASL incinerator off-gas are expected to be less than 2.3 g/std m<sup>3</sup> at 12% CO<sub>2</sub> while burning LASL design basis waste. This low particulate loading will ease some of the operational requirements of the wet off-gas cleaning system.

### Off-gas Cleaning Components

Effluents from the incinerator pass through the high efficiency off-gas cleanup train shown in Figure 2. High-temperature combustion gases are cooled to saturation conditions by multiple water sprays in the quench chamber. Particulate removal is primarily effected by the venturi scrubber. Mineral acids are removed in the packed column by counter-current contact with water. A condenser removes the bulk of water vapor from the scrubbed gas stream to reduce volumetric off-gas rates prior to filtration. Reheat of the gases downstream of the condenser prevents condensation of the HEPA filter media and the induced-draft fans. The quench chamber, venturi scrubber, and packed column scrubber were designed and fabricated by the John Zink Company, of fiberglass-reinforced plastic (FRP).

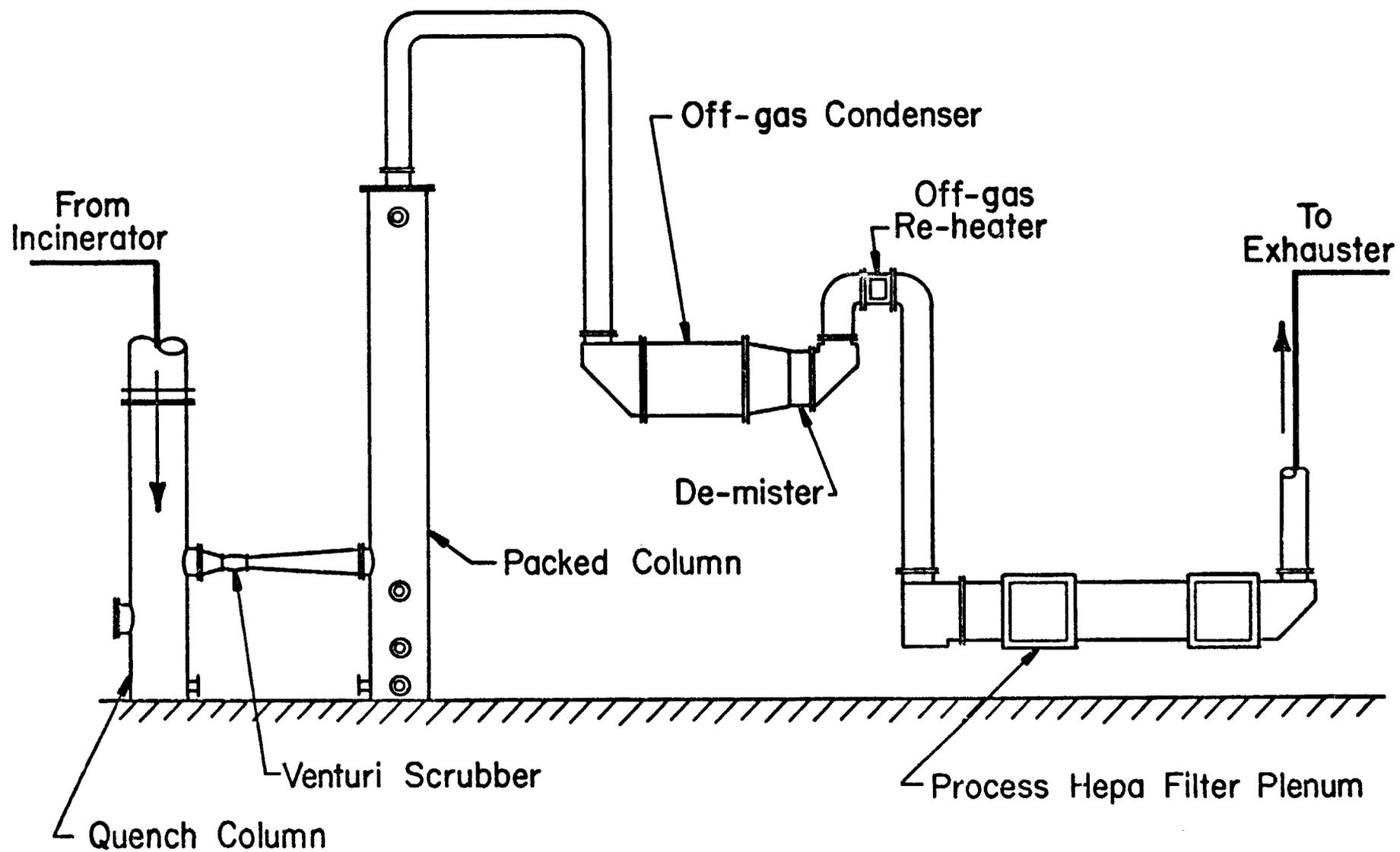


Figure 2. Off-gas cleaning system.

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The quench column, shown in Figure 3, is designed to cool combustion gases from 1100°C to 75°C by direct evaporation of recycled scrubbing solution. The column is divided into a contacting section and a separator. Approximately eight times the amount of scrub solution required for evaporative cooling is injected into the contacting section. Excess solution collects in the separator.

The contacting section consists of a 50-cm i.d. by 150-cm FRP pipe, refractory lined with a weir, three spray lances, and an exit nozzle. The weir is designed to keep the refractory wall fully wetted. Three spray lances, located below the weir, are used to atomize scrub solution for better gas-liquid contact. The weir, spray lances, and nozzles were fabricated from Hastelloy C-276 for corrosion resistance. The 20-cm i.d. FRP exit nozzle serves to 1) re-entrain the quench solution that runs down the refractory wall; 2) promote gas-liquid contact by creating a high velocity, high turbulence area; and 3) aid in separation by imparting a high downward kinetic energy to the liquid droplets.

The separator is a disengaging section to de-entrain the quench liquid. The high inlet velocity caused by the contactor exit nozzle aids in separation. Since the venturi inlet is located at approximately the same level as the contactor exit nozzle, the gas flow must reverse direction. De-entrainment is caused by the combination of the gas-phase flow reversal and the high kinetic energy of the liquid drops. The variable-throat venturi scrubber is located between the quench column and packed column. It is designed to remove up to 99% by weight of the assumed particulate distribution shown in Table III.

Table III. Particulate size distribution.

<u>Particle Diameter, <math>\mu\text{m}</math></u>	<u>WT. %</u>
Greater than 10	10
5-10	20
2-5	40
1-2	20
0.5-1	10
Specific Gravity	1.5
Particulate Loading	1.7 g/std m <sup>3</sup>

The venturi has a 33-cm long converging cone and a 125-cm long diverging cone both constructed with FRP. The throat is a 10-cm diameter, Teflon-lined, clamp valve, which allows the pressure drop to be varied between 28 and 150-mm Hg. Scrub solution is injected through a nozzle located upstream of the throat.

The packed column scrubber, shown in Figure 4, is designed to reduce the gas-phase HCl from 24,400 ppm to a maximum of 25-ppm (99.9% removal) by counter-current contact with condensate and/or fresh water. Polypropylene supports hold a 300-cm deep polypropylene Pall ring packing. Condensate and fresh water is introduced at the top through a polypropylene distributor.

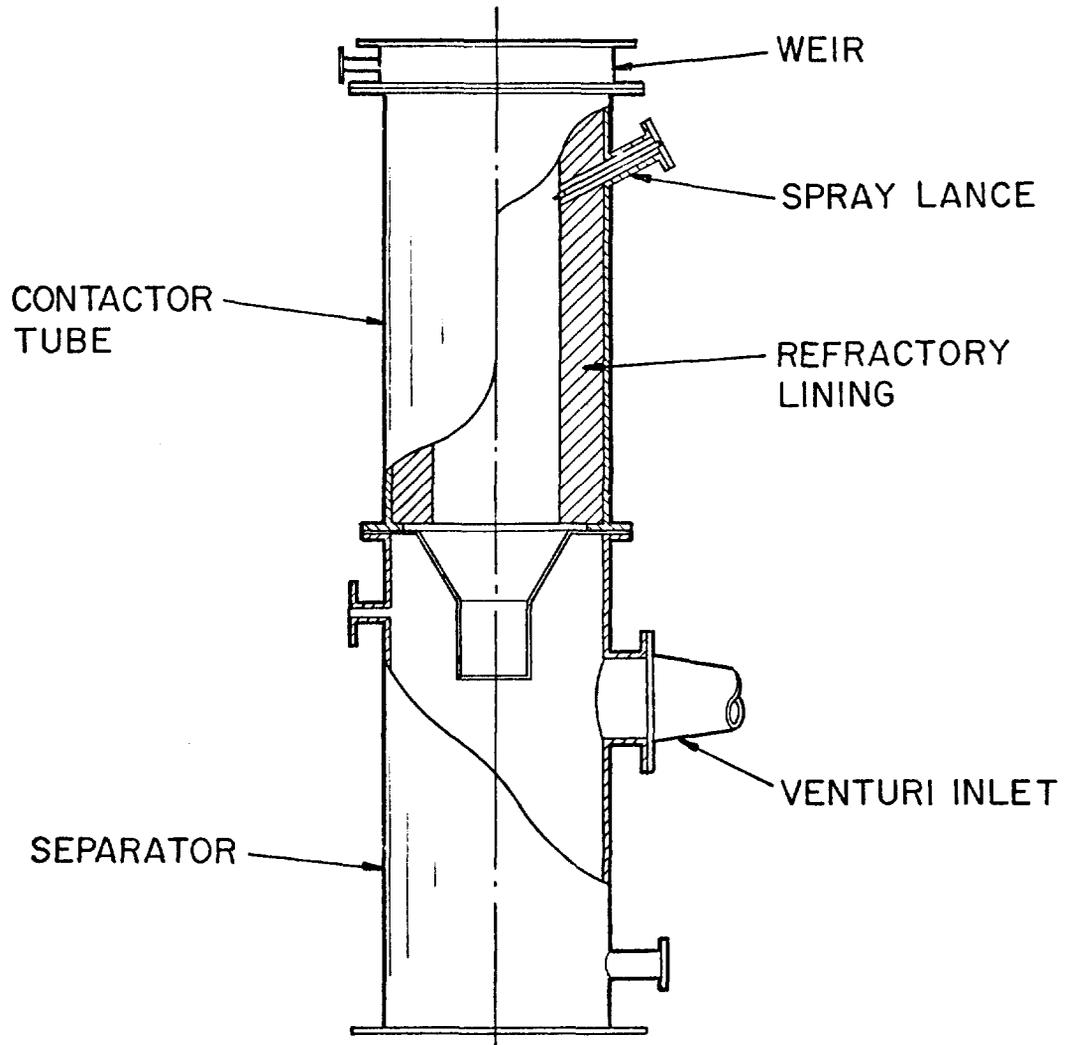


Figure 3. Quench column.

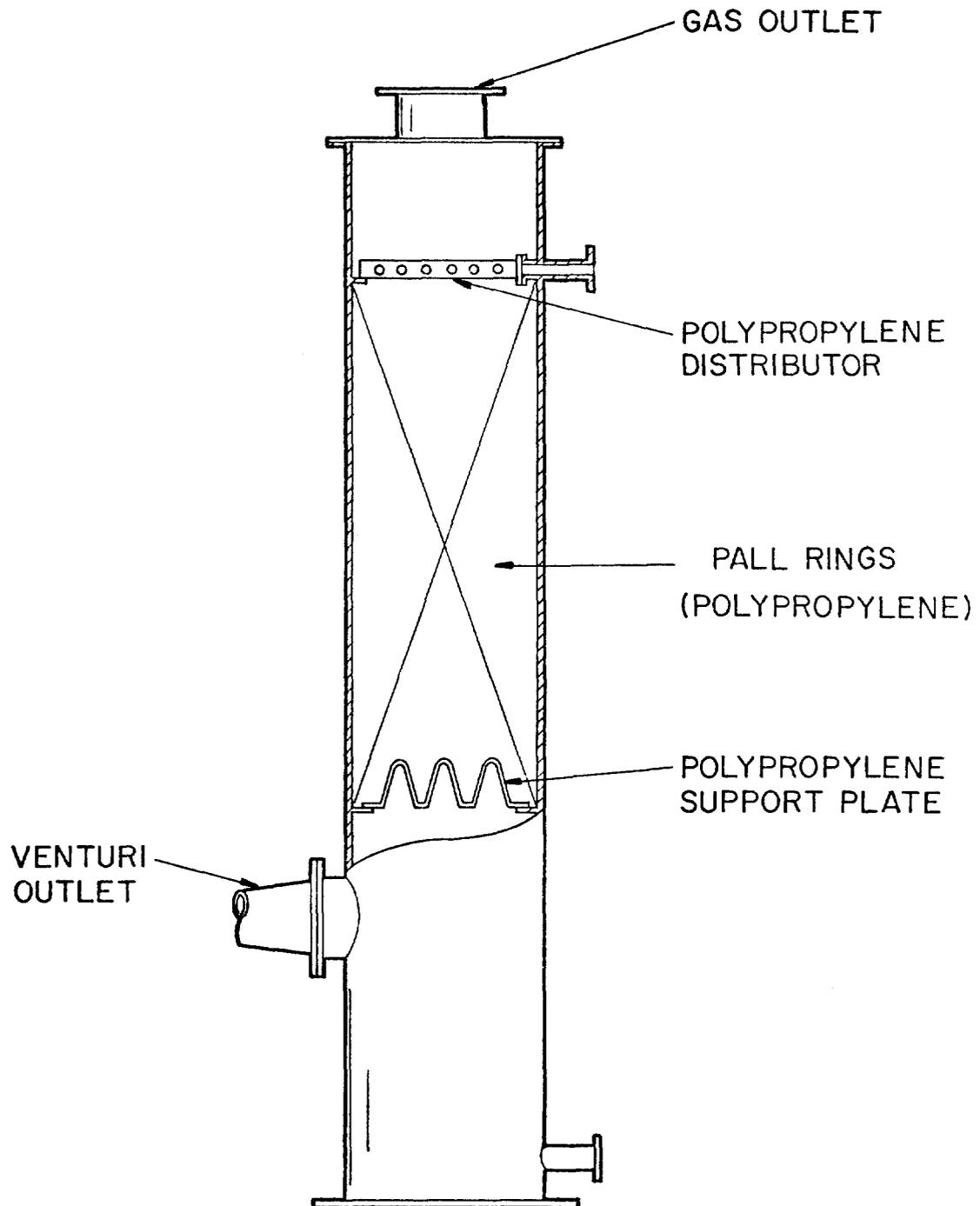


Figure 4. Packed column scrubber.

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The condenser, mist eliminator, re-heater, and HEPA filter frames were purchased from commercial suppliers. However, as these components were not designed to withstand the 160-mm Hg (3psi) vacuum of this process, special enclosures were designed by the LASL to meet the pressure requirements. These enclosures were designed to provide access for maintenance or replacement of contaminated components as dictated by process test results.

The condenser lowers the off-gas temperature from 66°C to 49°C. As the stream is saturated before reaching the condenser, it is necessary to remove approximately 12 l/min of condensate. The condenser core contains two coils consisting of several rows of finned tubes, which are coated with a baked phenolic to prevent chloride corrosion. The total capacity of the two coils is 278 kW. The mist eliminator is located downstream from the condenser. The epoxy-fiberglass frame supports ABS plastic elements.

The re-heater superheats the off-gas approximately 12°C above the saturation temperature to assure that neither condensation nor attendant corrosion will occur downstream in the HEPA filters or off-gas blowers. It is a 12 element unit with a 12 kW capacity. The heater housing is located above the centerlines of the condenser/mist eliminator module and the HEPA filter module to prevent radiant heating of the adjacent modules.

Redundant HEPA filtration is provided for final removal of particulates. The filter module houses two frames in series. The first frame uses a 122 X 61 X 15-cm prefilter and two 61 X 61 X 29-cm HEPA filters. The second frame is similar, but does not have prefilter provisions. Both frames are rated for 56.6 m<sup>3</sup>/min at 1.9 mm-Hg, and are supplied with bag-out doors. The support module is fitted with hatches to access the bag-out doors and with in-place dioctylphthalate (DOP) filter testing ports. Since there is little possibility of condensate reaching the HEPA filter module, it is fabricated of carbon steel.

The induced-draft blower produces 423 mm-Hg static pressure 53.8 m<sup>3</sup>/min with a discharge pressure of 580 mm-Hg (elevation at LASL is approximately 3540 m). If blower performance proves adequate, an identical backup blower will be installed. Redundant blowers are required before contaminated waste can be introduced into the process.

### Scrubbing Solution Recycle System

A scrubbing solution recycle system is used to minimize liquid blowdown from the aqueous gas-scrubbing system. The system uses full-flow liquid filters, a graphite heat exchanger, two evaporative cooling towers, a scrubbing solution receiver tank, a condensate receiver tank, and a caustic makeup tank. The solution drains from the bottom of the quench column to the packed column. Solution from the packed column sump is pumped through a full-flow filter and heat exchanger to the scrubbing solution receiver tank, where it is stirred to suspend small particulate that is not removed by the full-flow filter. The scrubbing solution is then pumped from the tank to the venturi and quench column. Solution returning to the weir is

filtered a second time to remove a smaller size fraction of particulates.

The blowdown rate from the 2600 l fiberglass scrubbing solution receiver tank is controlled by level and specific gravity. If the specific gravity of the scrubbing solution exceeds a specified value (currently set at 1.05), or if the tank level exceeds 80%, the blowdown rate is increased. Neutralized blowdown is sent to the LASL liquid waste treatment plant for cleanup.

Condensate from the condenser/mist eliminator module drains into a 750-l stainless-steel condensate receiver tank. The level in this tank is maintained at 80% by the addition of fresh water. This solution, being low in acid content, is pumped to the top of the packed column scrubber at a determined rate.

To control the scrubbing solution acidity, 20% caustic solution is added just upstream of the packed column sump pump. The addition rate is controlled by a pH sensor on the outlet of the scrubbing solution receiver tank. The caustic solution is held in a 850-l stainless-steel tank.

Full-flow filters were obtained for removal of suspended particulates. The fluorocarbon-coated housings use polypropylene cartridge-type filters and are enclosed in a glovebox to control contamination during filter changes. The cartridges are bagged-out and incinerated. Cold testing will determine the cartridge porosity requirements for each stream.

The scrubbing solution heat exchanger, a shell and tube model with graphite tubes, is designed to cool solution from 82°C to 49°C. The process (tube) side is operated at least 260 mm-Hg below the coolant side to guarantee in-leakage. Coolant is circulated through two ABS plastic evaporative towers.

#### IV. Future Plans

Start-up of the controlled-air incineration process will occur in two distinct stages: nonradioactive operations and radioactive operations. Testing of the primary system components with nonradioactive waste is scheduled to begin in October 1976. Objectives of these initial experiments will be to identify specific process design and component deficiencies. The addition, substitution, or modification of components will be greatly facilitated by the complete absence of contamination during these initial tests. Following attainment of satisfactory nonradioactive process performance, final provisions for transuranic containment and process ventilation will be completed in preparation for the introduction of radioactive wastes.

Testing of the process train with transuranic-contaminated wastes is presently scheduled for mid-1977. Challenge-level, i.e.,  $\sim 10$ -nCi/g wastes, will be used initially to assess the integrity of the containment systems and adequacy of the process enclosure ventilation system. Contamination levels in the charged wastes will gradually be increased to determine isotope distribution within the system. Major emphasis in the evaluation of controlled-air incin-

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eration will be in determining the effectiveness and reliability of each system component. Because this system relies heavily on existing, proven technology, development efforts will be limited to identified deficiencies related to the adaptation to radioactive service. Materials and design reliability, as well as containment adequacy, will receive primary attention. One exception to this approach is the scrub solution blowdown evaporator. No clear cut system has yet been identified for evaporation-to-dryness of this liquid effluent. Development efforts in this area will be toward reducing all process effluents to solid form.

Program output for this initial waste treatment process will contain design specifications and recommended operating procedures for the system essentially as described. Basic design modifications, e.g. a non-aqueous off-gas system, or a radically different incinerator configuration will be reserved for future development efforts beyond completion of this initial study.

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DISCUSSION

GRADY: The first question concerns the pressure through the unit involving the high energy Venturi and columns. Is your  $\Delta P$  around 50 or 60 inches of water?

NEULS: The maximum is a little higher than that. It is designed for approximately 3 psi. The variable-throat Venturi varies between 15 and 80 inches of water  $\Delta P$ .

GRADY: The second question refers to the treatment of waste prior to entering the incinerator. Do you have to shred it or sort it? What handling procedures are required?

NEULS: By the nature of the RAM feeder, it is not required to shred the waste. However, we do go through a feed preparation glovebox line that includes an assay and an x-ray system. The x-ray system spots things like bottles and metal parts. Most of the waste boxes are incinerated without being opened. The glovebox is described in other references that are given in the paper.

C. R. ALLEN: Can you tell me what mass of material is introduced with each cycle of the ram feeding device?

NEULS: The mass per cycle is a variable. It will be determined as part of the development of operating procedures. Obviously, a feed rate of 45 kg/hr is the only parameter we are trying to meet. The feed cycle time could vary over a substantial range.

ORTH: You mentioned that you were going to try to contain it sometime later. Containment isn't an easy thing. Have you designed this thing from the beginning to worry about containment or have you already completed design on how you will contain it?

NEULS: There are two answers. First, this is a process that was assembled from commercially available equipment. Therefore, the design was not made for the specific process to be contained. However, we have nearly completed the design for all the gloveboxes and containment equipment that is required. To simplify checking out the components during nonradioactive testing, we are not going to complete containment until after we are satisfied with the performance.

FREEMAN: How do you plan to repair or replace the contaminated refractory?

NEULS: First, we don't expect to repair or replace it. Refractories have come a long way in the last ten years. We expect that, by using proper operating procedures for the refractory, there will be little problem. It is industry standard to use refractory. The refractory lifetime should be approximately 5 years, or longer than the development program. This particular unit, I might add, will be dismantled and buried. It will not be used for production.

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AN INCINERATOR FOR POWER REACTOR  
LOW-LEVEL RADIOACTIVE WASTE

T.S. Drolet and J.A. Sovka  
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1.0 Introduction

Ontario is presently operating 2200 MWe of CANDU\* reactors (Table 1). A further 11000 MWe of CANDU is under design or construction.

Table 1

Ontario Hydro Nuclear Generating Sites

Name	Size	Number of Units	In Service Date	Location
<b>Operating</b>				
1. Nuclear Power Demonstration (NPD)	20 MWe	1 x 20	1962	Ottawa River
2. Douglas Point (DPGS)	200 MWe	1 x 200	1968	Bruce Site
3. Pickering 'A' (PGS 'A')	2000 MWe	4 x 500	1970	Pickering 18 Miles east of Toronto
<b>Under Construction</b>				
4. Bruce 'A' (BGS 'A')	3000 MWe	4 x 750	1976 (1st Unit)	Bruce Site
5. Pickering 'B' (PGS 'B')	2000 MWe	4 x 500	1980 (1st Unit)	Pickering
<b>Under Design</b>				
6. Bruce 'B' (BGS 'B')	3000 MWe	4 x 750	1983	Bruce Site
7. Darlington 'A'	3400 MWe	4 x 850	1984	60 Miles east of Toronto

By 1980, the nuclear portion of the Ontario Hydro system will be producing 2000 m<sup>3</sup>/yr of low-level combustible waste. To date, low and medium level radioactive waste produced from Ontario Hydro's Nuclear Stations has been stored in sophisticated, capital intensive, engineered structures. There is, therefore, an economic incentive to reduce the volume of this waste to a minimum as well as the safety criteria of preparing waste for storage in a non-combustible

\*CANDU - Canadian Deuterium Uranium: Heavy Water Moderated and Cooled Pressurized Reactors

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form for the long term. The technique chosen for volume reduction of combustible waste is incineration by a propane-fired unit. Non-combustible material (relatively high activity, metal content, etc) will be compacted into 200 litre drums (Fig 10). The Waste Volume Reduction Facility is located at the Bruce Nuclear Power Development Site on Lake Huron.

Figure 1, 2 - shows the building and its environment.  
 Figure 3 - shows the material flow in the radioactive portion of the WVRF.

## 2.0 Waste Description

### 2.1 Physical Composition

In order to segregate combustible waste from non-combustible waste a program of segregation of wastes at the producing nuclear stations has been instituted prior to in-service of the incinerator. The segregated combustible polyethylene bags of waste will contain: disposable coveralls, cotton coveralls, cotton and rubber gloves, cotton towels, rags, cardboard, paper, wood pieces, plastics (suits, bottles, syringes), vermiculites, mopheads, floor cleaning materials and other miscellaneous items. The use of clear PE bags allow a final visual inspection prior to loading. Metal and activity detectors complete the pre-incinerator inspection program. Other physical and chemical waste factors include:

Wt % Moisture	5 - 20
Wt % Ash	10
Wt % Combustible	90
Average Density lb/ft <sup>3</sup>	7 - 9
Average Btu/lb	7500 - 8500
Wt % Plastics	10 - 20
Wt % Halogenated	1/2% as PVC
Average Bag volume	1-1/2 - 2 ft <sup>3</sup>
Average bag weight	12 lb

### 2.2 Anticipated Waste Radioactivity Composition

Sampling of waste bags collected over several years have shown the average radiation field at contact to be approximately 2 mR/hr. Approximately 5% of bags have fields in the 5 - 20 mR/hr range.

Table 2 gives the relative number of times various radionuclides have appeared in bags of waste as measured at the nuclear stations.

Table 2

Relative Radionuclide Appearance in Waste

90% of bags	70% of bags	30% of bags	<10% of bags
Cs-134	Ru-106	Co-58	Sb-124 Ba-140
Cs-137	Mn-54	Cr-51	Cs-136 Mo-99
Ce-144	Zn-65	La-140	Cs-138 I-132
Nb-95	Fe-59	I-131	No-24 I-134
Co-60	Ru-103	Xe-133	Np-239 Rb-88
	Ce-141	Kr-88	Np-238

Table 3 gives the relative isotopic composition of a typical bag of solid waste.

Table 3

Relative Isotopic Composition of a  
Typical Bag of Solid Waste

Isotope	Half Life (days)	Percent of Total Activity due to Isotope
Co-60	1920	19
Cs-137	10950	17
Cs-134	730	6.7
Zr, Nb-95	66	17
Ce-144	284	17
Ce-141	33	2.3
Fe-59	45	0.8
Zn-65	245	3.4
Mn-54	300	0.5
Ru-106	368	12
Ru-103	40	1.6
I-131	8	0.4
Cr-51	28	1.7
Co-58	71	0.1
La-140	12	0.1
Total		99.6

There will be a normal delay period between waste collection at the stations to actual incinerator burn of 1 - 2 months.

### 3.0 Incinerator Description

The Waste Volume Reduction Facility contains five (5) areas:

- (a) Administration Wing
- (b) Non Radioactive Waste Incinerator
- (c) Radioactive Waste Incinerator
- (d) Service Area
- (e) Ventilation Equipment Area

Area (c) will be the subject of this paper.

Figures 4 and 5 show the equipment layout and Incinerator Schematic.

#### 3.1 Process Description

The system is based on batch type, controlled air incineration with secondary clean up equipment to reduce radioactivity release to the atmosphere.

The controlled air concept in incineration starves the air quantity in the 310 stainless steel primary chamber to obtain a partially oxidized effluent (800 to 1100°F) consisting of CO, CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, and Water Vapour. This is accomplished by limiting the air

flow to 30% of the air required for complete oxidization. This design with a gentle air flow pyrolyzes the waste and leaves most of the ash (which has completely oxidized by the end of the cycle) in the primary chamber.

With the ignition of the waste, the pyrolysis reaction proceeds gradually throughout the waste bed. First, the moisture and volatile matter (partially oxidized) are driven from the waste, leaving the fixed carbon in the waste for complete oxidation in the latter stages of the burning cycle.

The greatest volume change occurs in the initial stages when the volatiles are being driven off and partially oxidized. Half way through the cycle a 75% volume reduction has occurred with general waste as described above. The balance of the burn cycle is used to oxidize the fixed carbon content of the waste leaving radioactive ash.

Waste active oil can be burned in this facility. It will be injected into the unit approximately 4 hours into the cycle after the waste level has receded several feet below the liquid waste injection point. The waste oil is injected for three hours at a rate of 5 Imp gal/hr. The waste is injected as droplets (not finely atomized) through the starved air atmosphere to the hot waste bed. The liquid quickly vaporizes and then the fixed carbon residue is oxidized along with the fixed carbon in the solid waste. This disposal method is different to the normal concept of burning liquid droplets in suspension. An air purge is maintained on the liquid waste nozzle (when liquid is not being injected) to keep the nozzle from plugging with residual oil or overheating.

The partially oxidized effluent with small amounts of particulate is completely burned in a stainless steel afterburner where additional air (with an excess of 100%) and fuel is introduced to complete the oxidization. The afterburner temperature is 1600 to 1800°F.

Controlled air burning with a proper afterburner produces an effluent with particulates in the range of .05 grains per standard cubic foot (110 ppb) in the afterburner exhaust. This is sufficient to meet most environmental regulations considering only particulate emission. However, the particulates from radioactive waste usually contain a level of radioactivity that warrants further clean up. Besides handling the normal refuse, the system can also handle 15 gallons of oil based liquid waste each cycle.

Due to the maximum operating temperature level for the fabric filters, the effluent from the afterburner is cooled to 400°F by a shell and tube air cooled heat exchanger. Then the gases proceed through a precoated baghouse for additional particulate clean-up, and then release via the stack to atmosphere.

### 3.2 Primary Incinerator Assembly

The primary chamber is a vertical cylindrical unit with a cone on the bottom. The unit is a double shell design with a stainless steel inner shell to prevent build up of radioactivity.

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The area between the inner shell and outer shell provides an annulus through which air flow maintains the inner shell temperature above the dew point of the controlled oxidation products and below serious scaling and oxidation temperature of the inner shell.

The cone section at the bottom is replaceable.

The waste (2270 kg/5000 lbs) is loaded directly into the 500 cu ft primary chamber of the incinerator. The unit is only loaded when the incinerator is not burning. During the burning of the waste the loading chamber is under negative pressure direct to the baghouse. During loading the incinerator is under negative pressure. The top loading door is not opened until the sliding gate valve (used to dump the waste into the incinerator) is closed.

After loading, the waste is ignited with three burners equally spaced around the circumference of the primary chamber. Three burners are used to equalize the heat distribution which causes expansion on the inner shell.

The air for the primary incinerator is supplied through the bottom dump plate through nozzles which are self cleaning when the bottom dump plate (which also acts as a valve) is rotated 90°. This plate is also used to dump the ashes into a hopper below the incinerator.

The waste is gravity loaded and the ash gravity dumped.

Below the bottom dump plate and above the ash hopper, there is a sliding gate valve which remains closed except when dumping the ashes into the ash hopper after the cool down portion of the cycle.

The seals on the top sliding gate valve can be replaced from the top of the valve, and the seals on the bottom sliding gate valve can be replaced from the bottom of the valve.

### 3.3 Afterburner

The afterburner section is designed to ignite and burn the partially oxidized effluent from the primary chamber at a temperature of 1800°F for 1/2 second. The auxiliary burner is sized for  $1 \times 10^6$  Btu/hr required at start-up and is modulated by a temperature controller to maintain the 1800°F outlet temperature. Normally the auxiliary burner will be running at approximately 200,000 Btu/hr. Additional oxygen is introduced into the afterburner to complete the combustion of the waste. The secondary air comes from the annulus air exhaust from the primary chamber.

### 3.4 Cooling Heat Exchanger

Due to the temperature limitations of the cloth filter in the baghouse for off gas clean-up a heat exchanger is required to reduce the 1800°F effluent from the afterburner to 400°F. The temperature of 400°F is selected to keep the effluent temperature above the dew temperature.

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The heat exchanger is a shell and tube design with the effluent being cooled by forced ambient air. The air exhaust from the heat exchanger is directed through the system stack, when it is not used for heating the primary chamber inner shell. The tubes and inlet tube sheet are 304L SS because of the high effluent inlet temperature.

### 3.5 Baghouse Filter

The baghouse filter removes particulate matter from the exhaust gases at better than 99% efficiency by weight according to the American Filter Institute (AFI) weight method. (The efficiency of the filter represents the amount by weight that the filter removes).

The filter media is Nomex which has a temperature rating of 232°C (450°F). There are 96 bags in the baghouse, each bag being 0.15 m (6 in) in diameter, and 3.2 m (10.5 ft) in effective length. Normally the bag life for this application is approximately 5 years.

The filter is initially precoated with 91 kg (200 lb) of short asbestos fibres to achieve a high initial efficiency. The efficiency improves as the fly ash accumulates on the bags. The initial pressure drop is about 0.05 m (2 in) of water. At 0.13 m (5 in) of water pressure drop, the bags are to be shaken to remove the accumulated ash. At this time the bags must again be precoated before putting the filter back into service. The estimated time between shaking must be determined by operating experience, but is estimated to be approximately one year.

The failure of one filter bag could reduce the overall efficiency. Any failures may be detected by visual inspection. Significant leakage would be detected by the stack radioactivity monitor.

### 3.6 Induced Draft Fan and Stack

An induced draft fan is required by the system to maintain a slight negative pressure at the primary chamber outlet. This is controlled by a pressure indicating controller positioning an inlet damper on the induced fan which exhausts into a 75 foot carbon steel stack. The stack exhausts 25 feet above the top of the building.

### 3.7 Cycle

The incineration system operates on a timed sequence with safety interlocks to assure proper operation. The unit is operated essentially from a master control panel with the main flows, temperatures, pressures, pressure drops and valve positions tied into the interlock and the annunciator system. The main points of this cycle are:

- |   |             |
|---|-------------|
| 1. Waste Loading (Estimated)  | 1 hr 0 min  |
| 2. Pre-purge (after loading)<br>induced draft fan is started<br>-burner fans are on | 0 hr 12 min |

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Table 5

Maximum Permissible Concentrations in Air of Biologically Significant Radionuclides  
Maximum Permissible Concentration  
MPCa (Ci/m<sup>3</sup>)

Radionuclide	External Irradiation	Inhalation	Food Chain (Milk)
(1) Noble Gases	$6.4 \times 10^{-8}$ $\gamma$ Ci-MeV/m <sup>3</sup>	NA	NA
(2) I-131		$3 \times 10^{-11}$ *	$6 \times 10^{-13}$
(3) H-3		$3 \times 10^{-7}$	NA***
(4) Particulates:			
Cs-137		$1.5 \times 10^{-9}$	$5 \times 10^{-11}$
Cs-134		$1 \times 10^{-9}$	$1.5 \times 10^{-11}$
Sr-90		$4 \times 10^{-11}$	$1.5 \times 10^{-12}$
Sr-89		$2 \times 10^{-10}$	$1.5 \times 10^{-11}$
Co-60		$9 \times 10^{-11}$	NA
Ru-106		$4 \times 10^{-11}$	NA
Unidentified Particulates**	$4 \times 10^{-11}$	$1.5 \times 10^{-12}$	

\* Assumes 50% of the dose is from the shorter-lived radioiodines accompanying I-131.

\*\* The lowest MPC<sub>a</sub> value under "particulates" is used as the MPC<sub>a</sub> for unidentified particulates. Measurement of unidentified particulates activity in the stack effluent will be based on the counting efficiency for Cs-137, which approximates closely the counting efficiency of a typical radionuclide mixture.

\*\*\*Tritium is not considered to be a food chain hazard.

Table 6

Derived Release Limits for Both Direct and Indirect Exposure Paths

Radionuclide	Indirect Intake Path (Food Chain)		Direct Exposure Path (Inhalation or External Irradiation)	
	MPCa (Ci/m <sup>3</sup> )	Release limit (Ci/7 days)	MPCa (Ci/m <sup>3</sup> )	Release limit (Ci/7 days)
I-131	$6 \times 10^{-13}$	0.72	$3 \times 10^{-11}$	14
H-3	—	—	$3 \times 10^{-7}$	$1.4 \times 10^5$
Particulates:				
Cs-137	$5 \times 10^{-11}$	61	$1.5 \times 10^{-9}$	700
Cs-134	$1.5 \times 10^{-11}$	18	$1 \times 10^{-9}$	470
Sr-90	$1.5 \times 10^{-12}$	1.8	$4 \times 10^{-11}$	19
Sr-89	$1.5 \times 10^{-11}$	18	$2 \times 10^{-10}$	93
Co-60	—	—	$9 \times 10^{-11}$	42
Ru-106	—	—	$4 \times 10^{-11}$	19
Unidentified particulates	$1.5 \times 10^{-12}$	1.8	$4 \times 10^{-11}$	19

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3. Afterburner Warm-up -start afterburner in secondary chamber	0 hr 30 min
4. Burn Cycle -ignition burners start -afterburner operates on modulating temperature control	11 hr 0 min
5. Cooldown Cycle -all burners are shut off -induced draft fan continues to run	5 hr 0 min
6. Ash Removal (Estimated) -induced draft fan is operated during ash removal to avoid spread of ash	2 hr 0 min
Total Incinerator Cycle Time	19 hr 42 min

### 4.0 Dose Limits to the Public

The annual dose limits for individual members of the public, as recommended by the ICRP and endorsed by the Atomic Energy Control Board in Canada, are summarized in Table 4. In addition, the AECB also limits the population exposure to personnel in the surrounding area to the BNPD site by stipulating the following limits:

- $10^4$  man-rem per year whole-body exposure
- $10^4$  man-rem per year thyroid exposure

The dose integration must extend over all areas, outside of the site exclusion boundary, in which the individual dose could exceed 1% of the dose at the boundary. The annual dose limits are maximum limits which must not be exceeded.

The dose to the individual member of the public at the boundary, and not the integrated population dose, limits the releases of radionuclides from the BNPD Radioactive Waste Operations Site No 2.

**Table 4**  
**Dose Limits for Members of the Public**

Organs	Annual Dose Limit
Whole-body Gonads Red bon-marrow	0.5 rem
Skin, bone	3.0 rem
Thyroid	3.0 rem (Adults) 1.5 rem (Children up to age 16 years)
Other single organs or tissues	1.5 rem
Extremities	7.5 rem

5.0 Derived Release Limits for Airborne Effluents

The maximum permissible concentrations in air (MPCa) of the biologically significant radionuclides for continuous exposure of the public have been calculated (1) and are summarized in Table 5. The derived release limits for the continuous release of the specific radionuclides are calculated using the following relationship:

$$\text{Continuous release rate, } Q \text{ (Ci/sec)} = \frac{\text{MPCa}}{K_a}$$

where  $K_a$  is the average or weighted mean dilution factor for continuous releases reported by Bryant (2) and is a function of distance from the source and effective height of release.

The incinerator will be the only potential source of radioactive airborne effluents from the waste operations site under normal operating conditions. The height of the stack will be approximately 15 m. Since this will not be 2-1/2 times the height of adjacent buildings, the effective height of release will be less than 15 m due to downdraught. An effective stack height of 10 m is assumed. This is a conservative value as additional lift will result from the buoyancy of the hot gases and the velocity of discharge from the stack.

5.1 Continuous Releases of Specific Radionuclides

A dilution factor,  $K_a$ , of  $1.3 \times 10^{-6} \text{ sec/m}^3$  is used for a distance of 1 km from the point of release for direct exposure by inhalation. The combustible materials ashed in the incinerator will not contain significant quantities of noble gases so that release limits for this group of radionuclides are not calculated. Since the nearest grazing land is about 2 km from the site, a dilution factor of  $5 \times 10^{-7} \text{ sec/m}^3$  for the indirect exposure path is used.

The derived release limits for both the direct and indirect exposure paths for the various radionuclides are listed in Table 6. The limits are stated in units of Curies per seven day period. This approach has been adopted to accommodate transient releases of a somewhat higher level than those normally envisaged but still acceptable from the basic dose limitation standpoint.

The derived release limits for the airborne releases from the radioactive waste operations site are summarized in Table 7 with the most restrictive limit of the direct and indirect exposure paths for each radionuclide being applied.

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Table 7

**Derived Release Limits for  
Airborne Effluents from the BNPD  
Waste Operations Site**

Radionuclide	Release Limit (Ci/7 Days)
I-131	0.72
H-3	$1.4 \times 10^5$
Particulates:	
Cs-137	61
Cs-134	18
Sr-90	1.8
Sr-89	18
Co-60	42
Ru-106	19
Unidentified Particulates	1.8

## 5.2 Continuous Releases of More Than One Radionuclide

The calculated permissible releases of single radionuclides may be modified in practice to take into account releases of several radionuclides. It is necessary to ensure the dose limit for any organ is not exceeded. This requirement will normally be realized if the following summations are observed:

$$\frac{Q(\text{Sr-89})}{18} + \frac{Q(\text{Sr-90})}{1.8} \leq 1 \quad (\text{Critical organ - bone})$$

and,

$$\frac{Q(\text{H-3})}{1.4 \times 10^5} + \frac{Q(\text{Cs-137})}{61} + \frac{Q(\text{Cs-134})}{18} \leq 1 \quad (\text{Critical organ whole body})$$

where Q is the actual seven-day release of a radionuclide in Curies.

Operating procedures for the active incinerator will be established to ensure that the routine airborne releases, as measured by the stack monitoring, comply with the above summations.

## 5.3 Derived Release Limit: Design Target

In limiting the release of radioactivity from its nuclear sites to levels as low as practicable, Ontario Hydro has established a design target of 1% of the DRL limit (Table 7) per nuclear facility on a site.

## 6.0 Anticipated Releases from the Active Incinerator

From the measured relative mix of radionuclides listed in Section 2.2, it is anticipated that approximately 150 m Ci of mixed activated corrosion and fission products will be contained in one average batch load. Assuming a maximum particulate carryover of

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0.2% to the baghouse with a further reduction of 98% by the baghouse filters then 6  $\mu$ Ci of mixed activity will be released per burn. With 5 burns per week, a total of 30  $\mu$ Ci/7 days may be released up the stack.

The most restrictive DRL is for  $I^{131}$ . With a built in delay of at least 1 - 2 months, the quantity of  $I^{131}$  in the waste, as it is burned, is expected to be very low.

Using the 100% DRL for unidentified particulates (1.8Ci/7 days), the most restrictive category other than  $I^{131}$ , it is anticipated that releases could be in the order of:

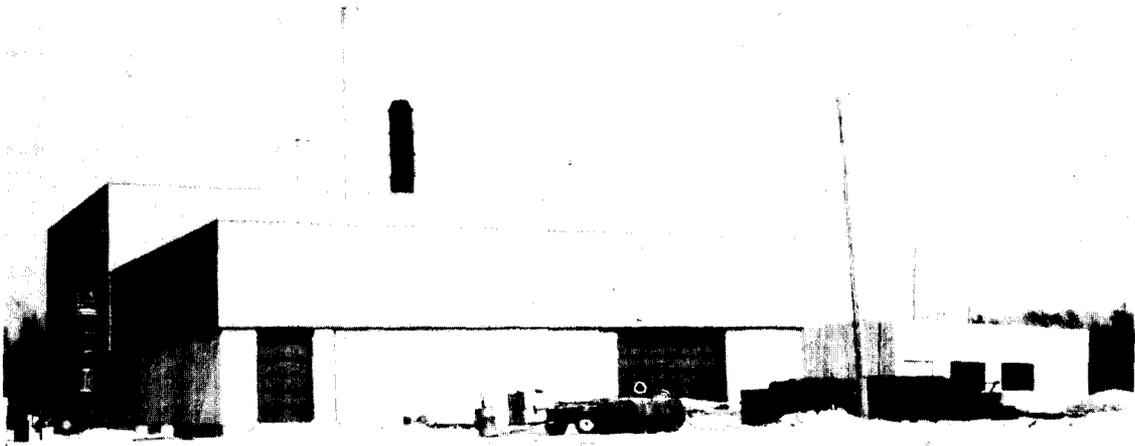
$$\frac{30}{1.8} \times 10^{-6} \times 10^2 = \underline{0.0016\% \text{ DRL}}$$

### References

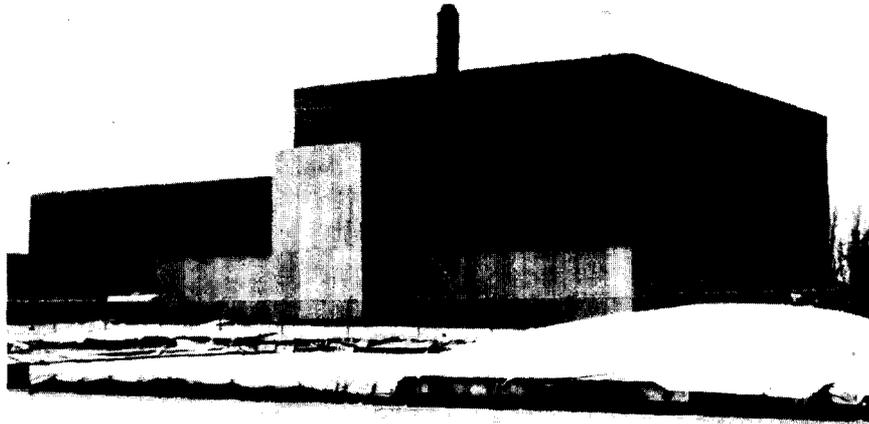
- (1) "Basis for the Derived Limits for the Release of Radionuclides in Gaseous and Liquid Effluents from Ontario Hydro's Nuclear Stations", K.Y. Wong, Ontario Hydro, August 1974.
- (2) "Methods of Estimation of the Dispersion of Windborne Material and Data to Assist in their Application", P.M. Bryant, 1964.

### Acknowledgement

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**FIGURE 1 THE BNPDS RADIOACTIVE WASTE VOLUME REDUCTION FACILITY VIEWED FROM THE SOUTHWEST**



**FIGURE 2 THE BNPDS RADIOACTIVE WASTE VOLUME REDUCTION FACILITY VIEWED FROM THE NORTHEAST**

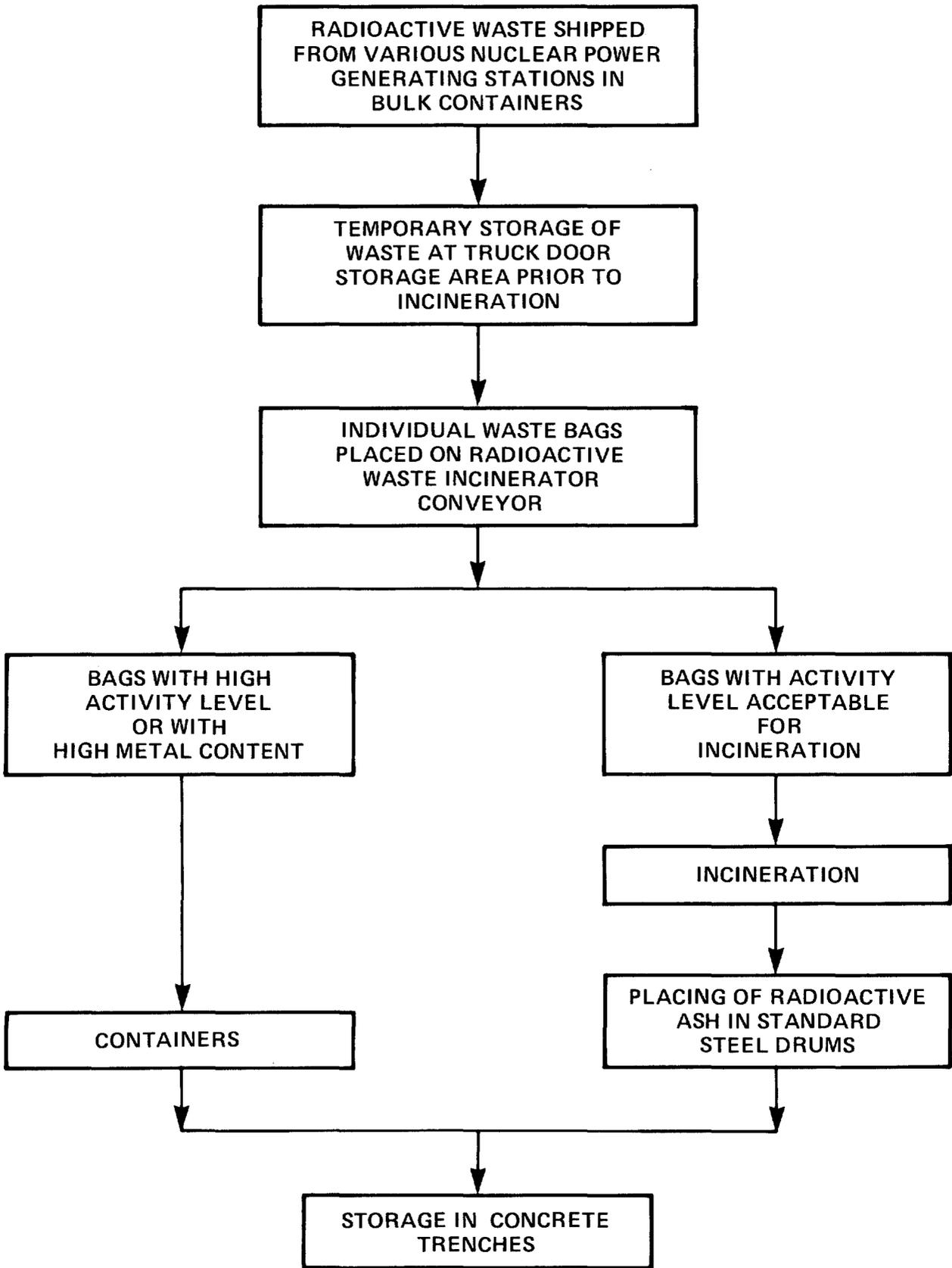


FIGURE 3 RADIOACTIVE WASTE PROCESS FLOW DIAGRAM

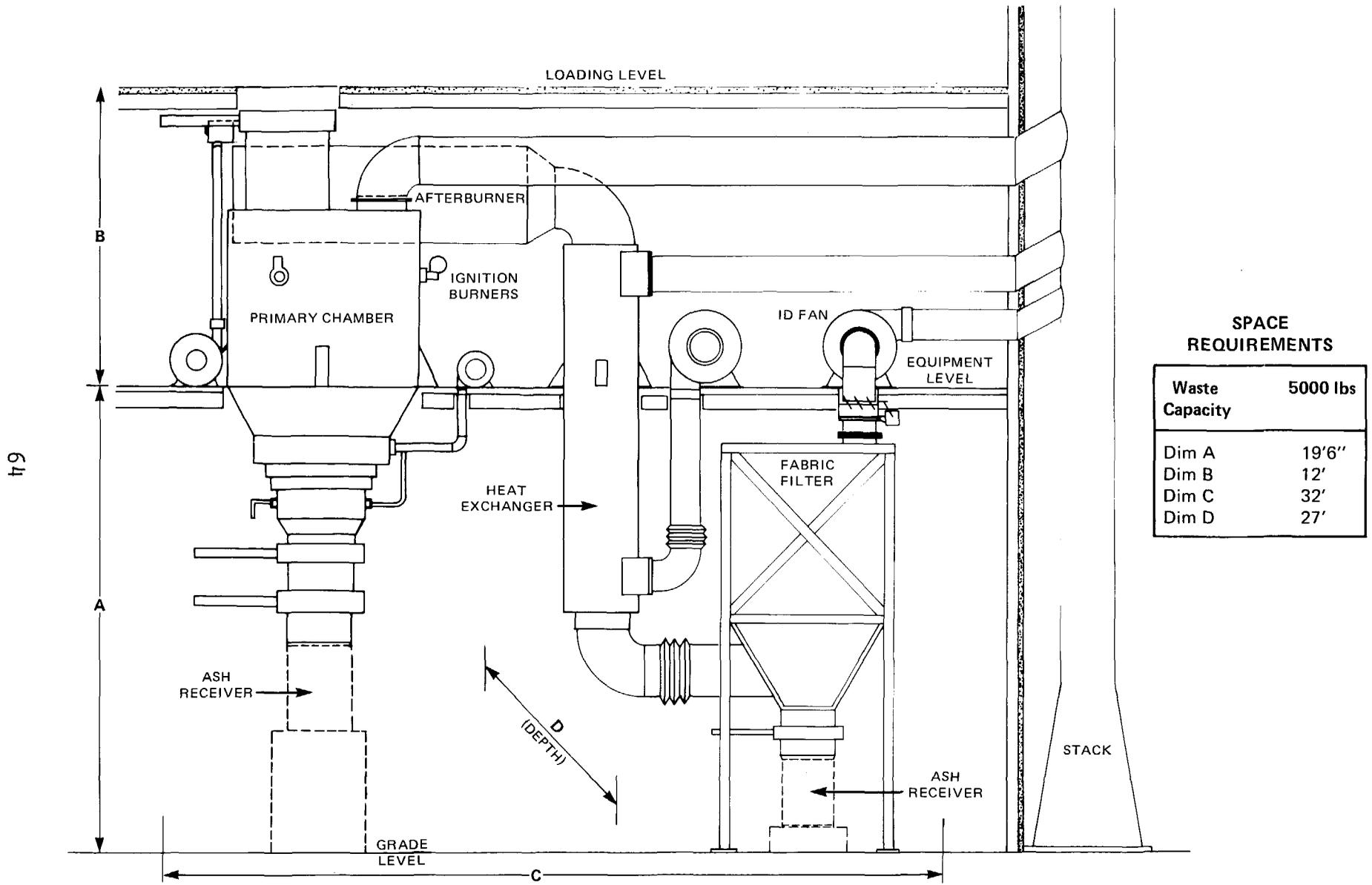


FIGURE 4 INCINERATOR EQUIPMENT LAYOUT

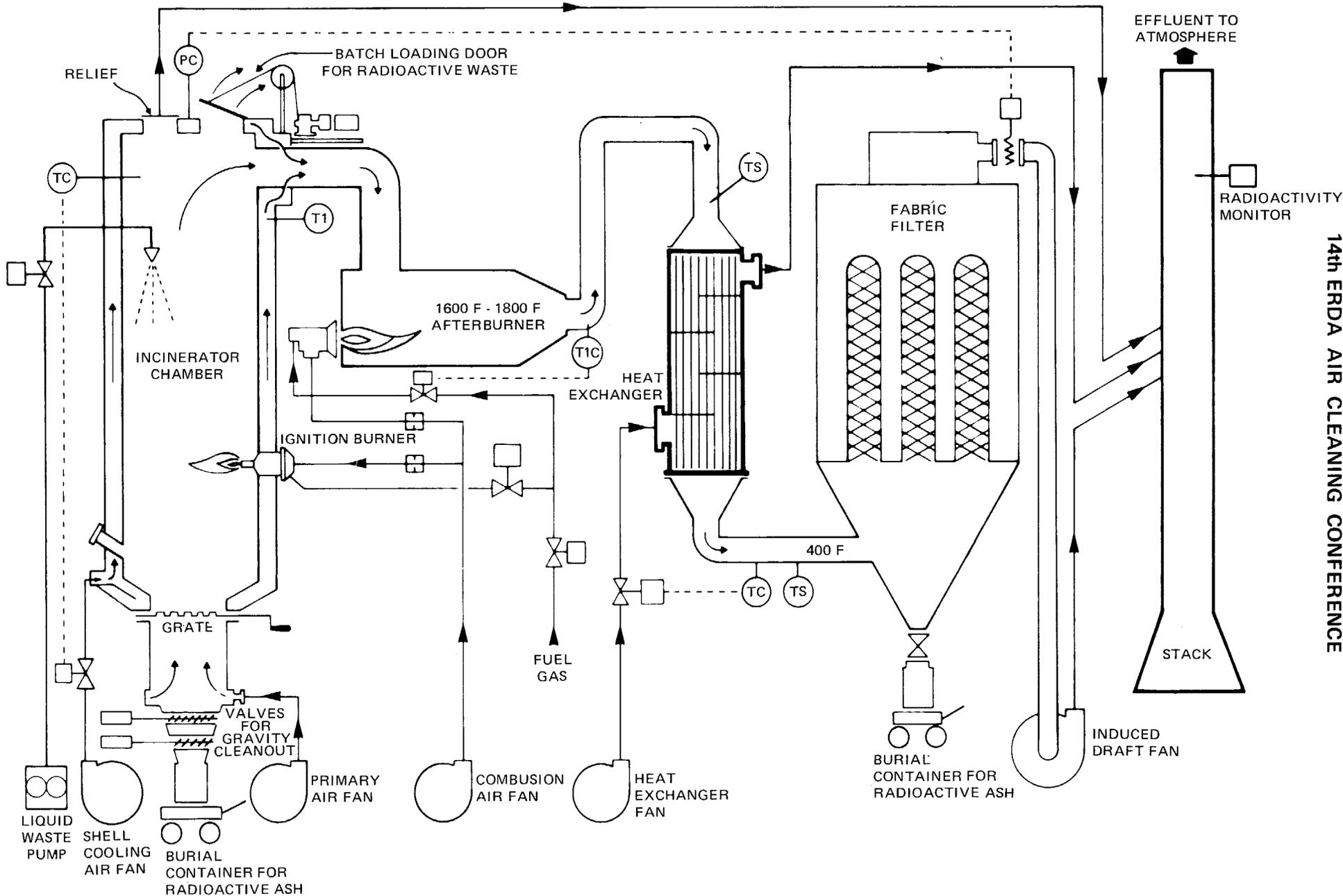
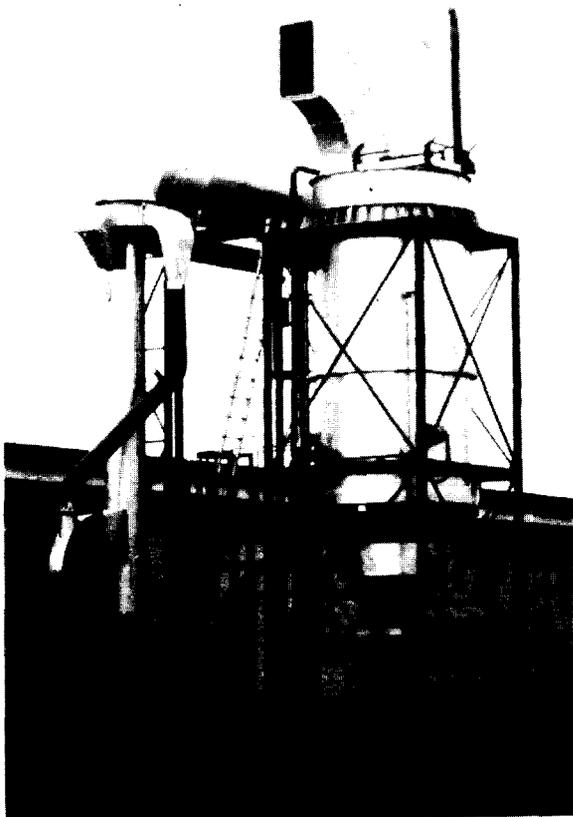
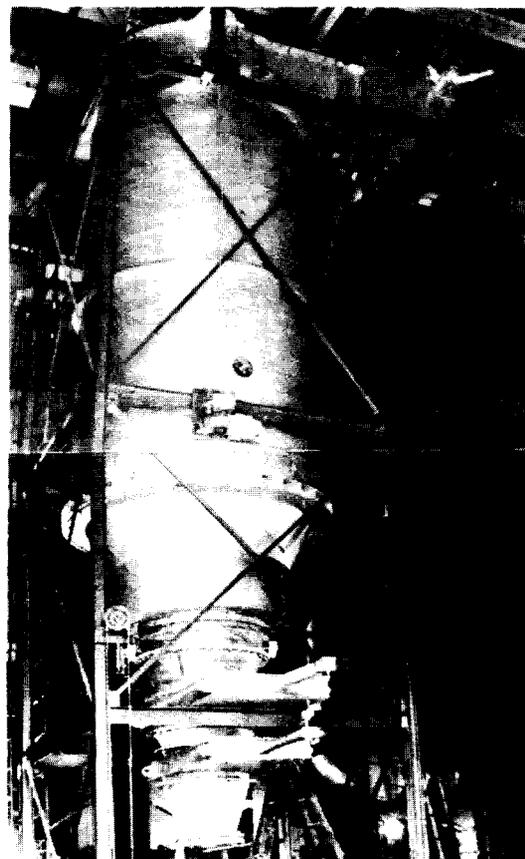


FIGURE 5 INCINERATOR SCHEMATIC



**FIGURE 6 THE BNPDS RADIOACTIVE WASTE INCINERATOR SHOWING THE PRECONSTRUCTION ASSEMBLY**



**FIGURE 7 THE BNPDS RADIOACTIVE WASTE INCINERATOR DURING CONSTRUCTION**

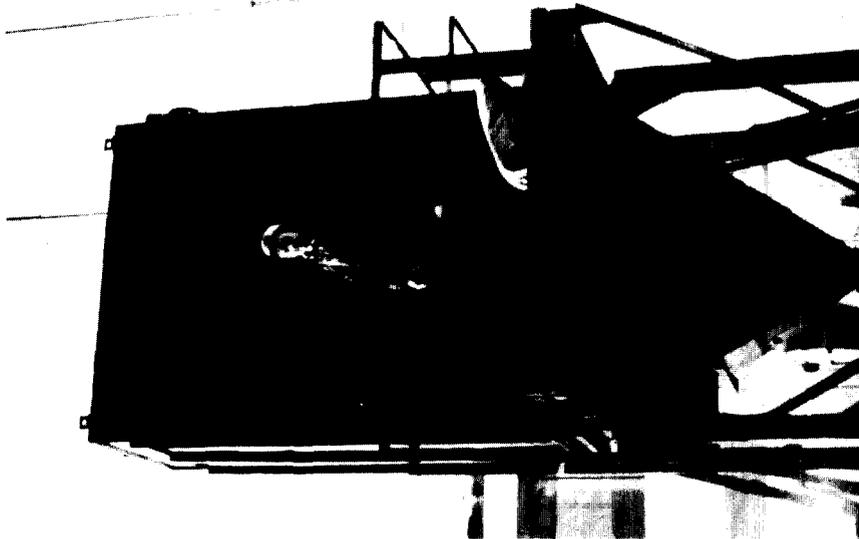


FIGURE 9 BAG HOUSE FILTER



FIGURE 8 THE BNPDS RADIOACTIVE WASTE  
INCINERATOR EXHAUST GAS  
FILTER BAG-HOUSE

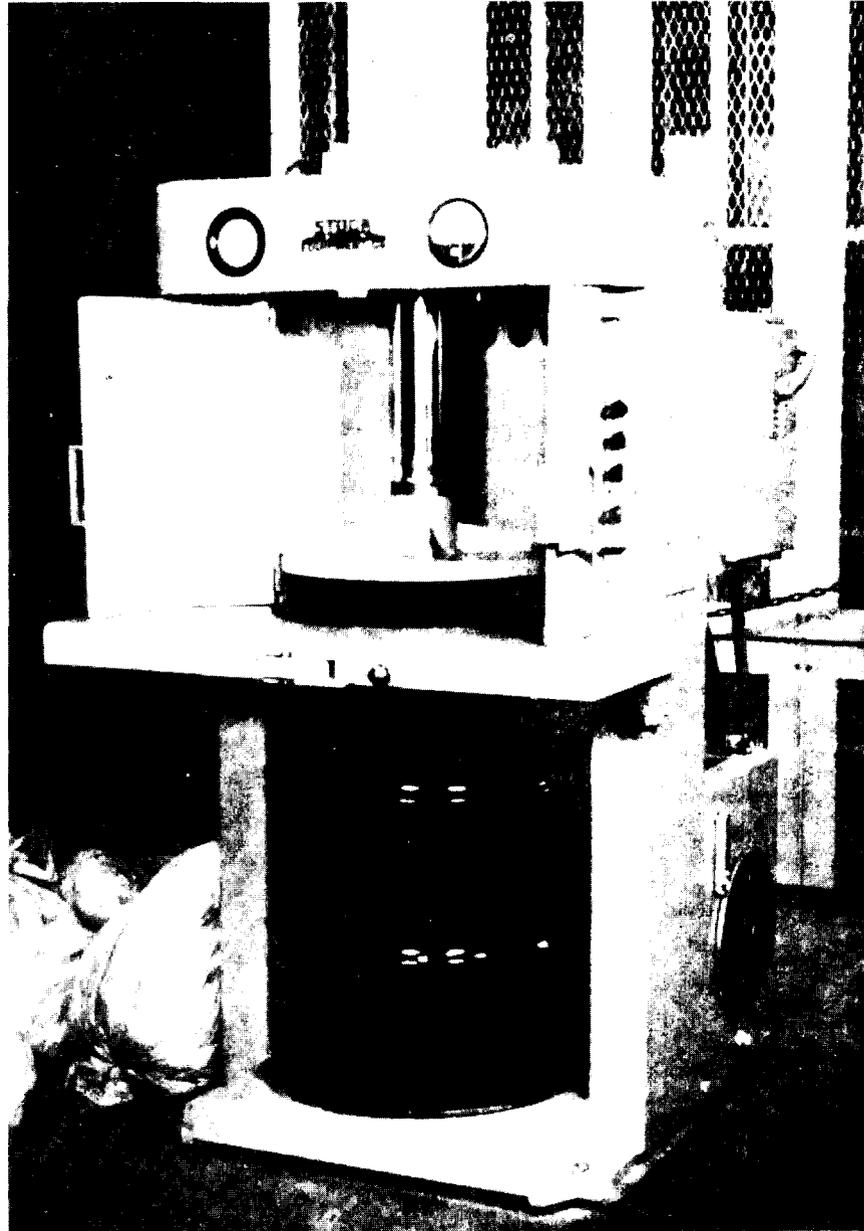


FIGURE 10 THE RADIOACTIVE WASTE COMPACTOR

DISCUSSION

BURCHSTED: Is the efficiency of the bag filters mass efficiency or number efficiency?

DROLET: Mass efficiency.

ETTINGER: My first question is somewhat similar. Is it correct that your paper indicated that you use the American Air Institute efficiency test, which is a mass efficiency for relatively large particles?

DROLET: Yes.

ETTINGER: What do you think the efficiency of the bag house with Nomex filters will be for submicron aerosols? The AFI test is heavily weighted, because of the test aerosol they use and the weight measurement method, to do well against large particles but relatively poorly for small particles. Do you have information on efficiency for some of the particles which are likely to be the source of contaminants coming out of the incineration?

The second question is: Do you think your dilution factor of  $10^6$  is fairly realistic and consistent with the Canadian regulatory requirements and ERDA or NRC regulatory requirements?

DROLET: To answer the second part first; yes, it is in line with accepted Canadian regulatory requirements and with Canadian experience to date, which we have gathered from the operating nuclear stations and from original R & D work at the Chalk River Nuclear Laboratories.

The first part of the question, no. We have no aerosol information to date. This incinerator is not yet on line. We have no research data to back it up. We will be measuring it after start-up and report it to you as soon as we can.

FREEMAN: Figure 3 shows the flow of bags with activity level acceptable for incineration going to incineration and high activity level being drummed for burial. What is the acceptable level?

DROLET: At Ontario Hydro we do it in terms of radiation doses on contact with each container. For concrete storage of these containers, our operating limit is 15 R.

FREEMAN: How is the waste checked to assure that this level is met?

DROLET: Individual monitoring of each container.

FREEMAN: It must be very low, as you stated later that even if the baghouse is breached, very little activity would be released.

DROLET: It is very low.

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## FLUIDIZED BED INCINERATOR DEVELOPMENT

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### Abstract

A fluidized bed incinerator is being developed for burning rad contaminated solid and liquid waste materials. In situ neutralization of acid gases by the bed material, catalytic afterburning, and gas filtration are used to produce a clean flue gas without the use of aqueous scrubbing.

### Introduction

The processing of radioactive materials generates waste, such as polyvinyl chloride (PVC) bags, polyethylene bags, surgeon gloves, paper wipes, and rubber drybox gloves. These waste materials must be processed for recovery of radioactive nuclides, such as plutonium. Conventional incineration, at temperatures of 800 to 1000°C, produces a refractory type of plutonium oxide which is difficult to dissolve. The combustion of chloride-containing waste in conventional incineration results in corrosion of the incinerator shell and of the flue gas scrubbing equipment. Recovery of plutonium from used refractory and the short life of refractory linings are major disadvantages of conventional incineration for this application.

To overcome some of the problems with conventional incineration, a project was initiated to develop a fluidized bed incinerator.<sup>(1)</sup> The major objectives of this incinerator system are as follows:

1. To produce a non-refractory plutonium oxide in the ash through the use of lower (550°C) operating temperatures.
2. To provide a system in which the corrosion of the incinerator and off-gas handling equipment is minimized with the use of in situ neutralization of acid gases generated by combustion of halogen-containing waste materials.
3. To provide a system which would minimize the complexity of the off-gas cleaning equipment through the use of in situ neutralization of the hydrogen chloride (HCl) and the use of catalytic afterburning of the flue gas.
4. To provide a system which would not require the use of refractory lined equipment because of lower operating temperatures in the reactor (550°C) and in the catalytic afterburner (525-650°C).

### Discussion

#### Equipment

The pilot plant incinerator was designed for a 9 kg/hr capacity.

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A flow diagram is given in Figures 1 and 2. The bagged solid waste is brought into a large sorting glovebox, bags cut open, and visible scrap metal removed before the waste is fed into a thick-bladed (16 mm) cutter type shredder. Coarse shredded waste drops onto a conveyor belt and is carried to an air classifier. Heavy particles fall into a collection glovebox, while the lighter fraction is air conveyed to a cyclone positioned over a second shredder. The cyclone-separated waste is ground in this thin-bladed (6 mm) shredder and falls into the incinerator feed screw hopper, while the air stream is recirculated back through the air classifier.

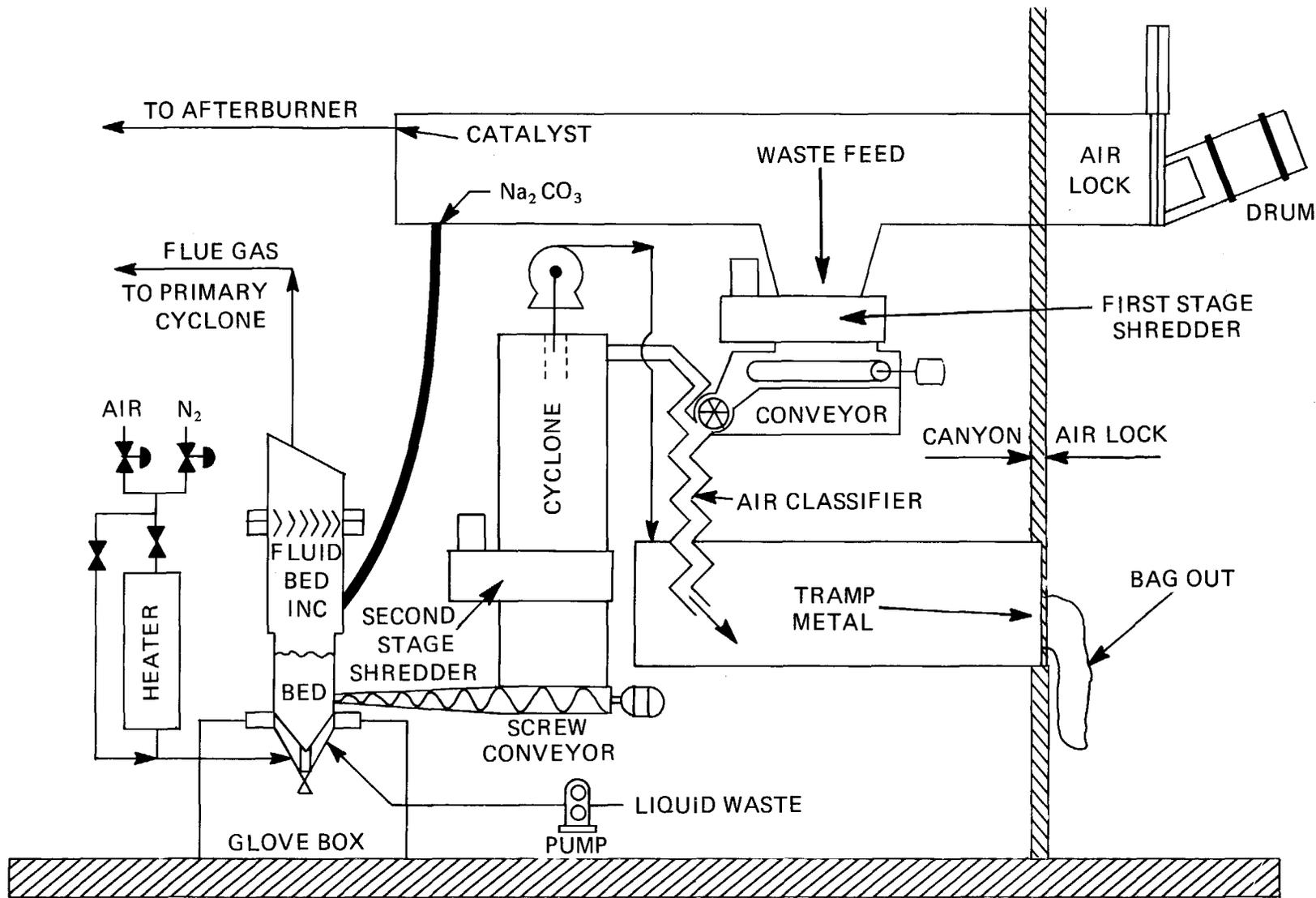
Shredded waste is fed by a tapered screw conveyor into a bed of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) which is fluidized by air or an air-nitrogen mixture introduced through a distributor plate and passing through the bed of granular solids. At a temperature of about  $550^\circ\text{C}$  the waste is burned or decomposed and the HCl produced by decomposition of waste PVC reacts with the bed material to form sodium chloride (NaCl).

The flue gas exiting the primary bed passes through a cyclone; this is the major point of residue removal. After most of the elutriated solids are removed by the cyclone, the flue gas passes through a fluidized bed of oxidation catalyst for complete combustion of the contained flammable gases.

The flue gas exits the reactor through a cyclone and sintered metal filters for the final removal of elutriated solids. Gas flow through each of the five filters can be stopped and the dust removed by reverse flow. From the filters the gas passes through an air jet ejector which provides motive force for gas flow through the incinerator. The entire incinerator system operates under a negative pressure to prevent leakage of hazardous materials. The process offgas is blended with  $64 \text{ m}^3/\text{min}$  of room air to produce a gas temperature below  $70^\circ\text{C}$  before it passes through four stages of high efficiency filtration for release to the atmosphere. Normal operating conditions and material compositions are presented in Table I.

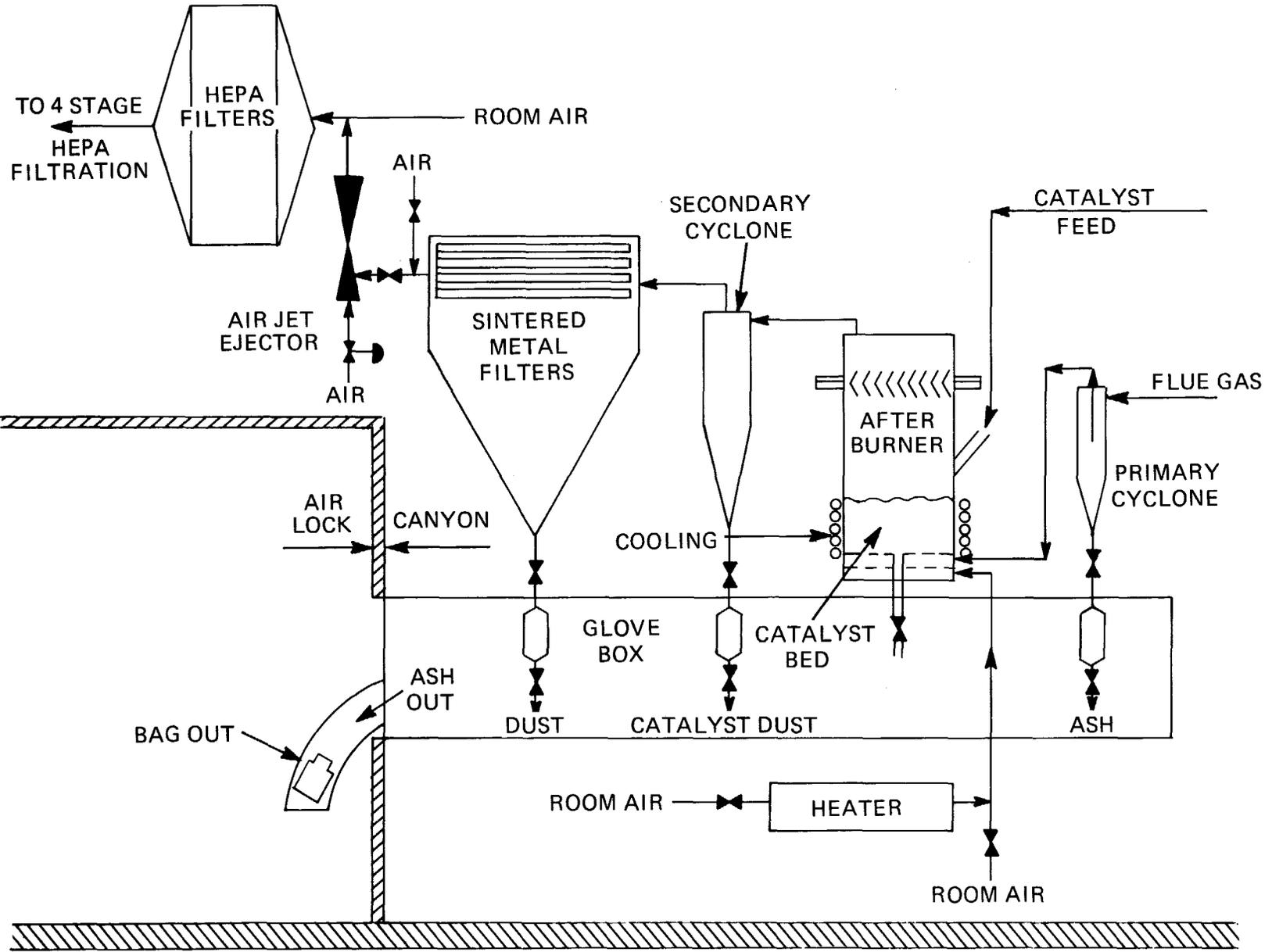
Table I. Operating conditions and materials for solid combustible waste incineration.

	<u>Incinerator</u>	<u>Afterburner</u>
Temperature, $^\circ\text{C}$	525-575	525-650
Gas Velocity, m/sec	0.35-1.0	0.35-1.0
Feed Rate, kg/hr	9	
Bed Depth, m	0.45	0.4
Construction Materials	Hastelloy C276 <sup>®</sup> stainless steel	and 304
Bed Materials	Sodium carbonate, 500-1000 micron	
Catalyst	23% chromic oxide on alumina 500-1000 micron	



FLOW DIAGRAM FOR PILOT PLANT FLUIDIZED BED INCINERATOR

FIGURE 1 - FEED END



FLOW DIAGRAM FOR PILOT PLANT FLUIDIZED BED INCINERATOR

FIGURE 2 - ASH END

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### Feed Preparation

The waste fed into any type of incinerator requires preliminary handling that includes sorting and getting the waste in the proper form for adding to the incinerator. For the fluidized bed incinerator, the preparation includes sorting, shredding, and air classification to remove tramp metal.

The shredders now in use were selected after testing shredders proposed by five different manufacturers. Two drums of waste materials, including all materials normally found in Rocky Flats Plant (RFP) waste such as surgeon gloves, plastic bags, wood, and high efficiency air filters, were shipped to each manufacturer. These materials were shredded in a vertical shaft hammer mill with ring type hammers, a horizontal shaft hammer mill with fixed hammers, a rubber chopper, and two low speed cutter type shredders. At the time these were tested, the Shred-Pax, <sup>®</sup> low speed cutter type shredder was found to offer the best combination of product size, minimum space requirement, and cost. It was equipped with an over-torque device to protect the equipment from damage due to tramp metal introduced with the waste material. Two of these units equipped with a hydraulic drive system have been installed in series to prepare feed for the pilot plant incinerator.

### Incineration of Liquid Wastes

The fluidized bed incinerator (FBI) is now provided with tankage and an associated pumping system for the incineration of liquids. Two pencil tanks with critically safe dimensions are filled from inside an airlock. The liquid is circulated through a loop for thorough mixing and a controlled amount injected, with admixed air, into a primary bed of oxidation catalyst. If the mixed waste being burned contains some halogenated hydrocarbons, a mixed primary bed of  $\text{Na}_2\text{CO}_3$  and catalyst is used for acid gas neutralization.

The two pencil tanks are provided with an automatic nitrogen pad that fills the void space as liquid is withdrawn from the tanks. This prevents the buildup of an explosive vapor mixture above the liquid surface. Injection rate and the selection of which tank is being circulated and/or filled is controlled from the master control panel. Level controls provide for automatic shut off when the tanks are full, along with warning lights on the control panel when a tank is near empty.

A dual system allows for the injection, at the same time, of two different liquids at individually controlled rates. This is advantageous for the destruction of a waste such as hydrazine. The hydrazine is noncombustible, but when injected into the incinerator while burning a waste naphtha mixture, the hydrazine is destroyed.

The enclosing of the FBI in a canyon, with residue removal isolated by a glovebox, allowed the incineration of alpha contaminated wastes. A large number of drummed contaminated flammable liquids, mostly from maintenance activities, had collected with no viable method of disposal. The disposal operation was started by pumping the liquid from the storage drums into drums fitted with bottom drains. At this time, as much water as possible was separated from

the organic fraction; the special drums filled with the organic were then sampled for analysis and connected to the incinerator tankage system. The analysis was made to determine if any especially hazardous or halogenated hydrocarbon materials were present.

Analytical data compiled from these typical runs are given in Table II.

Table II. Liquid waste incineration.

Run Number	kg Burned	Rate kg/hr	Residue, wt, kg.	Weight Reduction %
2	326	4.2	11.2	95.8
12	342	6.1	19.9	94.2
14	590	5.8	20.4	96.5

The increased burning rate in Runs 12 and 14 were attainable after the redesigned air ejector was installed. A greater amount of gas could be handled; this allowed the adding of more combustion air and the exhausting of the increased volume of flue gas produced.

#### Chloride Reaction with Bed Material

One of the major objectives of this process is to neutralize the HCl at the point of generation so as to eliminate the need for flue gas scrubbing to remove acid gases. To accomplish this, the chloride-containing waste is burned in a bed of sodium carbonate which reacts with the HCl to produce sodium chloride. The chloride is thus removed from the system without the complexity of a scrubbing system and with a minimum of chloride corrosion of the equipment.

The efficiency of chloride removal or reaction as a function of the efficiency of sodium carbonate usage has been evaluated in several experimental runs on the pilot unit. Presented in Figure 3 are the results of neutralization efficiency for experiments conducted with continuous waste feeding to a single bed of  $\text{Na}_2\text{CO}_3$ . For these tests, fresh  $\text{Na}_2\text{CO}_3$  was continuously fed and bed material continuously discharged from the fluidized bed. Essentially 100% efficiency of HCl reaction was obtained up to a level of about 26%  $\text{Na}_2\text{CO}_3$  utilization; the chloride reaction efficiency decreases and significant quantities of HCl are released with the flue gas after this point.

The data were generated with 500-1000 micron size sodium carbonate bed material. Analysis, by x-ray microscopy, of the used bed material, indicates that the particle is composed of a dense shell of high concentration NaCl surrounding a core of unreacted  $\text{Na}_2\text{CO}_3$ . This finding seems to indicate that using smaller particles would tend to improve the neutralization efficiency at higher levels of  $\text{Na}_2\text{CO}_3$  utilization. This also suggests that abrasion of the NaCl shell to expose the core  $\text{Na}_2\text{CO}_3$  may improve the  $\text{Na}_2\text{CO}_3$  utilization.

Presented in Figure 4 are data generated with batch operation of the bed material and continuous feeding of the waste. That is, no  $\text{Na}_2\text{CO}_3$  was fed and no bed material discharged during the test. All the data represented by the lower line were generated without

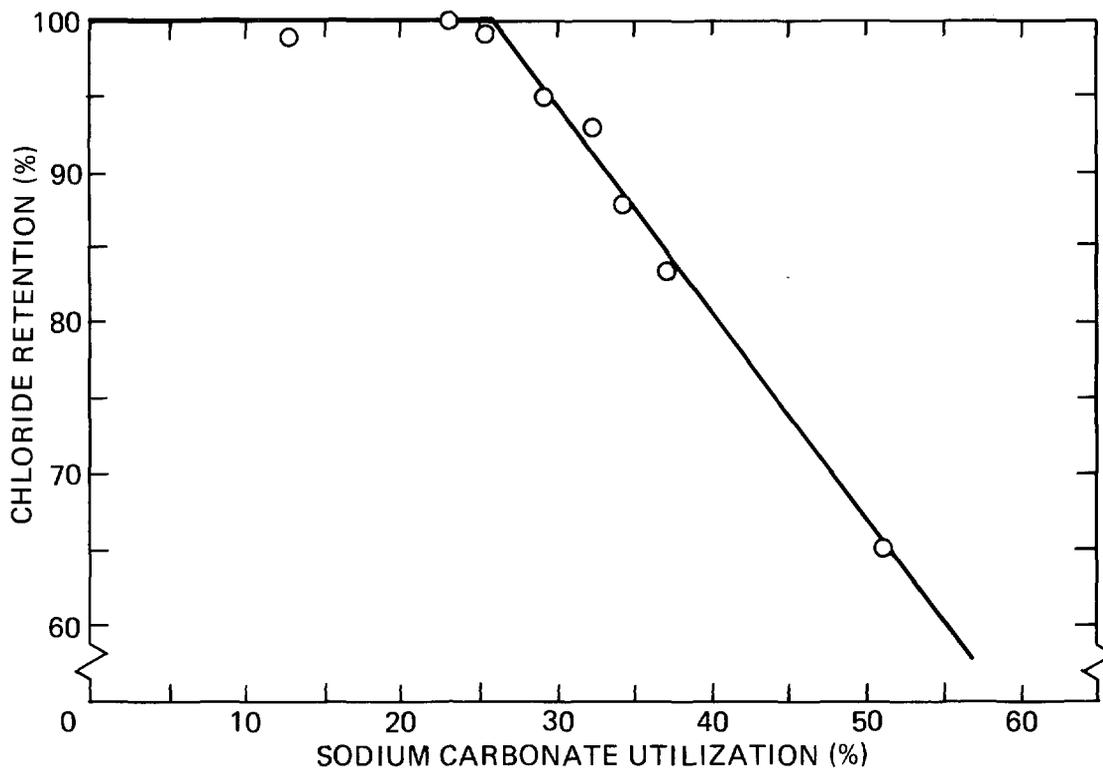


FIGURE 3  
HCl REACTION EFFICIENCY FOR CONTINUOUSLY OPERATED FLUIDIZED BED

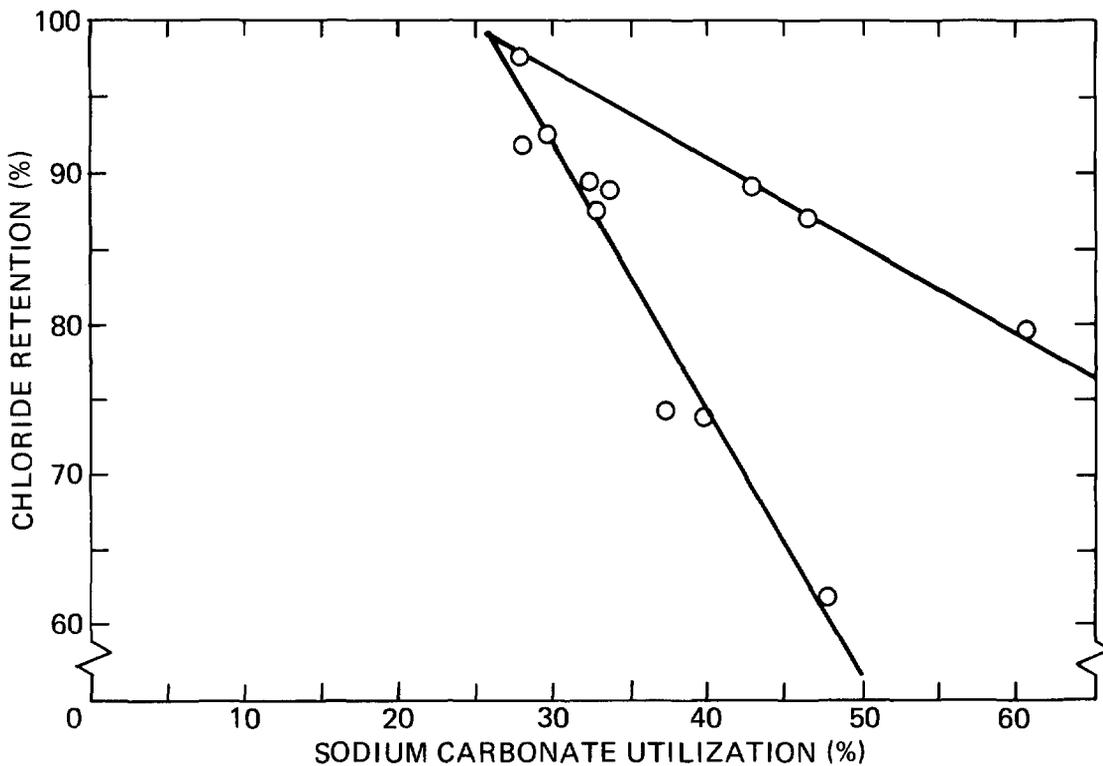


FIGURE 4  
HCl REACTION EFFICIENCY FOR BATCH OPERATED FLUIDIZED BED

interruption of the tests. The data represented by the other line were generated by runs which were interrupted during the test. For these runs, the bed material was reacted to an intermediate level of  $\text{Na}_2\text{CO}_3$  utilization, the bed material cooled to room temperature, and then reheated and carried to completion of the test. This intermediate cooling and reheating tends to increase the neutralization efficiency at equivalent utilization levels. This could be caused by thermal stress cracking of the sodium chloride shell and partial exposure of the core  $\text{Na}_2\text{CO}_3$ . Both of these lines intersect the 100% chloride retention level at about 26%  $\text{Na}_2\text{CO}_3$  utilization.

The fluidized bed depth did not have a significant effect on neutralization efficiency. Data from both deep and shallow bed experiments are included in Figures 3 and 4. This suggests that the HCl is generated and reacted shortly after the waste is introduced. Several tests were made using a secondary bed of  $\text{Na}_2\text{CO}_3$ . The secondary bed did not improve the neutralization efficiency at comparable  $\text{Na}_2\text{CO}_3$  utilization levels, again supporting the theory of rapid HCl generation and neutralization.

Over a year of operational tests of the pilot plant with plutonium contaminated RFP generated waste has proven that excellent chloride retention can be obtained with  $\text{Na}_2\text{CO}_3$  utilization levels up to about 70 percent. These improved results during week-long incineration runs burning actual waste were obtained with a waste stream containing a lower PVC content than feed material used in previous tests. This, in effect, provided increased grinding time per unit addition of chloride to remove the sodium chloride shell formed on the outside of bed particle.

### Flue Gas Afterburning

When the gas was filtered prior to the afterburner to remove elutriated bed material, the sintered metal filters became plugged with condensing hydrocarbons or tars. Because of this filtration problem, tests were conducted with the filters installed downstream of the fluidized bed catalytic afterburner. This allows the particulate to percolate through the catalyst bed and the filtration to be performed on a gas stream free of significant concentrations of hydrocarbons.

Catalytic oxidation provides several important features for this process. The catalyst is effective at lower temperatures than are required for open flame afterburning. Therefore, the elutriated bed material will not be melted and coated on reactor walls which could occur in conventional open flame afterburning. The low temperature operation of the catalyst also eliminates the need for refractory lined equipment. The catalyst is effective in producing a high quality flue gas. A typical flue gas composition for the fluidized bed afterburner operation is presented in Table III.

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Table III. Typical flue gas composition exiting afterburner.

	<u>Fluidized Bed</u>
Oxygen (%)	7.8
Carbon Dioxide (%)	8.3
Carbon Monoxide (ppm)	400
Total Hydrocarbons (ppm)	100

### Particulate Elutriation

The majority of the ash generated is elutriated from the bed and collected in cyclone and filtration system. Most of the tests resulted in 70 to 80% of the ash being elutriated from the bed. The remaining 20 to 30% of the ash was removed with the bed material.

With the fluidized catalytic bed afterburner, some of the catalyst is elutriated from the reactor. The rate of catalyst loss is dependent on gas fluidizing velocity and the mesh size of the catalyst used. These data are presented in Figure 5. This type of information is needed to properly size the fluidized bed afterburner to minimize catalyst usage.

### Conclusions

1. The operating temperatures in the incinerator and the afterburner are low enough to eliminate the use of refractories.
2. The performance of waste shredding and feeding of shredded material has been demonstrated to be satisfactory.
3. Efficient HCl neutralization has been accomplished up to a level of about 70%  $\text{Na}_2\text{CO}_3$  utilization. This eliminates the need for an aqueous scrubbing system.
4. Catalytic afterburning produces a flue gas with minimal levels of unburned hydrocarbons.

### Reference

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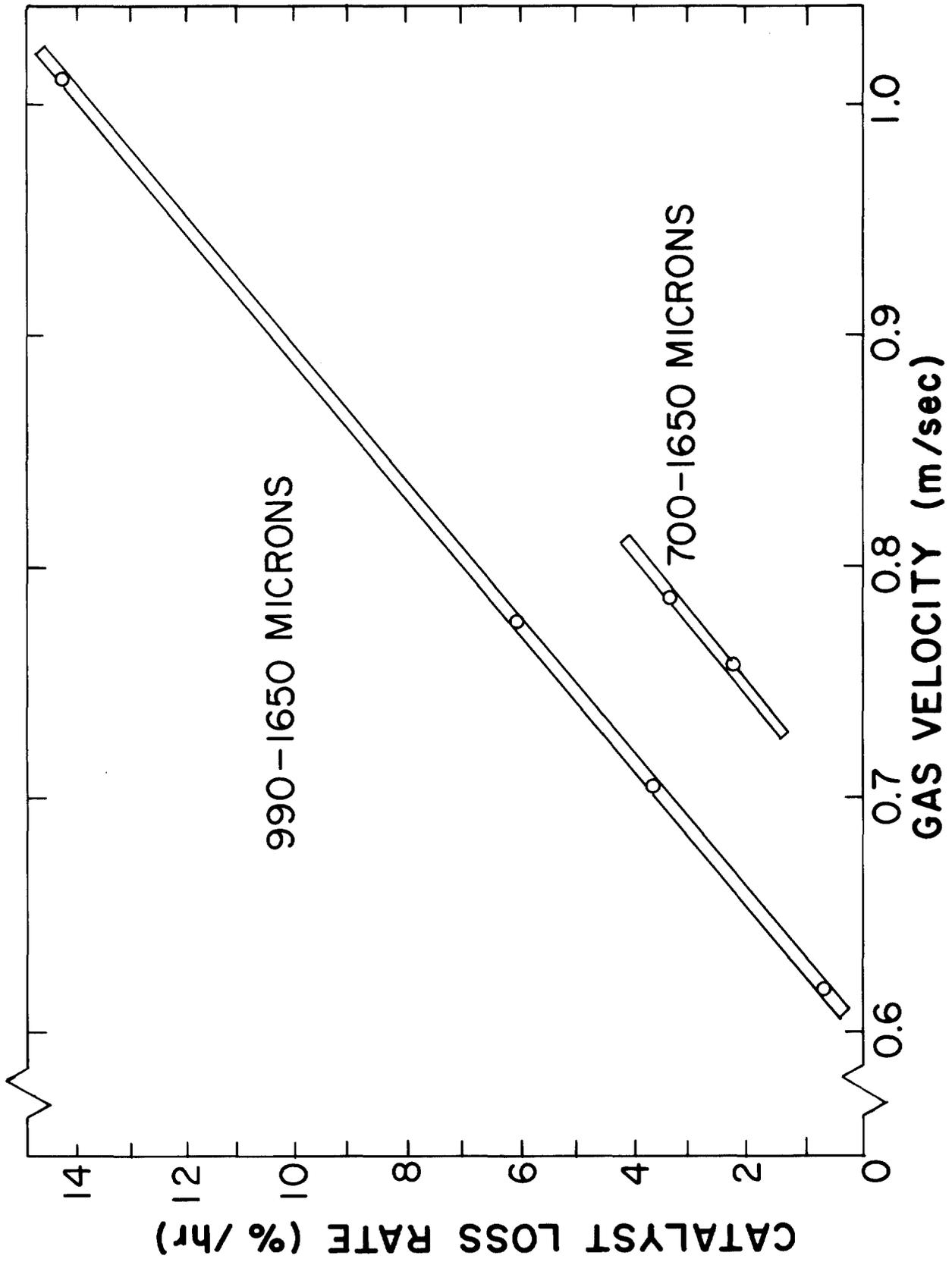


FIGURE 5

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### PARTICULATE COLLECTION IN A LOW LEVEL RADIOACTIVE WASTE INCINERATOR

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#### Abstract

As designed, sintered stainless steel filters will clean the gas from the secondary cyclone at a low level radioactive waste incinerator. Using bench scale apparatus, asbestos floats and diatomaceous earth were evaluated as filter aids to prevent clogging of the sintered metal interstices and to decrease filter penetration. Both precoats prevented irreversible pressure drop increase, and decreased cold DOP penetration from 80% to less than 1%. To collect the same quantity of fly ash, less diatomaceous earth was needed than asbestos floats.

A back-up study evaluated a moving bed of sodium carbonate pellets in lieu of the sintered metal filters. Since identical sodium carbonate pellets are used to neutralize hydrogen chloride in the incinerator, their use in a moving bed has the advantages of trouble free disposal and cost free replacement. Co, counter, and cross-current beds were studied and gave fly ash penetrations less than 0.1% at moderate pressure drop.

#### I. Introduction

Volume reduction of solid wastes contaminated with radioactive materials, such as plutonium, in high temperature fixed hearth incinerators has been practiced for about 25 years. These incinerators have experienced rapid deterioration and have required frequent expensive maintenance and repair services because of high combustion temperatures and the presence of corrosive gases from the decomposition of halogen-containing substances, such as PVC. To overcome these problems, a program was undertaken at the Rocky Flats Plant to develop a low temperature (550°C) fluidized bed incinerator utilizing sodium carbonate pellets to react with acid gases and minimize corrosion of the gas incinerator and offgas system.<sup>(1)</sup> The primary flue gas cleaning system of the pilot scale incinerator consisted of a cyclone collector followed by a bank of sintered metal filters. After some hours of incinerator operation, the air flow resistance of the sintered metal filters increased substantially, and they could not be restored to a serviceable condition by chemical or physical cleaning methods nor by high temperature exposure for prolonged periods. The exact cause of the permanent plugging of the sintered metal filters could not be determined with certainty, but remedial measures were required as these filters are very costly.

Two methods of overcoming the plugging problems experienced with sintered metal incinerator flue gas filters were investigated:

(1) the use of filter aids to protect the sintered metal filter surfaces from direct contact with the particulate matter in the incinerator offgases and (2) substitution of a high temperature granular moving bed filter for the sintered metal filters.

## II. Filter Aids for Sintered Metal Filters

When fine particles enter and become wedged into the comparatively large pores of sintered metal filters, they may become fixed in place and impossible to remove. This leads to irreversible increase in pressure drop and premature filter replacement. To prolong filter life, the use of filter aids to shield the sintered metal surface, and enhance collection efficiency, was investigated. To satisfy all design criteria and operate successfully, it was required that the filter aid selected (1) separate easily and uniformly from the sintered metal surface during cleaning (2) form a layer with low pressure drop but high collection efficiency for the incinerator dust (3) coat the filter well with a small amount of filter aid relative to the amount of incinerator dust collected to minimize the disposal of radioactive waste (4) withstand 500°C, the temperature of the incinerator exhaust gases (5) disperse easily into the filter inlet air stream and (6) be easy and safe to handle. Several filter aids were reviewed against these criteria. Two of these, asbestos floats and diatomaceous earth, were low in cost, easily obtainable, and appeared to satisfy most requirements. They were selected for further testing.

### Equipment

Three sintered stainless steel filter tubes, each 1 1/2 in. O.D. and 5 3/4" long, were used for evaluation. The filter tubes were mounted in parallel within a stainless steel housing and so arranged that gas flow passed through the filters from the outside to the inside, allowing filter aid and dust to collect on the outside surfaces. Filtered air passed through solenoid valves to an exhaust manifold, and then in turn to an orifice flowmeter, flow control valve, blower, and to the laboratory air exhaust system. Pulses of back-flow cleaning air were admitted by closing solenoid valves connected to the exhaust manifold and then opening solenoid valves connected to a compressed air reservoir. The three filters were operated and cleaned simultaneously. Measured quantities of filter precoat and test dust were fed in to the filter housing by a dust feeder. (2)

Diatomaceous earth has been widely used as a precoat for liquid filters and asbestos floats have been used as a precoat for fabric filters controlling low concentrations of toxic dusts, such as beryllium, which must be collected with exceptionally high efficiency. Cumulative size distributions by count for the diatomaceous earth and asbestos floats precoat materials used in this study are given in Figure 1. Both materials have a count median diameter about 1 micrometer and similar size distributions.

Measurements

A series of tests was performed to determine cleanability of these precoat materials from the sintered metal surface. Air at room temperature was passed through the filters at a face velocity of 20 feet per minute and sufficient precoat added to raise filter pressure drop from 6.5 to 10.5 in. w.g. Cottrell-precipitated fly ash having the size distribution shown in Figure 1 was then added to the pre-coated filters until system pressure drop reached 20 in. w.g.

Filter aid and dust were then removed from the sintered metal filter surface by a one second pulse of 15 psig air directed from inside the filter tubes toward the outside. No decrease in residual pressure drop was found when the length of the cleaning pulse was increased from 1 to 15 seconds.

Twenty repetitions of the loading and cleaning cycle were carried out with asbestos floats and with diatomaceous earth as a precoat. Figure 2 is a plot of pressure drop after cleaning, against cycle number for each filter aid. The residual pressure drop for filters precoated with diatomaceous earth was about one in. w.g. higher than for asbestos floats. For both asbestos floats and diatomaceous earth, residual pressure drop appears to have remained stable over twenty cycles, demonstrating that the filter aid plus fly ash can be cleaned effectively from the sintered metal surface.

A second set of experiments was performed to determine the loadability, (i.e. fly ash to precoat mass ratio) of each filter aid and to indicate its ability to prevent fly ash from entering the sintered metal pores. First, cold DOP, generated with a single Laskin nozzle and having a mass median diameter of 0.8 micrometers and standard geometric deviation of 1.65<sup>(3)</sup> was fed to the cleaned filters. Penetration was read directly using a total light scattering photometer. Next, precoat was added, in gram increments, to the filter surface until system pressure drop increased by 4 in. w.g. and then a second DOP test was performed. Finally, fly ash was added, in gram increments, until total system pressure drop reached 20 in. w.g. and a third DOP test was performed. Figure 3 shows pressure drop vs pounds per square foot of filter aid (areal density) when pre-coated with asbestos floats or diatomaceous earth. The pressure drop loading characteristics of both filter aids are almost identical while precoat is being fed, but when fly ash is added, pressure drop builds up much more slowly on the filters precoated with diatomaceous earth.

With a precoat of asbestos floats, 35% of the total filter aid-fly ash mixture cleaned from the filters was asbestos whereas with diatomaceous earth, only 15% of the total mass was precoat. Therefore, filters using asbestos floats would have to be cleaned and recoated more than three times as often as filters using diatomaceous earth, and over three times as much asbestos would have to be used and disposed of.

The results of the DOP penetration tests are shown in Table 1. Clean sintered metal filters show a DOP penetration close to 100% and are inefficient filters for submicrometer particles without the

presence of a filter cake. Additions of both asbestos floats and diatomaceous earth, as precoats, decreased penetration to 0.3 - 0.4%. After loading with fly ash, DOP penetration decreased to less than 0.01% with the asbestos floats precoat, but to only 0.1% with diatomaceous earth.

### Discussion of Results

The differences in loadability and DOP penetration of sintered metal filters between filter aids can be explained by differences in the properties of the cake that is formed on the clean filter. Asbestos floats contain a significant fraction of small diameter fibers that are excellent collectors of small fly ash and DOP particles. As a result, when using asbestos floats, most fly ash collection takes place upon the upstream surface of the deposit. The fly ash filter cake that develops rapidly at the precoat surface is a very efficient fly ash collector but has a rapid pressure drop rise. Diatomaceous earth is composed, instead, of cubic and spiny round particles with very few fibers. As a result, fly ash may penetrate below the surface of the diatomaceous earth precoat and deposit within the interstices of the diatomaceous earth cake, thereby delaying the formation of a fly ash filter cake at the precoat surface. Although penetration is not as low as when the fly ash cake forms immediately on the surface of asbestos floats, pressure drop across the filter system increases much more slowly, at least until a homogeneous fly ash cake is established on the surface of the diatomaceous earth. After the fly ash filter cake is fully established, pressure drop should increase at a rate that is independent of the nature of the filter aid. One criterion of the effectiveness of a filter aid is how well the pressure drop increase can be delayed. The data presented here suggest that diatomaceous earth is effective than asbestos floats in this regard.

Both asbestos floats and diatomaceous earth can be used to protect sintered stainless steel filters from irreversible plugging without causing an increase in cleaned filter pressure drop over many cleaning cycles. Although a deposit of diatomaceous earth and fly ash gives greater DOP penetration than one of asbestos floats and fly ash, loadability of the diatomaceous earth coated filter is much better.

### III. Moving Bed Granular Filter

The feasibility of using a moving bed granular filter containing sodium carbonate pellets, as an alternative to the use of sintered metal filters to clean the offgases from a fluidized bed incinerator burning low level radioactive wastes, was also studied. Sodium carbonate pellets were selected for the granular filter because they are being utilized in the incinerator to neutralize hydrogen chloride formed during the combustion of chlorine-containing wastes and it was considered possible that the sodium carbonate pellets from the filter could be cycled back to the incinerator, thereby eliminating one radioactive waste stream.

Two types of pellets, in use in a prototype incinerator built at Rocky Flats, Colorado, were tested as candidates for a granular filter. The larger pellets are isometric and close to monodisperse, i.e., they have a geometric mean diameter by count of 1.2 mm and a geometric standard deviation (GSD) of 1.2. The smaller pellets are cylindrical and have a geometric mean length equal to 0.21 mm by count (GSD = 2.0) and geometric mean diameter equal to 0.12 mm (GSD = 1.7).

### Granular Bed Configurations

Filtration in fixed granular beds, used for the initial studies, is a non-steady-state process inasmuch as both pressure drop and collection efficiency will vary with time and the bulk of the collected dust will be concentrated on or near the upstream face of the filter whereas a moving bed granular filter is a steady-state unit once equilibrium has been reached. Moving granular beds, often referred to as gravity beds, are used for catalytic cracking units, pebble heaters, shaft furnaces, and blast furnaces. Gas flow through a moving granular bed may be cocurrent, countercurrent, or perpendicular (cross-flow) to the direction of movement of the solids. For cocurrent and countercurrent arrangements, gas flow can accelerate or impede the flow of solids. In either case, the porosity of the flowing granular medium, (4) will be the same as the loosest possible packing in a fixed bed.

A cocurrent arrangement is advantageous as a particulate filter because dirty gas initially contacts clean pellets that have low collection efficiency, but as the gas travels deeper into the bed it meets granules that are more heavily laden with collected particles and hence have higher dust collection efficiency. This arrangement is analogous to a deep bed filter using successively finer and more efficient filtering media and makes it possible to distribute the collected material throughout the entire depth of the bed. Cocurrent flow also eliminates the possibility of bed fluidization, a major hazard of a countercurrent flow granular filter. Fluidization occurs when the pressure drop associated with the upward flow of gas is sufficient to overcome the weight of the granular medium, i.e., when

$$\frac{\Delta P}{L} = \rho_B g \quad (1)$$

where  $\Delta P/L$  is the pressure drop per unit height of bed,  $\rho_B$  is the bulk density of the bed, and  $g$  is the acceleration of gravity. For a moving bed of granules, the weight of collected dust will not significantly increase bulk density but will have a profound effect on the pressure drop. For both small and large sodium carbonate pellets, the maximum pressure drop attained per length of bed before fluidization occurs is equal to about 1.0 in. w.g. per inch of bed height. Because this condition can be reached easily, a countercurrent granular bed filter is not desirable.

One disadvantage of cocurrent (and countercurrent) flow is the need for large length-to-diameter bed ratios to assure plug flow of the granules. This is generally not a problem with cross-flow operations.

Fixed Granular Bed Filter

Sodium carbonate pellets supported on a screen in a two-inch diameter column were gently tapped until their volume was minimized. The pressure drop across this bed vs gas velocity for various bed depths is shown in Figures 4 and 5 for large and small pellets, respectively. For the larger pellets, the experimental data were compared to the Ergun equation<sup>(5)</sup>, a relationship commonly used to predict pressure drop in porous media, i.e.:

$$\Delta P/L = 4.17\mu VS^2(1-\epsilon)^2/\epsilon^3 + 0.292\rho V^2S(1-\epsilon)/\epsilon^3 \quad (2)$$

where  $\Delta P$  is pressure drop,  $L$  is bed depth,  $\mu$  is gas viscosity,  $V$  is superficial gas velocity,  $S$  is external specific surface area of the granular medium,  $\epsilon$  is interpellet porosity of the bed, and  $\rho$  is gas density. Using the method of Chalkly, et al.<sup>(6)</sup>, the external specific surface of the larger pellets was determined to be  $7.6 \text{ mm}^{-1}$  from photographs of bed cross-sections. Interpellet porosity was evaluated from bed cross-sections and found to be 0.33. The internal specific surface and intrapellet porosity of the porous pellets have an insignificant effect on the flow and do not influence these measurements.

For air at ambient conditions, equation (2) reduces to

$$\frac{\Delta P}{L} = 2.91 \times 10^{-2}V + 1.35 \times 10^{-4}V^2 \quad (3)$$

where  $\Delta P$  is in inches of water,  $L$  is in inches, and  $V$  is in fpm. Equation (3) is plotted in Figure 4 and is in excellent agreement with our experimental data.

Cold DOP aerosol was used to determine the collection efficiency of small and large sodium carbonate pellets and the results are shown in Figures 6 and 7 as a function of superficial velocity. For the large pellets, a maximum penetration was detected at about 20 fpm. No maximum was evident for the small pellets in the range of velocities studied.

Cocurrent Moving Bed Granular Filter

The experimental bench scale, cocurrent moving bed granular filter is shown schematically in Figure 8. Sodium carbonate pellets moved downward by gravity through a two-inch diameter glass column. Dirty gas entered the filter at the top of the bed and flowed cocurrent with the pellets. A large funnel served as a pellet feed hopper. The length of the funnel stem protruding into the column was adjustable to give various bed heights. Another funnel served as a gas-pellet separation section. Spent pellets were discharged to a hopper and pellet flow rate was controlled by a rotating drum located in the spent pellet hopper. The distance between the drum and the pellet outlet port and the speed of the drum motor determined the pellet flow rate.

To minimize end effects, the cross-section of the feed hopper

outlet was small compared to the column cross-section and the separation section cross-section was large compared to that of the glass column. Because of its unique geometry, the bottom of the bed was a combination of cocurrent, countercurrent, and cross-flow.

The moving bed granular filter was operated at a superficial gas velocity of 20 fpm, a pellet velocity of 0.016 fpm, and an inlet fly ash concentration of 18 grains/ft<sup>3</sup>. The size distribution of the fly ash is shown in Figure 1. Pressure drop and DOP penetration as a function of time of operation are shown in Figure 9. The pressure drop increased from an initial value of 1.0 to 10 in. w.g. in about 25 minutes, after which it remained essentially constant. For plug flow of the pellets, steady-state conditions should be reached after 21 minutes (i.e., bed length divided by pellet velocity).

A relatively high pellet velocity (0.016 fpm) was required to attain steady-state conditions in a short period of time and it became necessary to use a very high inlet fly ash loading (18 grains/ft<sup>3</sup>) to provide an adequate steady-state collection efficiency. At steady-state conditions, the percentage of fly ash in the pellet bed, which depends only on the fly ash feed rate and pellet velocity, was 5.2 wt.%. If the same steady-state value were obtained at lower inlet fly ash concentration and lower pellet velocity, the steady-state efficiency and pressure drop would remain essentially unchanged assuming the effect of dust loading on collection efficiency is minimal.

The fly ash penetration was extremely low for the entire run. ( $\leq 0.02$  wt. %) Inasmuch as pulverized coal fly ash contains many large particles that are relatively easy to collect, the penetration of weight would be expected to be low. DOP penetration, which provides a more severe test of filter efficiency, gave considerably higher penetration values, as shown in Figure 9. DOP penetration decreased from an initial value of 55% for a clean pellet bed to 2% after the pellet bed reached steady-state conditions.

#### Cross-Flow Moving Bed Filter

A schematic diagram of an experimental cross-flow moving bed granular filter is shown in Figure 10. The filter consisted of a rectangular "cross" in which the pellet bed moved downward by gravity and the gas flowed horizontally. The upper portion of the "cross" served as a pellet feed hopper. A shielded glass window installed in the vertical section of the "cross" permitted a view of the motion of the pellets. Pellet flow was controlled by a motor-driven rotating drum. This cross-flow moving bed granular filter was operated at a superficial gas velocity of 20 fpm, a pellet velocity of 0.006 fpm, and a fly ash concentration of 9 grains/ft<sup>3</sup>.

Neither pressure drop across the filter nor DOP penetration equilibrated with time because an air pocket formed in the pellet bed after about 10 minutes. The pocket was first detected at the base of the upstream side of the filter (labeled "A" in Figure 10) but, with time, the pocket grew until it reached across the entire filter and the pellets above the plane labeled "B" in Figure 10 no longer flowed downward. Nevertheless, pellets continued to be

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removed at a steady rate by the rotating drum and a fly ash filter cake was clearly visible at the boundary of the air pocket. It was found that when the unit was operated at the same gas flow rate but with dust free air, the pellets moved steadily, with no gas pocket formation. At first, it was believed that the fly ash cemented the pellets together, preventing further motion, but this is incorrect because the pellets fall and fill the air pocket when air flow is discontinued. Therefore, it was concluded that the pressure drop across the fly ash cake is sufficiently large to support the pellets.

Because the pellets flowed freely when clean air was passed through the filter a test was made using lower fly ash concentrations but reducing the fly ash concentration to 1 grain/ft<sup>3</sup> had little beneficial effect. Oven dried pellets gave similar results.

As it seemed likely that the pressure drop across the dirty pellets was sufficiently large to support the pellets, the apparatus was modified so that the gas entered the filter at a higher elevation than it exits but an air pocket still formed in the pellet bed. A heavy-duty vibrator was strapped to the pellet bed housing, but it, too, yielded no improvement. Apparently the dirty pellets arranged themselves in such manner that an upward component of the pressure drop still supported part of the pellet bed. Similar results were obtained for both large and small pellets.

### Discussion

Air pockets form in that portion of a cross-flow granular bed in which fly ash has deposited and the pellets no longer flow. When pellets move cocurrent with air flow, fly ash deposition on the pellets will not inhibit their movement, but scale-up of a unit to operating size (3500 ACFM) would be difficult. If the volumetric flow rate were to be increased by increasing the cross-sectional area of the bed, the length to diameter ratio would become very small and when the L/D ratio becomes very much less than one, "ratholing" occurs, whereby the pellets do not move in plug flow fashion. Also, pellet addition to and removal from a cocurrent pellet bed becomes particularly troublesome. Our bench scale moving bed filter has a L/D ratio of two and a volumetric flow rate of about 0.5 ACFM. It is unlikely that this ratio can be decreased very much without degrading the operation of the filter. If the length of the bed is significantly increased to compensate for an increase in diameter, the pressure drop even for a clean pellet bed would become excessive. Hence, it would be necessary to modify the cocurrent moving bed filter shown in figure 8 if a full scale unit were constructed.

### IV. Summary and Conclusions

Laboratory studies of filter aids for sintered metal filters have demonstrated their ability to protect the porous metal structure from permanent plugging with products contained in incinerator off-gases. In addition, they have shown that the use of appropriate filter aids can greatly reduce penetration of particulate matter through sintered metal filters and, thereby, provide added protection for heat exchangers and absolute filters downstream of the sintered metal filters.

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Moving bed granular filters have excellent characteristics for incinerator offgas treatment, i.e., they operate at constant gas flow resistance, have high temperature tolerance, can store large amounts of dust in the pores of the bed with low pressure drop increase, and are capable of high collection efficiency. For all of these reasons, they have good potential for use in conventional high temperature incinerators as well as for low temperature fluidized bed units.

### Acknowledgement

This work was supported by Contract E(11-1)-3049 from the Energy Research and Development Administration.

Table I. Cold DOP Penetration.

<u>Filter Aid</u>	<u>Sintered Metal Filter Condition</u>		
	<u>After Cleaning</u>	<u>After Filter Aid Additions*</u>	<u>After Filter Aid Plus Fly Ash Additions**</u>
Asbestos Floats	90%	0.4%	0.01%
Diatomaceous Earth	80%	0.3%	0.10%

\*Filter aid added until pressure drop of clean sintered metal filters increased 4 in. w.g.

\*\*Cottrell-precipitated pulverized coal fly ash added on top of the filter aid until total pressure drop reached 20 in. w.g.

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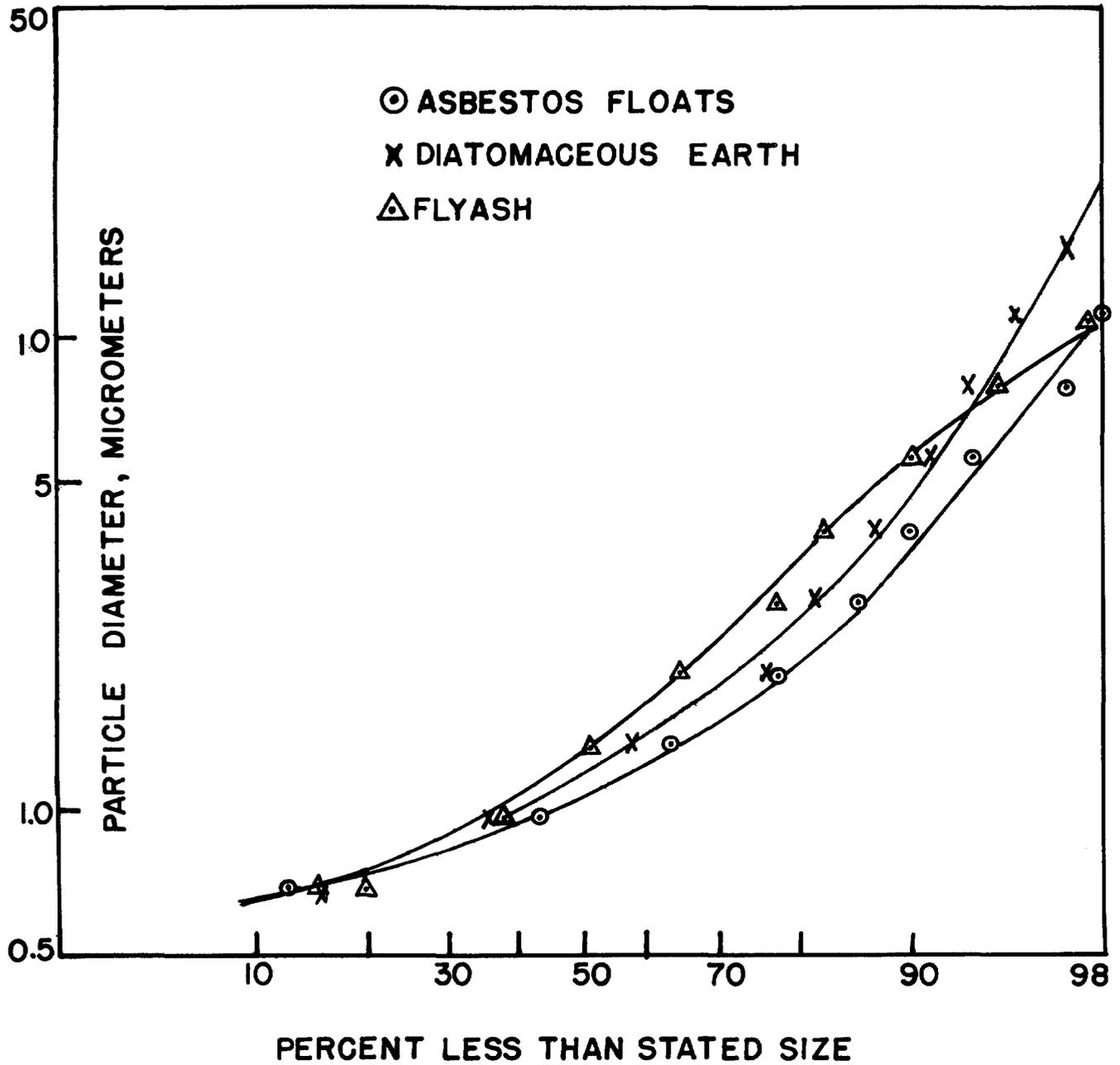
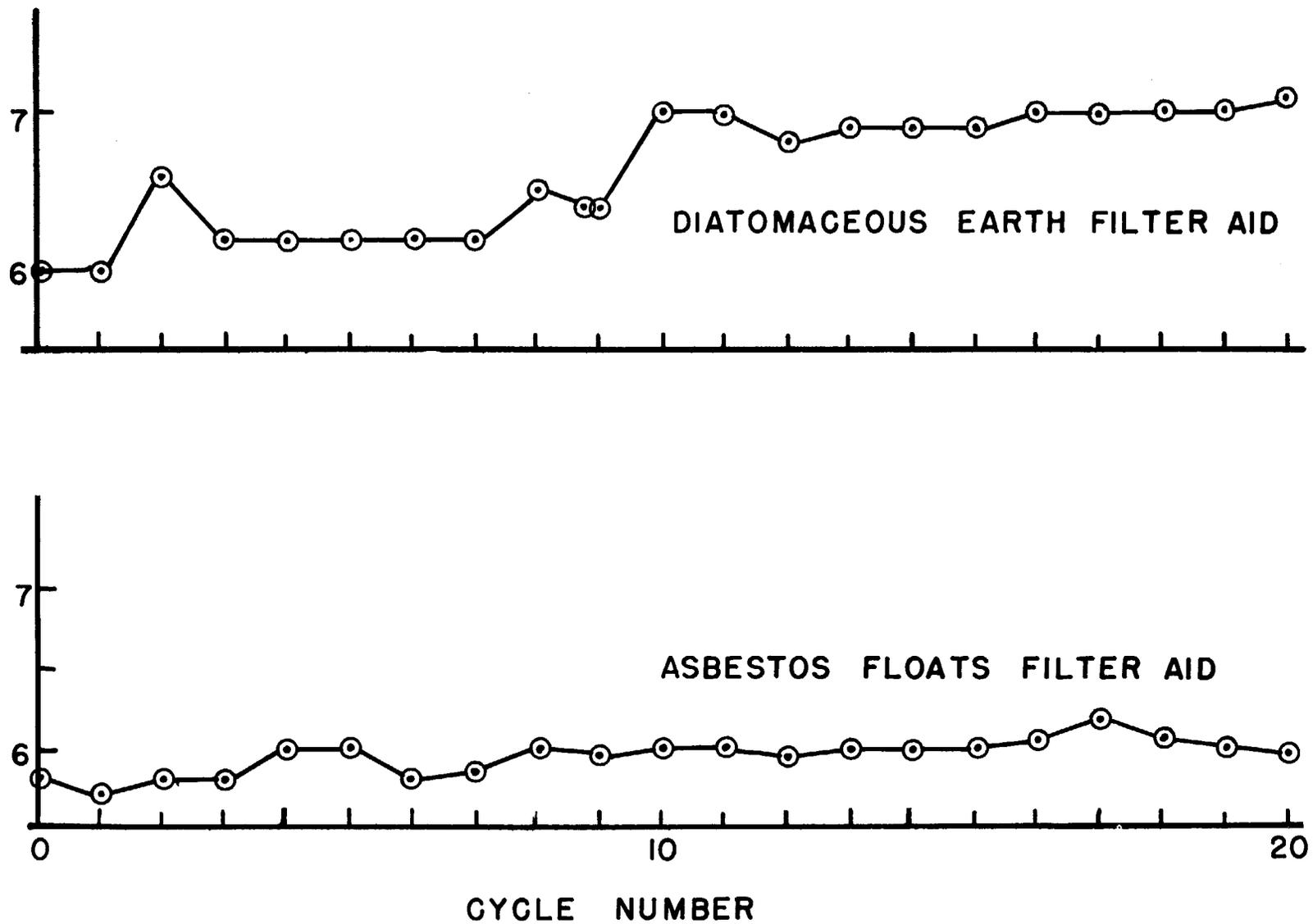


FIGURE 1 CUMULATIVE SIZE DISTRIBUTIONS BY COUNT FOR ASBESTOS FLOATS, DIATOMACEOUS EARTH AND FLY ASH.

RESIDUAL PRESSURE DROP, INCHES OF WATER GAUGE

FIGURE 2 RESIDUAL PRESSURE DROP AFTER CLEANING, DIATOMACEOUS EARTH FILTER AID (ABOVE) ASBESTOS FLOATS FILTER AID (BELOW)



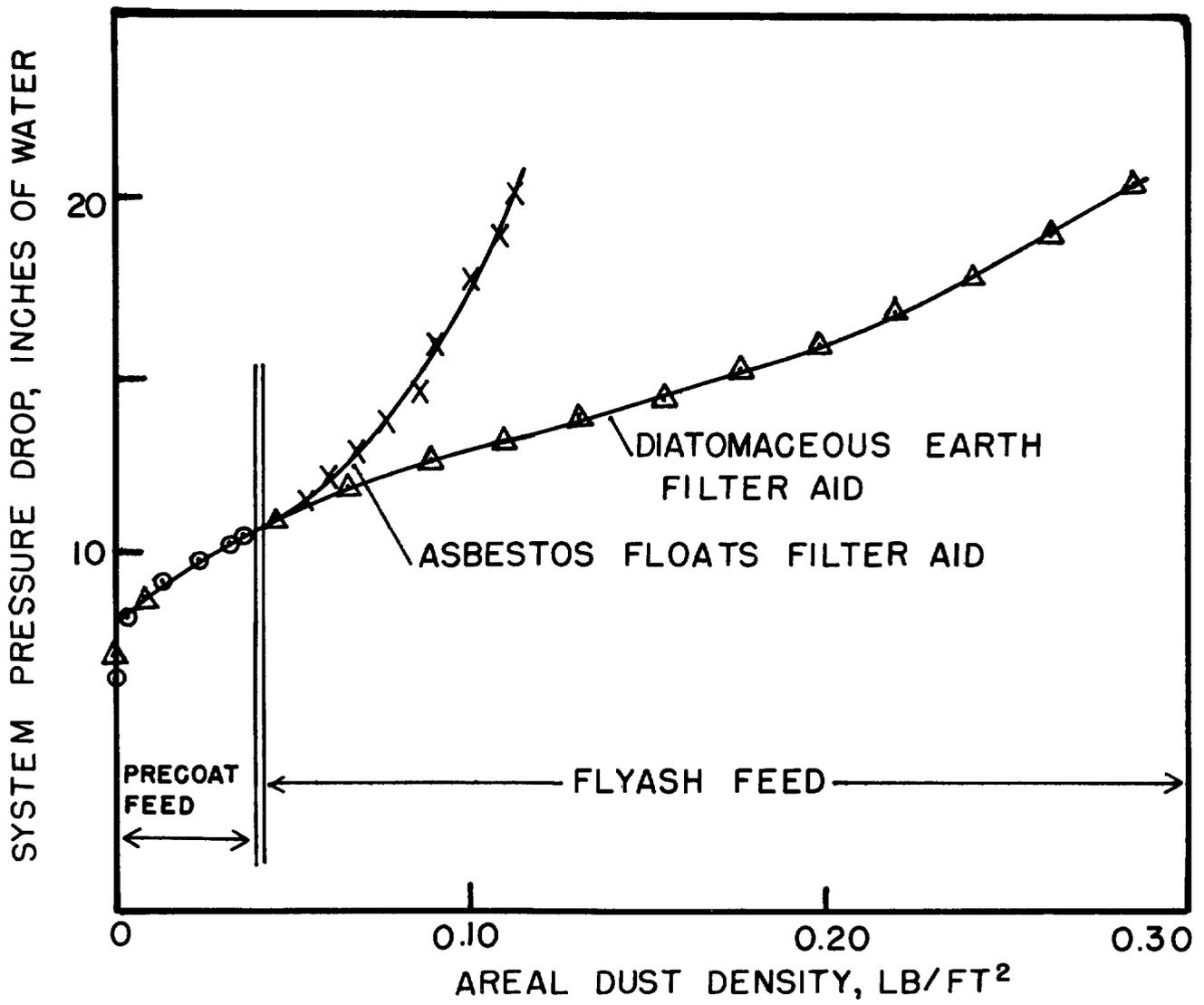


FIGURE 3 PRESSURE DROP VS AREAL DENSITY FOR FILTERS PRECOATED WITH ASBESTOS FLOATS AND DIATOMACEOUS EARTH.

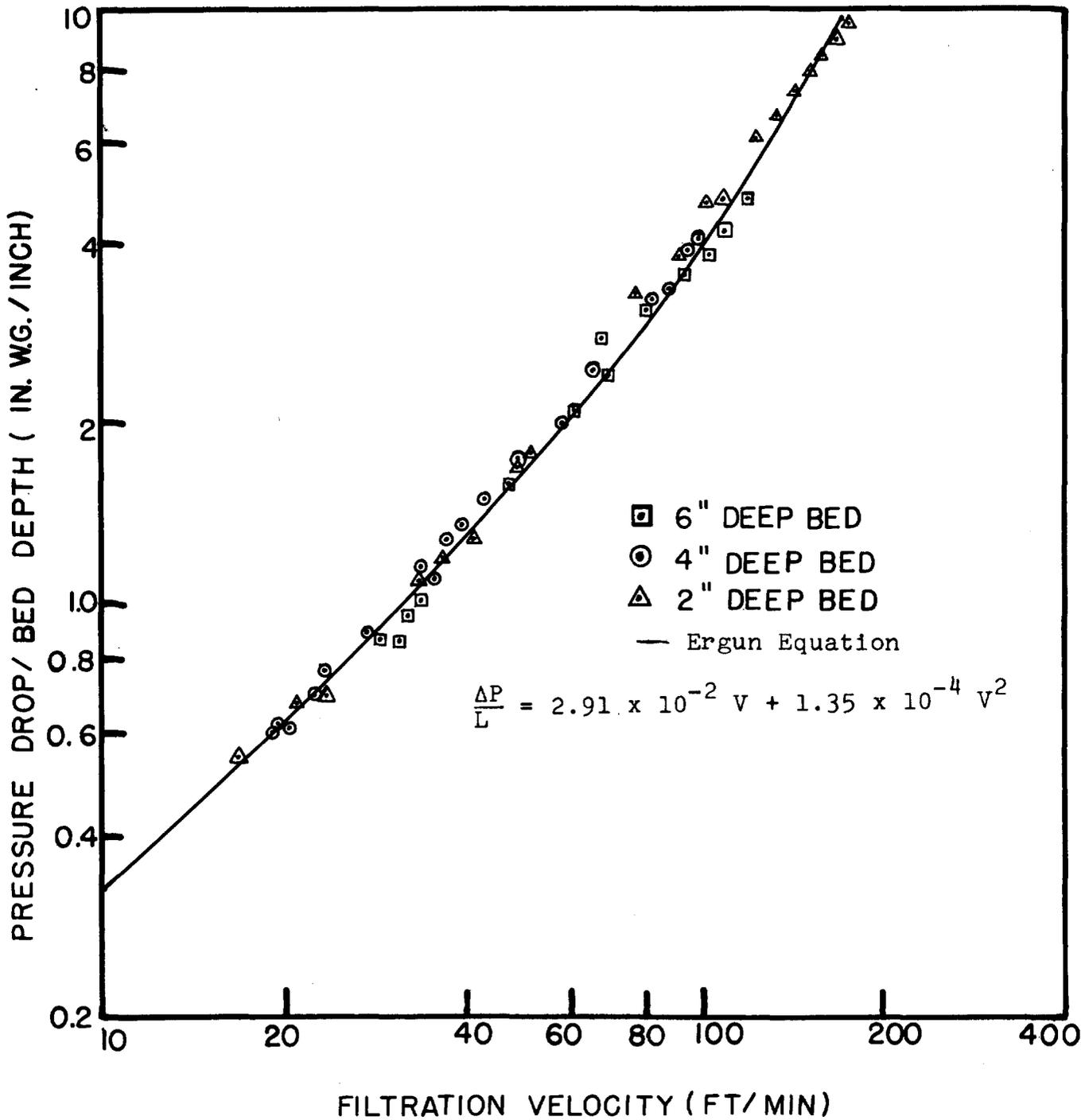


FIGURE 4 PRESSURE DROP PER UNIT BED DEPTH VS FILTRATION VELOCITY, LARGER  $\text{Na}_2\text{CO}_3$  PELLETS, FIXED BED.

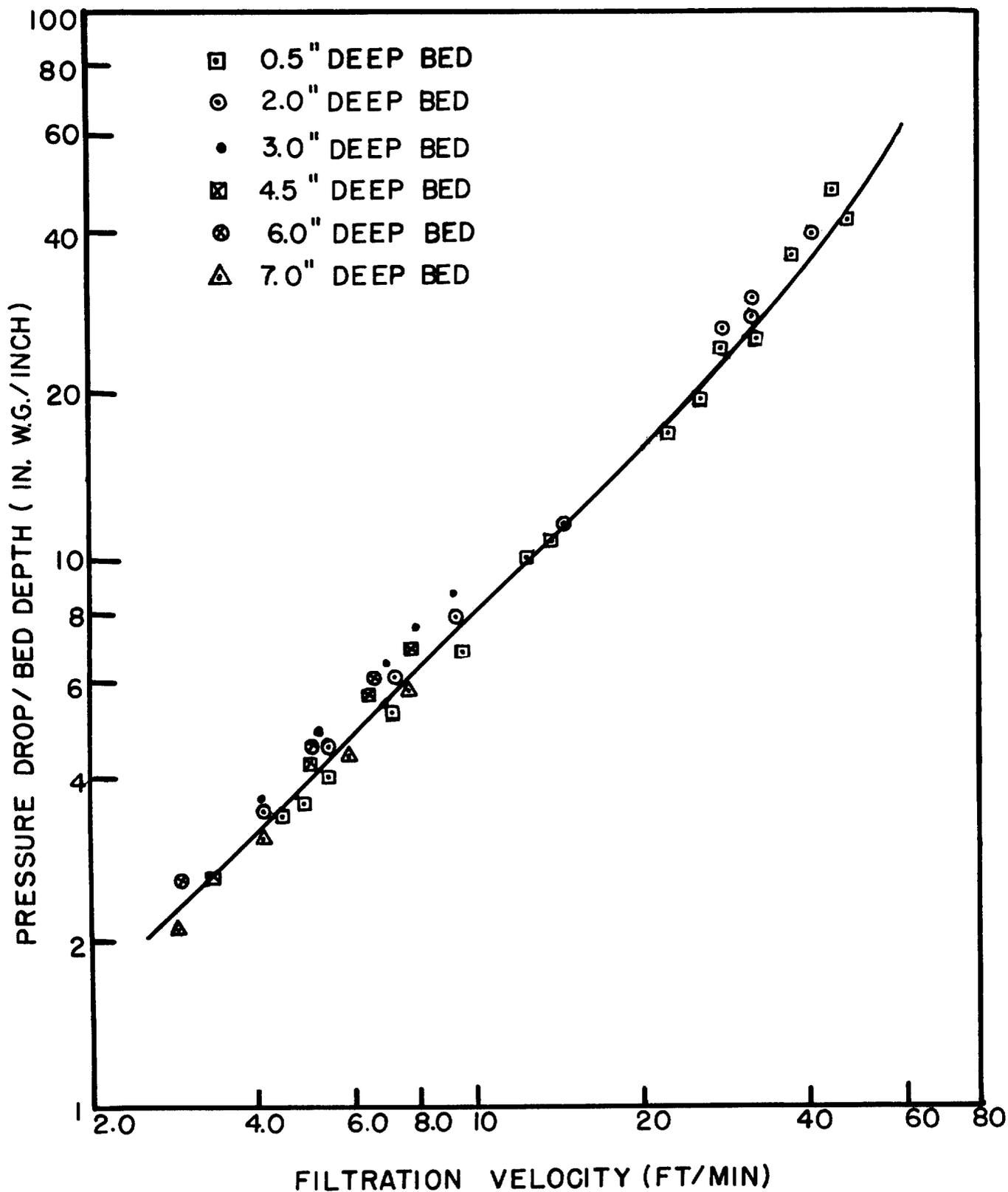


FIGURE 5 PRESSURE DROP PER UNIT BED DEPTH VS FILTRATION VELOCITY, SMALLER  $\text{Na}_2\text{CO}_3$  PELLETS, FIXED BED.

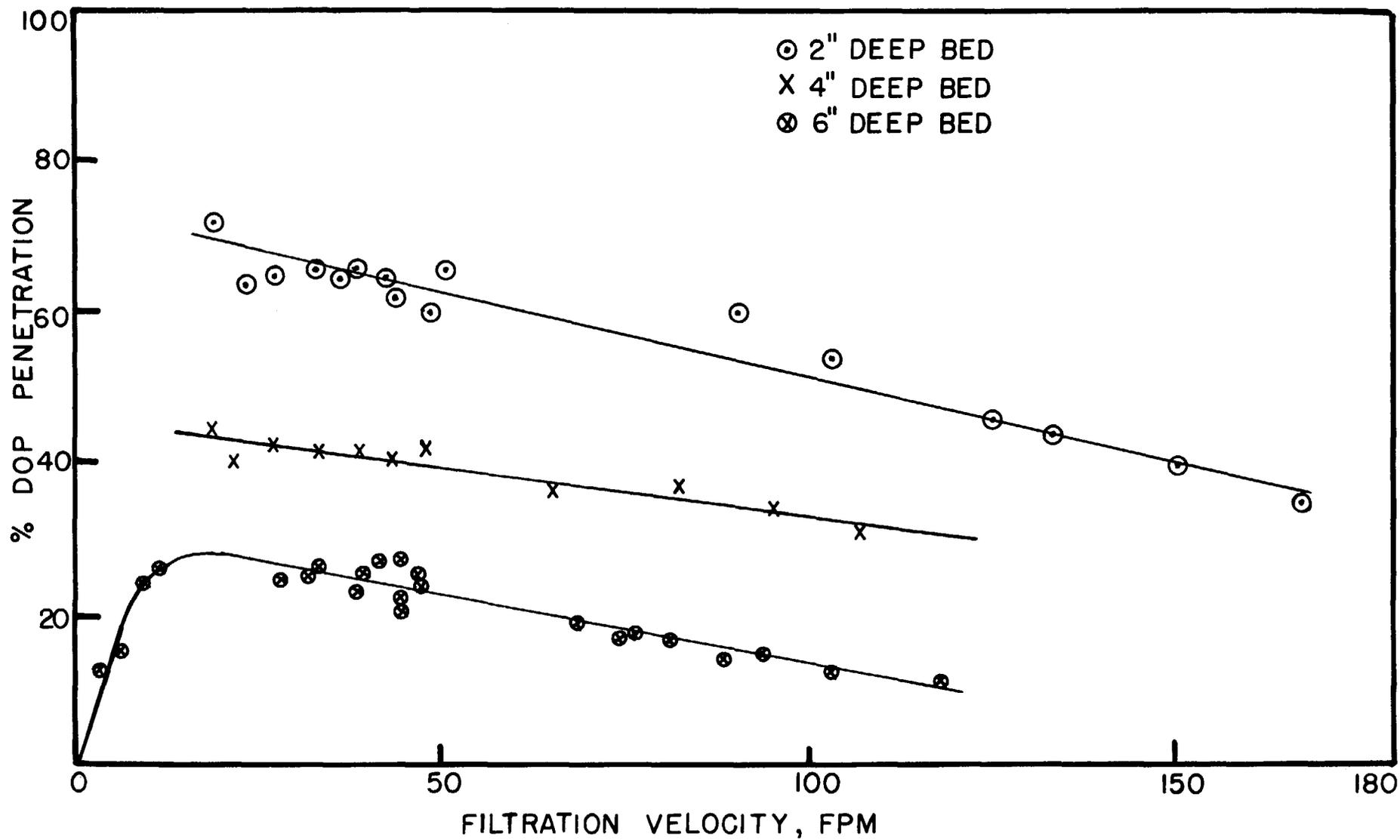


FIGURE 6 COLD DOP PENETRATION VS FILTRATION VELOCITY, BEDS OF LARGER  $\text{Na}_2\text{CO}_3$  PELLETS.

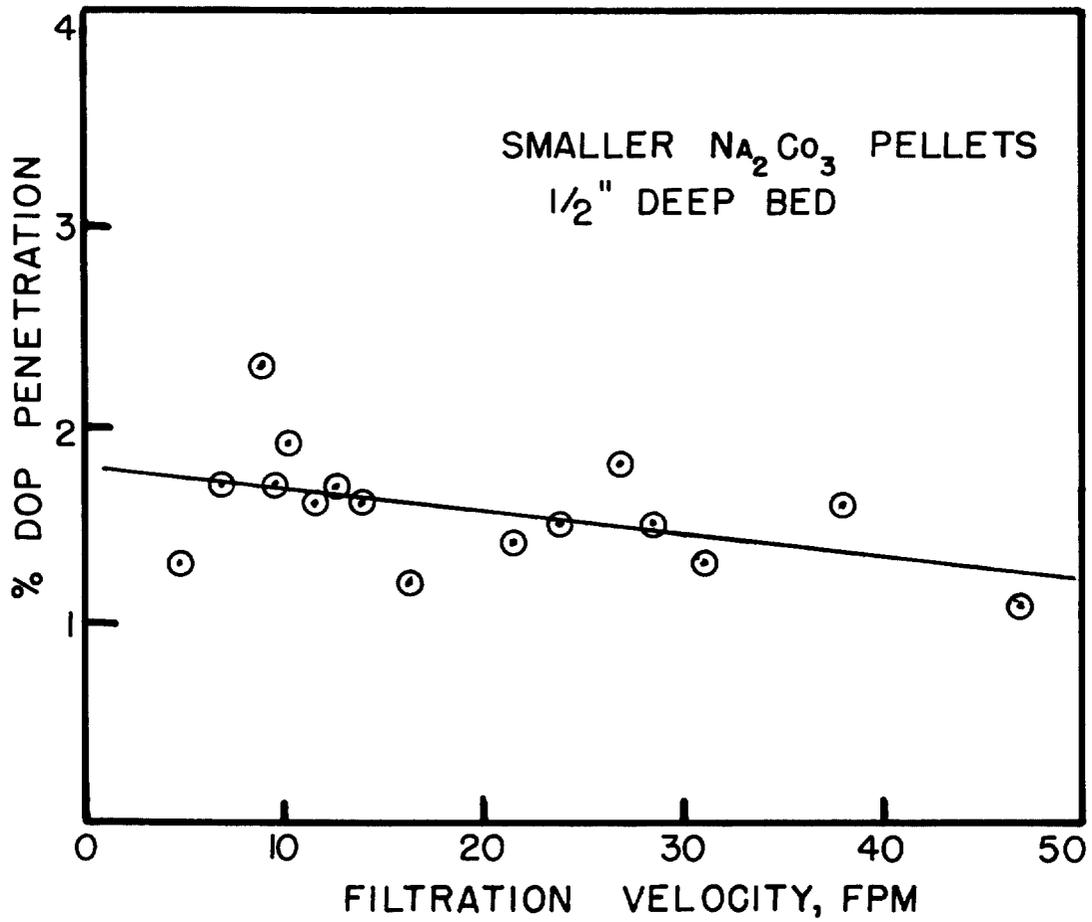


FIGURE 7 COLD DOP PENETRATION VS FILTRATION VELOCITY, BED OF SMALLER  $\text{Na}_2\text{CO}_3$  PELLETS.

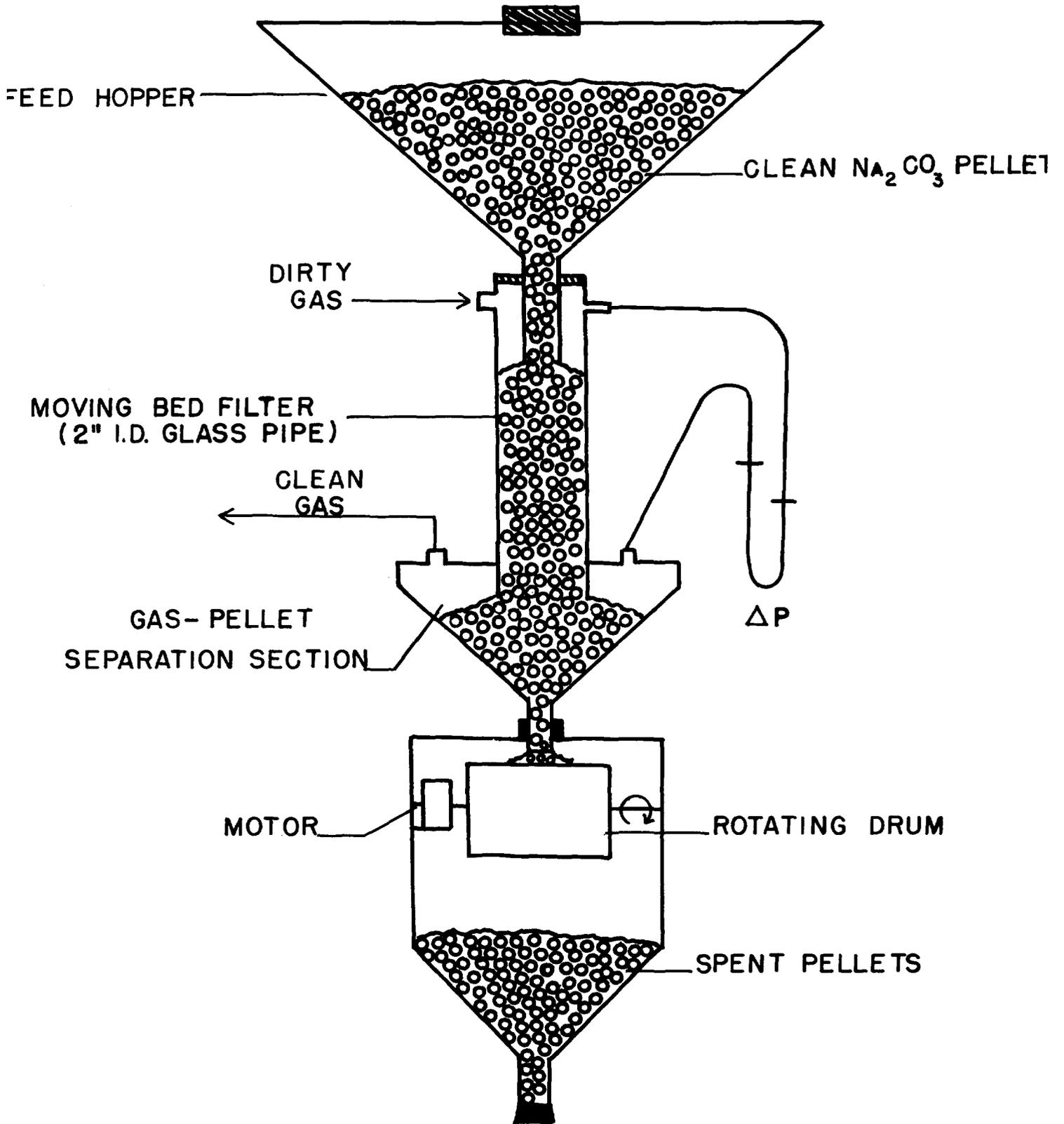


FIGURE 8 Cocurrent moving bed filter.

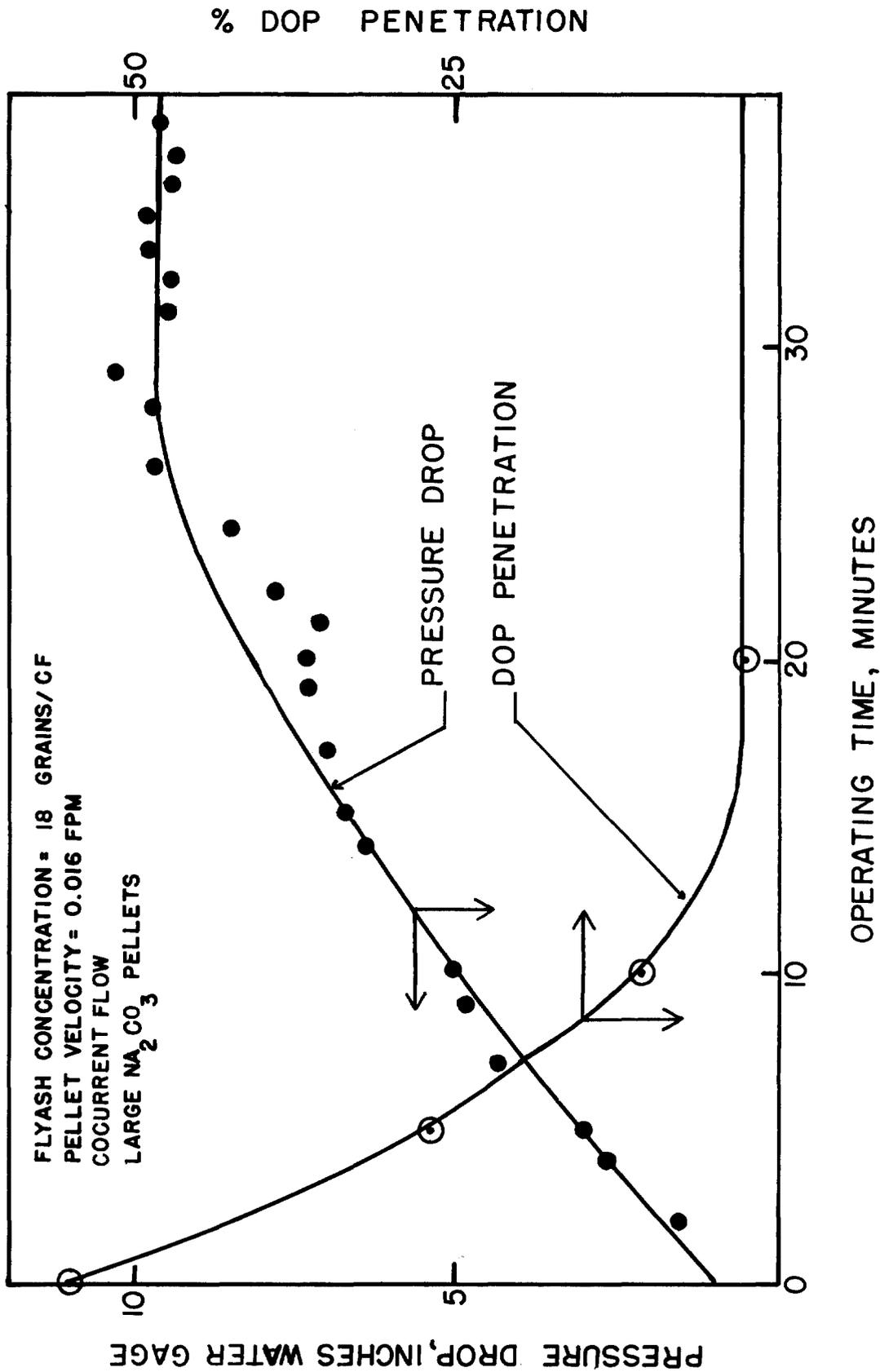


FIGURE 9 PRESSURE DROP AND COLD DOP PENETRATION VS TIME, COCURRENT MOVING BED FILTER

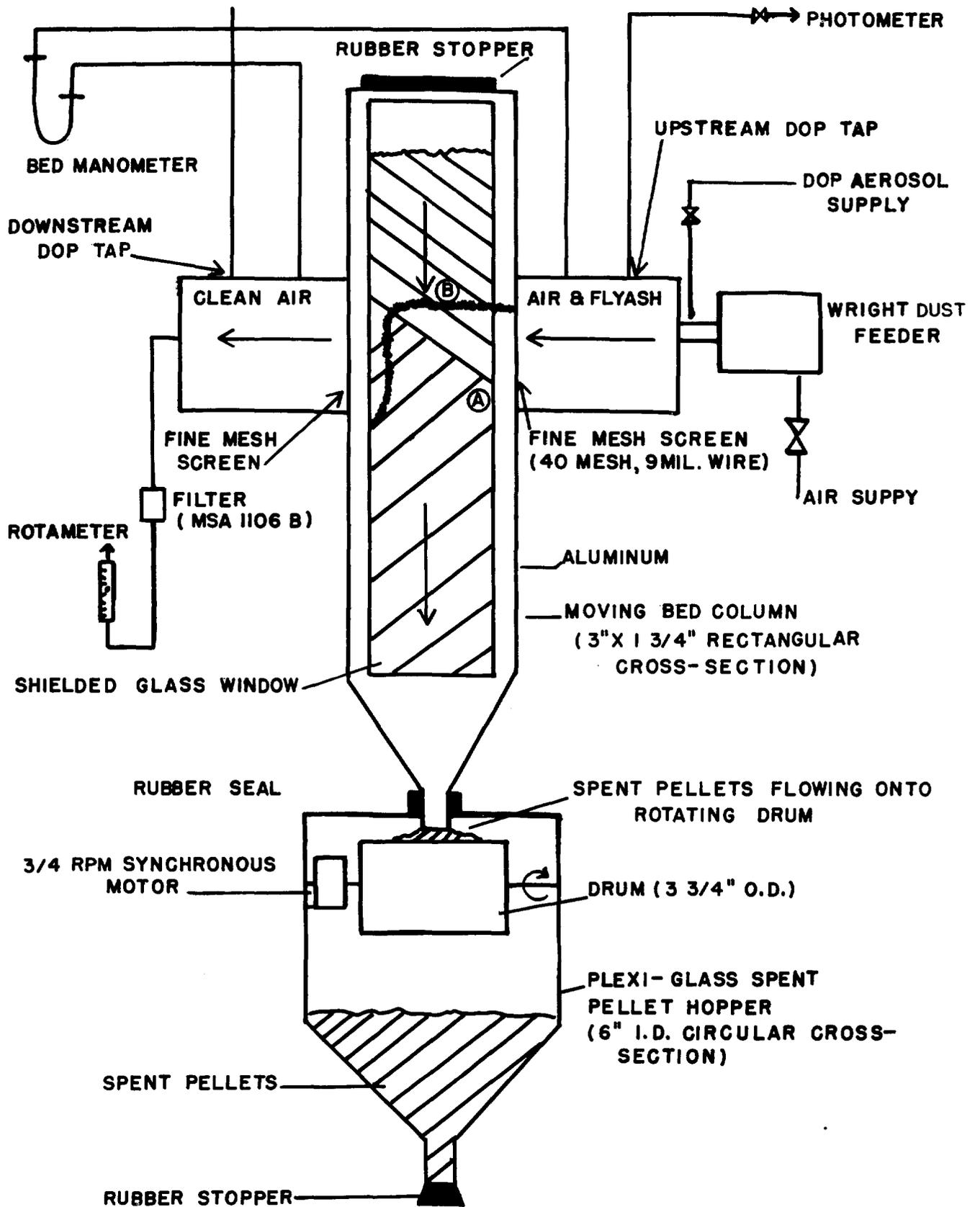


FIGURE 10 CROSSCURRENT MOVING BED FILTER

DISCUSSION

NOTZ: Why did you not test a countercurrent moving bed?

LEITH: The chief problem with a countercurrent bed is that if the gas velocity and pressure drop across it become too high, the bed can fluidize. We did not want to fluidize the bed.

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### DESIGN OF OFF-GAS CLEANING SYSTEMS FOR HIGH-LEVEL WASTE VITRIFICATION\*

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#### Abstract

Vitrification of high-level waste to a glassy or ceramic form is being evaluated as a method for final control of high-level nuclear wastes. During vitrification other lower level effluent streams are generated. To obtain complete control of high-level nuclear wastes, all effluent streams from the vitrification system must also be controlled. Off-gas cleanup for the vitrification system poses special problems. The cleanup system must be capable of meeting stringent regulations on both radioactive and nonradioactive pollutants.

High-level wastes are generally nitric acid solutions. Vitrification converts the nitrate salts to oxides, forming nitrogen oxides ( $\text{NO}_x$ ) as a by-product. These  $\text{NO}_x$  releases can be controlled by nitric acid recovery or by conversion of the  $\text{NO}_x$  to an acceptable species for release, such as  $\text{N}_2\text{O}$  or  $\text{N}_2$ . The off-gas system must also be capable of controlling any fission products which may be volatilized in appreciable quantities and may be controlled in the off-gas system by absorption or adsorption. Whichever method is used, the recovered fission products must somehow be converted to a safe disposal form. Proposed off-gas systems are described, and areas requiring research and development are discussed.

#### Introduction

Vitrification of high-level waste to a glassy or ceramic form is being evaluated as a method for final control of high-level nuclear wastes. High-level waste is the concentrated remains of chemical solutions used in the reprocessing of nuclear fuels, and contains virtually 100% of the fission products. Although the solutions are aqueous, they do contain undissolved material. Fission products are distributed in both phases.

The conversion of high-level aqueous wastes to solids results in one or more effluent streams with lower levels of activity. The radioactive content of these effluents must be reduced to low levels so that they can be discharged safely. Thus, auxiliary equipment supporting the waste solidification system must be designed to assure sufficient decontamination of effluent streams. Off-gas cleanup must be of sufficient quality to allow the cleaned gas to be released to the atmosphere. Further, the system must be capable of meeting stringent release regulations on both radioactive and nonradioactive constituents.

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\*Work performed under ERDA Contract E(45-1):1830.

\*\*Presently employed at Atlantic Richfield Hanford Company,  
Richland, Washington.

One requirement for the design of the off-gas system is the sufficient cleanup of off-gas to ensure safe operation of the facility. The off-gas system designs depend on many variables: design and operating philosophy, types of solidification equipment, high-level waste composition, allowable release limits, etc. The system can be designed for acid recovery or destruction and many options are available for fission product control.

### Process Description

High-level aqueous wastes are generally nitrate salts in nitric acid ( $\text{HNO}_3$ ) solutions. The wastes are the aqueous raffinate from the first solvent extraction step in the Purex process and contain undissolved solids. Fission products are distributed in both the liquid and solid phases. Solidification of these aqueous wastes to insoluble products involves heating the wastes to temperatures above the decomposition temperature of the nitrate salts. This is accomplished by atomizing the waste in a calciner. Various types of calciners are being developed although only two types will be discussed: indirect- and combustion-heated calciners. In an indirect-heated calciner the energy for calcination is provided by resistance or induction electrical heating. A method of indirect heat calcination is spray calcination, in which the high-level waste is atomized into an electrically heated chamber (see Figure 1). In a combustion heated calciner such as a fluidized bed (Figure 2) the energy is provided by the combustion of an organic fuel such as kerosene. Calcining is usually

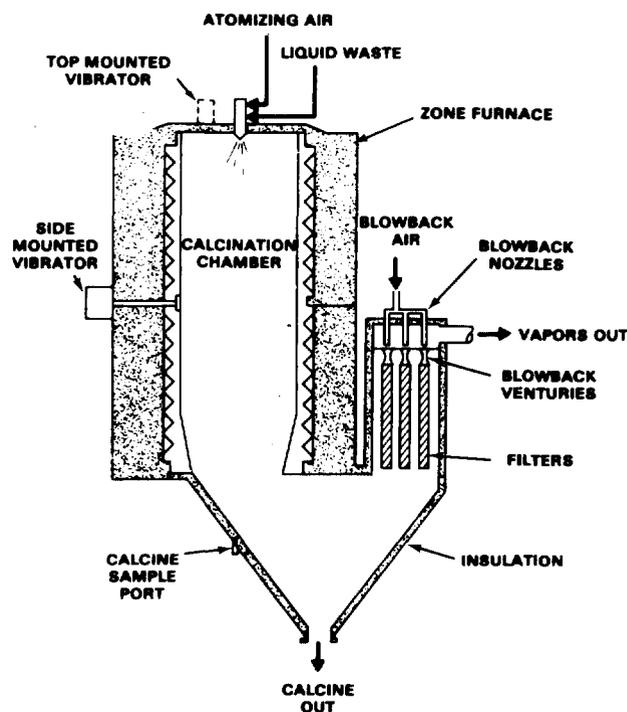


Figure 1 Spray calciner.

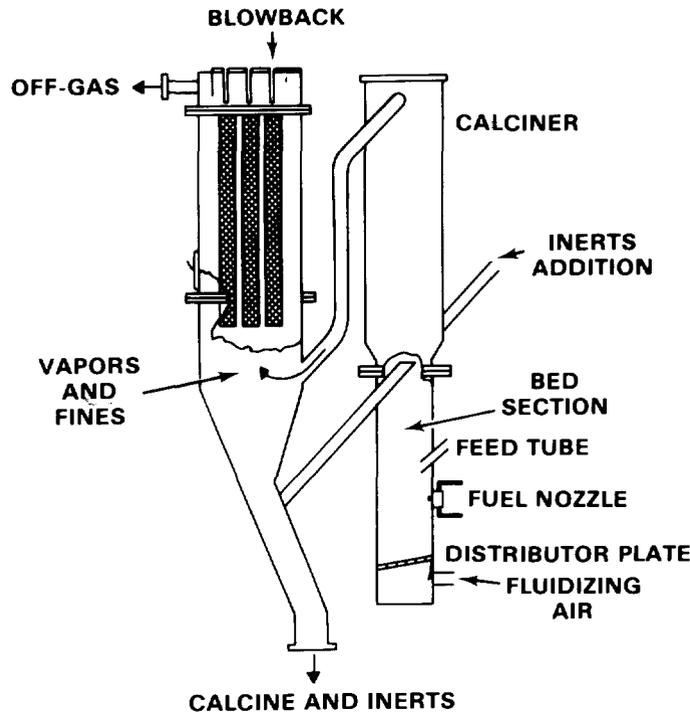


Figure 2 Fluidized bed calciner.

done at a temperature of approximately 500°C. After calcination, the waste is combined with glass-forming materials and falls into a melter where this glass is melted and the waste (now in oxide form) goes into solution with the glass. Melting takes place at approximately 1000°C and the energy for melting is provided by resistance induction, or joule heating (see Figures 3 and 4). Off-gases from the melting process generally pass back into the calciner chamber. These combined melter-calciner off-gases consist of H<sub>2</sub>O, nitrogen oxides (NO<sub>x</sub>), air, and small amounts of fission products which may be volatilized. As the gas passes through the calcining chamber a large portion of the calcine is entrained. This entrained calcine is then collected on porous sintered metal filters while the process off-gas passes through to the cleanup system. The calcine deposits are periodically blown off the filters by pulses of high-pressure air directed back into the filters by small venturi-type nozzles. The dislodged calcine then falls back into the calciner-melter for processing.

#### Normal Off-Gas Quantities and Compositions

A 1500-MTU\*/yr fuel reprocessing plant will have a typical high-level waste concentration of approximately 378 l/MTU after evaporation. This results in  $5.67 \times 10^5$  l of high-level waste to be processed per year. For an operating time of 300 days/yr, the vitrification facility must process about 80 l/hr of waste. At a feed rate

\*Metric tonnes uranium.

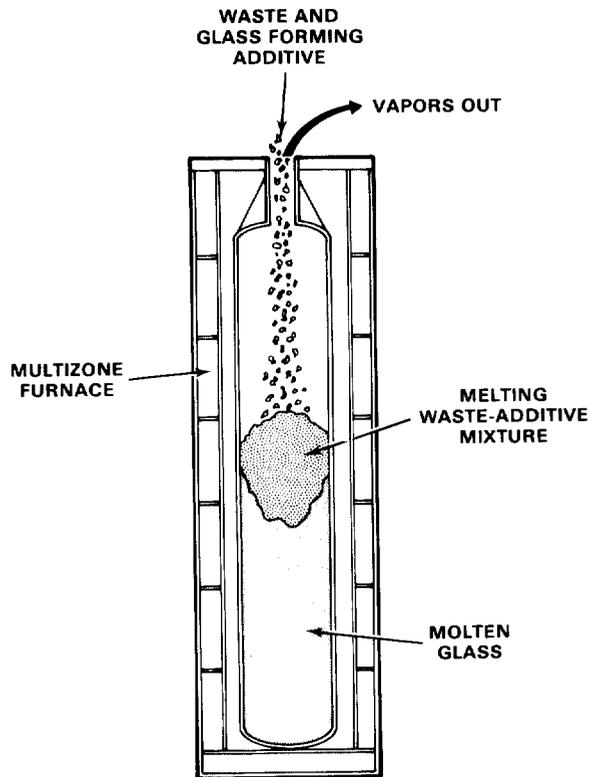


Figure 3 Resistance or induction heated in-canister melter.

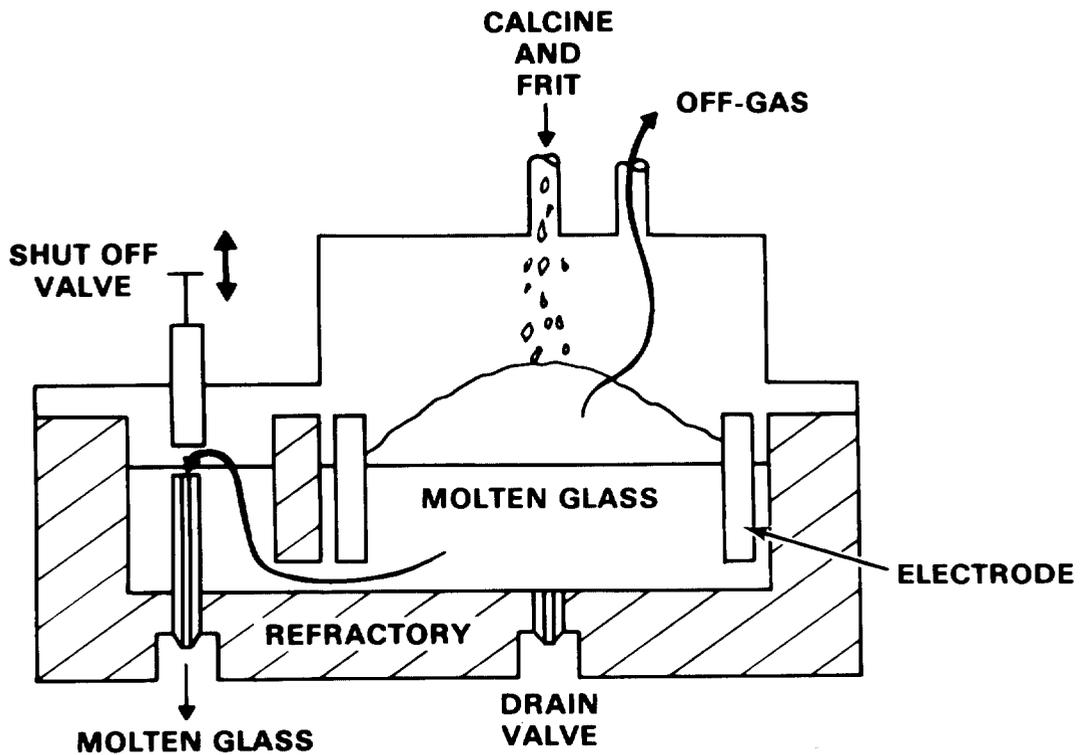


Figure 4 Joule heated ceramic melter.

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of 80  $\ell$ /hr the off-gas quantity will be approximately 176 actual cubic feet per minute (ACFM) at 350°C and -20 in. H<sub>2</sub>O pressure (about 132 ACFM off-gas/ $\ell$  of feed at these conditions).

Of the 176 ACFM gas produced, about 25 ACFM will be noncondensable with the remainder condensable, mainly steam and NO<sub>x</sub>. The volatilized fission products are of extremely small volume when compared to the total volume of gas. As can be seen in Table I, the gas consists mainly of steam, NO<sub>x</sub>, and air. The steam and the NO<sub>x</sub> are from evaporation and the decomposition of the nitrate salts in the waste while the air is from the pneumatic atomization of the feed as well as from other sources. For example, air may be used for the fluidizing medium in the fluidized bed calciner. Another source of air in the off-gas is inleakage. Since the calciners are operated at less than atmospheric pressure for safety considerations, some air will leak into the system through gaskets and connections.

Table I Typical off-gas composition.\*

	Indirect Heating, mole %**	Combustion Heating, mole %
N <sub>2</sub>	49.0	46.2
NO <sub>x</sub> <sup>†</sup>	<0.1	0.3
N <sub>2</sub> O	0.1	0.09
H <sub>2</sub> O	35.0	35.0
O <sub>2</sub>	15.2	10.4
CO <sub>2</sub>	--	7.4
CO	<0.07	0.6
CH <sub>4</sub>	--	0.01

\*Excluding fission products

\*\*Resistance or induction

†Includes N<sub>2</sub>O<sub>4</sub>

An important constituent of the off-gas is the very small amounts of fission products which may be volatilized or entrained as particulate or droplets in the gas stream. The fission products of particular concern are ruthenium, iodine, and cesium while other potentially troublesome fission products include tellurium and selenium. The following discussions will use fission products levels at discharge of fuel to be conservative. In an actual facility, the waste will be aged and the fission product activities will be lower.

It can safely be assumed that all of the iodine in the high-level waste will pass through the solidification system to the off-gas cleanup system. The high level waste contains about 2% of the iodine in the spent fuel. The waste from a pressurized water reactor (PWR) fuel of 33,000-MWd/MTU burnup at 30-MW power will contain about 5.5 g/MTU of iodine (2.34 x 10<sup>5</sup> Ci/MTU).<sup>(1)</sup> At the previously discussed conditions a processing rate of 80  $\ell$ /hr will therefore give

1.16 g/hr ( $4.95 \times 10^4$  Ci/hr) of iodine being discharged to the off-gas system. Since these levels are at discharge, and it is highly improbable that any fuel this fresh will be processed, a more realistic set of values can be found by discounting the activity of the short half-life isotope  $^{131}\text{I}$  (half-life of 8.041 day). Discounting this activity (using a waste age of one year) gives to the off-gas system an activity of  $1.59 \times 10^{-4}$  curies/hr of iodine.

Ruthenium volatility varies widely depending upon the process, the product, and the operating conditions. The formation of borosilicate glass from waste using spray calcination and in-canister melting in the WSEP program<sup>(2)</sup> indicated less than 2% ruthenium volatilities. A typical number of 1% ruthenium volatilization will be used in following discussions. The waste from PWR fuel of 33,000-MWd/MTU burnup at 30-MW power will contain about  $2.35 \times 10^3$  g/MTU<sup>(1)</sup> ( $3.71 \times 10^6$  Ci/MTU) of ruthenium. Given the previously discussed conditions and a processing rate of 80 g/hr of waste with 1% losses from the calciner, 4.97 g/hr ( $7.85 \times 10^3$  Ci/hr) of ruthenium will go to the off-gas system.

Cesium losses from volatilization ranged from 0.002 to 0.07% in the WSEP program.<sup>(2)</sup> With 0.07% losses and the same conditions used in the iodine and ruthenium discussions, about 0.4 g/hr ( $1.04 \times 10^3$  Ci/hr) of cesium will go to the off-gas system. Volatility of tellerium and selenium will probably be very low<sup>(2)</sup> and these materials are only mentioned because of their potential to cause problems.

It is assumed that the entrained particulate is a mixture of all the fission products present in the feed excluding the gases (hydrogen, iodine and the noble gases) and the volatilized elements previously discussed. With a conservative vitrification system particulate DF\* of  $10^3$ ,<sup>(3)</sup> approximately  $2.43 \times 10^4$  Ci/hr of particulate will go to the off-gas system.

In summary, Table II shows the typical amounts of fission products leaving the calciner-melter filters and going to the off-gas system. The degree of decontamination required prior to release is based upon the amount of the isotope present and on the established effluent limit. However, allowable release rates are not well defined in today's licensing environment. The allowable release

Table II Fission products going to off-gas cleanup system.\*

<u>Element</u>	<u>Amount, g/hr</u>	<u>Activity, Ci/hr</u>
I	1.16	$4.95 \times 10^4$
Ru	4.97	$7.85 \times 10^3$
Cs	0.4	$1.04 \times 10^3$
Other (Particulate)	--	$2.43 \times 10^4$

\*PWR fuel 33,000 MWd/MTU, 30 MW, 3.3% enriched uranium, at discharge.

\*Decontamination factor, as used in this paper, is defined as the ratio of the activity per unit time in the dirty effluent to the activity per unit time in the clean effluent leaving a given unit.

limits were estimated as follows. The 10 CFR-20 limit may be applied to the stack concentration. Since the solidification process is only a part of the whole reprocessing system, its effluents should not represent more than 10% of the allowable limit. The release limit is further reduced for individual isotopes because the limit applies to the total release. Since several isotopes may be present in comparable concentrations the limit for each is somewhat arbitrarily set at 20% of the total. From these factors the allowable stack concentration is 2% of the 10 CFR-20 limit. The DF requirements, based on a stack flow rate of 50,000 cfm, are shown in Table III.

Table III DF requirements for critical isotopes.

<u>Isotope</u>	<u>DF at 6 Months</u>	<u>DF at 2 Years</u>
I - 129	2500	2500
Ru - 106	$2.5 \times 10^{11}$	$0.9 \times 10^{11}$
Cs - 137	$6 \times 10^{10}$	$3.5 \times 10^{11}$
Particulate	$1 \times 10^{12}$	$1 \times 10^{12}$

### Off-Gas System Design

The off-gas cleanup equipment supporting the waste solidification system must be designed to assure sufficient decontamination of gaseous effluent streams. The off-gas system must clean the gas sufficiently to meet stringent release regulations on both radioactive and nonradioactive constituents.

Nearly all of the gaseous effluents are condensable. Most that are not can be adsorbed or absorbed (excluding air from atomization, inleakage, etc.). Both condensable and noncondensable streams must be treated to remove radionuclides. The noncondensable streams must be continuously discharged to the atmosphere following treatment. Liquid effluents from the off-gas cleanup system must be treated so they are acceptable for recycle (to a fuel reprocessing plant, for example) or for final release to the environment.

Generally, off-gas cleanup systems can be divided into two categories: with and without acid recovery. Since the aqueous high-level waste is nitric acid based, and the nitrogen oxides from the decomposition of the nitrate salts in the wastes cannot be released to the atmosphere untreated, there is incentive for acid recovery. Also, if the solidification plant is integrated with a fuel reprocessing plant, as will be assumed in this discussion, the recovered acid can be used for fuel dissolution and/or solvent extraction scrub streams. Design of the off-gas cleanup equipment without acid recovery would be reasonable if, for some reason, the acid could not be recycled.

The first stage in the off-gas cleanup is condensation or quenching and, depending upon the type of equipment used, particulate removal. There are two general types of equipment used for the first

stage of cleanup: condensers and scrubbers. The choice would be made depending upon the particular calciner to be used. If the calciner system has potential for high solids loading in the off-gas then an open type scrubber such as a venturi should be used. If the potential for particle loading is low then a shell and tube condenser or a packed bed quench scrubber will be of higher efficiency.

If a shell and tube condenser is used, a single pass with the process fluid on the tubeside allows easy maintenance. Downdraft flow of the vapors in the tubes should be chosen to provide good aerosol de-entrainment, some self-cleaning and good acid absorption. The condenser should be constructed of a highly corrosion resistant material, such as titanium. Shell and tube condensers typically give DFs of  $10^3$  to  $10^4$  for ruthenium and  $10^3$  for particulate. (2,3)

A packed bed type quench scrubber has the advantage of being able to produce high decontamination because of its inherent scrubbing capability. The scrubber can also be divided into two or more sections, accomplishing quenching in one section and scrubbing in another. A packed scrubber has the disadvantages of relatively high pressure drops and plugging potential. Gases entering a packed bed heavily laden with particulate may tend to gum and clog the packing material.

The venturi scrubber can handle relatively high particulate loadings while doing some quenching, and achieves fairly good particulate removal. Acid absorption is not as good as in packed beds. Pressure drop generally varies from high to less than zero depending upon operation (inversely with particulate removal efficiency). Ruthenium DFs of 10 and particulate DFs of 50 to 100 are typical for the venturi scrubber. (4-6)

Of the three pieces of equipment discussed in the previous paragraphs, the venturi scrubber is probably the best choice because of its ability to handle high particulate loadings. In a calciner system using sintered metal filters the possibility of a filter failing does exist. The failure of a filter would allow relatively large volumes of particulate to pass before the equipment could be shut down. If a cyclone separator is used instead of filters, removal efficiency will be normally low. Whenever the possibility of passing large amounts of calcine to the off-gas system does exist, the system should be able to handle it without plugging.

In the next stage of the off-gas cleanup, entrained aerosols are removed. This is accomplished by a knock-out pot or a fiber-type mist eliminator, depending upon what quench technique is used. A venturi would probably require a knock-out pot prior to a mist eliminator to prevent flooding. A mist eliminator type setup will give no volatile ruthenium removal but will give a DF of about  $10^3$  for particulate. (7)

Assuming that a venturi scrubber followed by a knock-out pot are the first and second stages (Figure 5), the next item in the off-gas train is a condenser which will remove any condensables left after the venturi quenching. This condenser will be similar to the one previously described: a single-pass, downdraft shell and tube condenser with the process fluid on the tubeside.

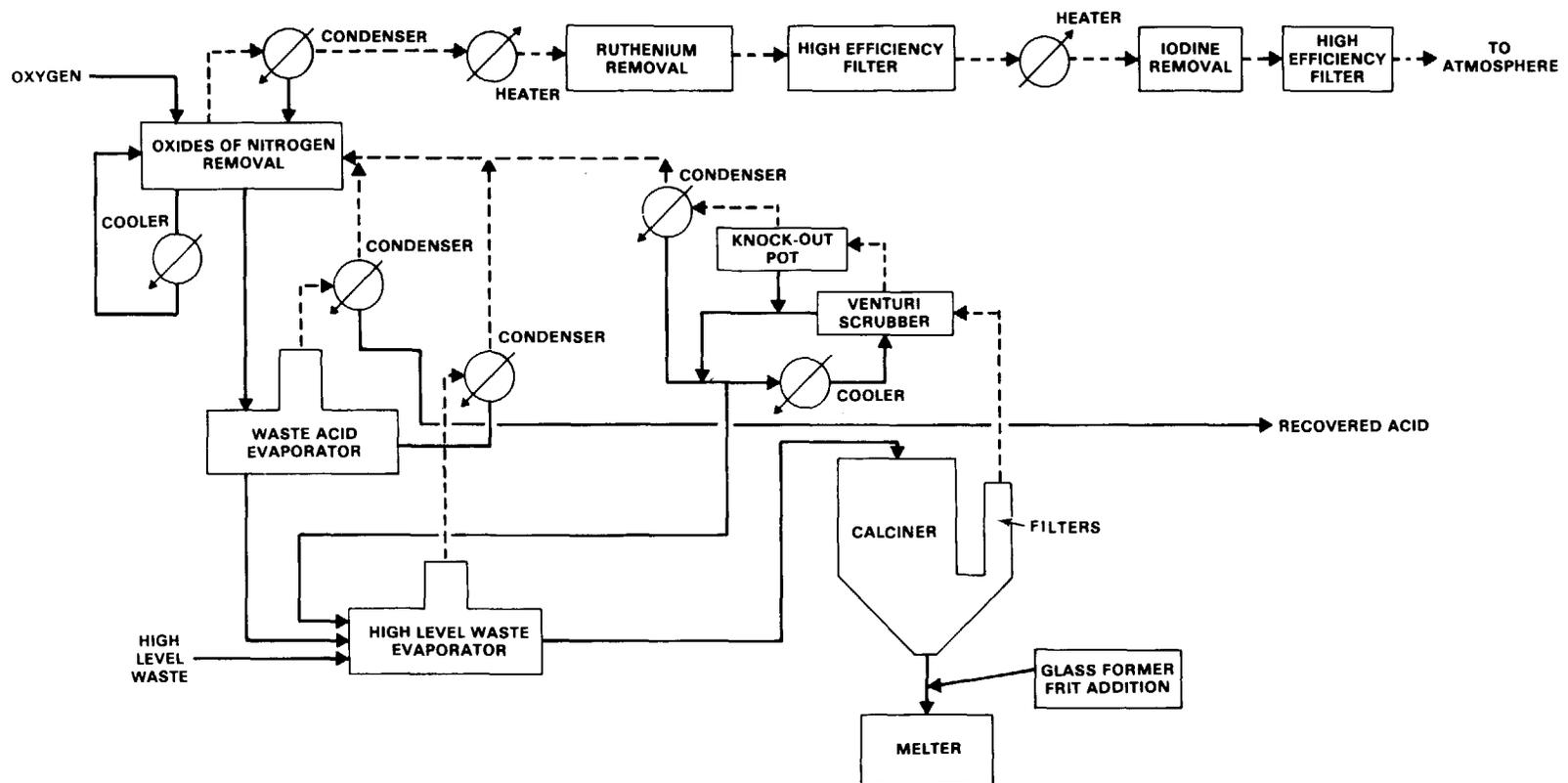


Figure 5 General flow diagram.

Nitrogen Oxide Control

During the next stage in the off-gas train (nitrogen oxide control), the acid will be recovered or destroyed. Control methods may be grouped in three major classes: absorption, conversion, and adsorption.

Absorption. Absorption consists of contacting the gases with liquid, absorbing the  $\text{NO}_x$  into the liquid. If water or nitric acid is used as the scrubbing liquid, nitric acid may be recovered. Using other liquid scrubbing agents generates a new liquid waste stream.

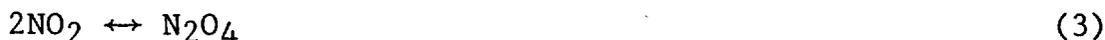
Absorption of  $\text{NO}_2$  into acid solutions takes place as follows:



NO must be oxidized to  $\text{NO}_2$  before it can react:



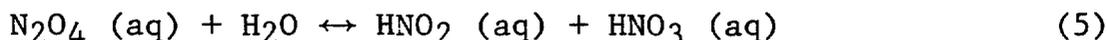
$\text{N}_2\text{O}_4$  is an equilibrium product of  $\text{NO}_2$  and will react in place of  $\text{NO}_2$  in Equation (1):



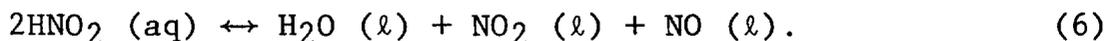
The overall reaction in Equation (1) takes place in several steps. Wendel and Pigford<sup>(8)</sup> studied  $\text{NO}_2$  absorption and analyzed the results using the penetration theory. The absorption process begins with the dissolution of  $\text{N}_2\text{O}_4$  gas in water:



This reaction is considered fast; the equilibrium constant is related to the Henry's law coefficient. After entering the liquid phase, the  $\text{N}_2\text{O}_4$  diffuses away from the gas-liquid interface and reacts with water:



This reaction is considered to be the rate limiting step in the absorption of  $\text{NO}_x$  in aqueous solutions.<sup>(4)</sup> The  $\text{HNO}_2$  is unstable in acid solutions and decomposes into  $\text{H}_2\text{O}$ ,  $\text{NO}_2$  and  $\text{NO}$ :



The  $\text{NO}$  is highly insoluble in water and escapes back to the gas phase. Thus, the evolution of  $\text{NO}$  from the liquid to the gas phase presents a significant limitation on absorption efficiency of  $\text{NO}_2$  by acid solutions. Each absorbed mole of  $\text{NO}_2$  produces 1/3 mole of  $\text{NO}$  which must be oxidized before it can be reabsorbed. This oxidation reaction can also be considered as a rate limiting step in the absorption of  $\text{NO}_x$  into aqueous solutions.

Peters<sup>(9)</sup> researched  $\text{NO}_2$  absorption efficiency in various absorbers. He found that venturitis and spray towers were the poorest absorbers, while packed scrubbers gave intermediate performance, and

bubble cap towers and fritted bubblers gave the best performance. For all of the scrubbers,  $\text{NO}_x$  removal efficiency decreased with decreasing concentration of  $\text{NO}_2$  in the entering gas.

Further, Peters<sup>(9)</sup> found that the addition of NaOH has only a minor effect on  $\text{NO}_x$  removal efficiency. Pennak et al.<sup>(10)</sup> also found that using NaOH in the scrub solution only gave a minor increase in the efficiency of  $\text{NO}_x$  removal. Also, the use of NaOH is unattractive because the acid is not recovered and another liquid waste stream is produced.

Efficiencies in removing nitrogen oxides by aqueous scrubbing are typically low. Very few scrubbers<sup>(9-11)</sup> have shown more than 90% removal of  $\text{NO}_x$ ; most range from 20 to 70%. Absorption will give a DF of about 10 to  $10^2$  for ruthenium and 10 for particulate.<sup>(12)</sup>

A mist elimination step will be required following the absorber to remove any entrained liquid.

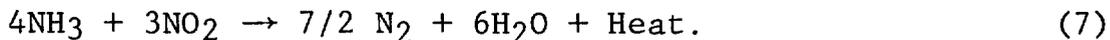
Conversion. Conversion involves the reaction of  $\text{NO}_x$  to form  $\text{N}_2$  and other innocuous gases. A reactant and sometimes a catalyst is required to accomplish the conversion, and acid is destroyed. The three major conversion methods are thermal reduction with hydrocarbon fuel, catalytic reduction with hydrocarbon fuel, and catalytic reduction with ammonia.

Thermal reduction with hydrocarbon fuel involves reducing  $\text{NO}_x$  to  $\text{N}_2$  and  $\text{H}_2\text{O}$  by using a fuel such as propane or natural gas. Temperatures are typically high (1800 to 2000°F).<sup>(13)</sup> An  $\text{NO}_x$  concentration reduction of 90% is possible using 8% combustibles ( $\text{C}_3\text{H}_8$ ).<sup>(13)</sup> Fuel costs are high because all oxygen in the stream must be consumed before the  $\text{NO}_x$  is reduced.

Gillespie et al.<sup>(14)</sup> and Reed and Harvin<sup>(15)</sup> have studied the use of natural gas in the presence of noble metal catalysts to reduce  $\text{NO}_x$ . In this case the catalyst operates at temperatures of about 1200 to 1400°F. This enables the catalytic reducer to operate with less fuel than the thermal reducer. However, catalyst life may be short because the operating temperatures are near the catalyst's upper limit capability.

The reduction of  $\text{NO}_x$  with ammonia over a catalyst is probably the most promising conversion system. The reaction takes place at relatively low temperatures, ammonia reacts only with  $\text{NO}_x$ , and high degrees of conversion are possible. The process consists of mixing gaseous  $\text{NH}_3$  with the process off-gas and passing the mixture through a heated catalyst. Typical catalysts are metal-impregnated alumina and silica,<sup>(14,15)</sup> metal exchanged zeolite,<sup>(16)</sup> and hydrogen and sodium forms of zeolite.<sup>(11)</sup> The reaction forms the products  $\text{N}_2$  and  $\text{H}_2\text{O}$ , and sometimes  $\text{N}_2\text{O}$ . A system similar to this is presently being used by Exxon Nuclear Company to eliminate  $\text{NO}_x$  in the off-gas from the dissolution of uranium oxides. The operation is described by Mays and Schwab.<sup>(17)</sup> This off-gas is similar to off-gas from the waste solidification process in terms of  $\text{NO}_x$  emissions. The 25-cfm off-gas stream requires a bed of 10 in. in diameter and 8 in. deep. The catalyst used is 1/16 in. diameter zeolite extrudates. The off-gas is mixed with 50 to 100% excess ammonia and passes down through the bed at a

temperature of 750°F. The conversion reaction(16,17) is:



The reaction rate must be carefully controlled since the bed temperature increases significantly during the conversion (up to 1400°F) due to the exothermic reaction. Conversion efficiencies greater than 99% have been reached.(17) Explosion hazards do exist due to the potential formation of  $\text{NH}_4\text{NO}_3$  below 600°F. Some type of temperature control is necessary to maintain required bed temperatures and cut the feed if the bed temperature should drop.

Adsorption. Adsorption involves the removal of  $\text{NO}_x$  from the gas stream by uptake on the surface of solids. Since the process must be cyclic, involving solids regeneration or disposal, two or more sorption beds are required to allow simultaneous adsorption and regeneration or disposal. If the beds are regenerated, the desorbed  $\text{NO}_x$  would be of relatively high concentration and  $\text{NO}_x$  control by adsorption would be necessary. The absorption would now be of higher efficiency due to the higher  $\text{NO}_x$  concentrations. Although high adsorption efficiencies are possible, large beds are required.

Final Off-Gas Cleanup. Up to this point, the gas stream has been treated to remove most of the condensables and the entrained particulate while the  $\text{NO}_x$  has either been recovered as acid or destroyed. Final cleanup must now be made to remove any fission products that have come through the system, either as volatiles or as particulates. As was stated earlier, the two fission products of primary concern are ruthenium and iodine which can come through the previous parts of the off-gas cleanup system. Since iodine removal methods also tend to remove some ruthenium, but ruthenium removal methods trap little iodine, the ruthenium is trapped first.

Ruthenium Adsorbers. Wet scrubbing is an inefficient method of ruthenium removal, so adsorption is generally used. The adsorbent must be able to: 1) adsorb large quantities of ruthenium while reducing ruthenium concentration in the off-gas effectively, 2) be resistant to attack from the off-gas, and 3) withstand the radioactive environment. There are two ways to handle the adsorption: with and without adsorbent regeneration. If the adsorbent is to be regenerated, it must permit ruthenium desorption quite easily, be resistant to attack from the desorption agent, and have the ability to adsorb effectively after regeneration. If the adsorbent is not to be regenerated, it must be disposable. Since the ultimate disposal method would be to place the adsorbent into the waste glass, the adsorbent should hold most of the adsorbed ruthenium at high temperatures.

Potential ruthenium adsorbers include silica gels, ferric oxide, hydrous zirconium oxide gel, phenolic based ion exchange resins, styrene-divinyl-benzene ion exchange resins, acid resistant molecular sieves, porous glass, impregnated alumina, copper sulfide, zirconium oxide hydrate-dithionite, etc. Of these, silica gel and ferric oxide best meet the requirements for the adsorbent.

- Silica Gel. Barnes and Newby(18) studied the ruthenium adsorption characteristics of silica gel for use in the New Waste Calcining

Facility at the Idaho Chemical Processing Plant. They obtained ruthenium adsorption capacities of greater than  $4.8 \times 10^{-3}$  g ruthenium/cm<sup>3</sup> of gel (6-12 mesh particle size bed) and determined that decontamination factors of  $10^3$  or better are possible, depending upon the depth of the bed. Further, they found that the silica gel can be effectively regenerated (about 80% of the ruthenium can be removed) and that regenerated silica gel adsorbs ruthenium as well as nonregenerated gel. The best operating conditions were found to be at a temperature slightly above the dewpoint of the gas and with a superficial velocity of about 0.4 ft/sec, giving pressure drops of about 1.0 in. of water/in. of bed height. Other investigators have shown similar results. (19,20)

- Ferric Oxide. Elliot et al. (21) found that DFs of  $10^3$  could be obtained with ferric oxide as the adsorbent. The adsorbent was at a temperature between 150 and 250°C and the superficial velocity about 3 ft/sec. The adsorbent was found to have a capacity greater than  $4 \times 10^{-2}$  g ruthenium/cm<sup>3</sup> of bed (18 to 25 mesh particle size bed). Elliot described a system in which the spent adsorber could be put into the glass canister. (21) Barnes and Newby (18) found that ferric oxide cannot be effectively regenerated and the material does not effectively adsorb ruthenium after regeneration. Based on this data, ferric oxide must be used as a nonregenerable adsorber to be disposed in the glass when saturated. The cost of ferric oxide is low, allowing this type of operation.

Depending on whether regeneration is attractive, either silica gel or ferric oxide will effectively remove ruthenium from the off-gas stream.

- Iodine Control. Iodine control is best obtained by using solid adsorbents. Inorganic adsorbents are chosen over wet scrubbing methods and organic adsorbents because they allow a simple design, are relatively noncorrosive, and can be put into permanent storage or recovered as necessary. Adsorbents having potential for use include silver and other metal-exchanged zeolites, silver impregnated, amorphous silicic acid, aluminum and silver oxides, and silver and other metal cation impregnated alumina. Impregnated carbons have potential but may react violently with NO<sub>2</sub>. Although only about 15% of the adsorbent is utilized before breakthrough (22) only small amounts are used: 4.2 ft<sup>3</sup>/yr of iodine containing adsorbent would be accumulated at the previously discussed processing rates. After NO<sub>2</sub> and moisture are removed the product is ideal for long-term storage and decay heat will not be a major problem since the decay energy of <sup>129</sup>I is low. If silver is used in the adsorbent, high costs may warrant recovery for reuse. Recovery costs will be dependent upon the degree of contamination of the adsorbent by other fission products and the ease of desorption. Should the adsorbent be recovered, some method of disposal must then be found for the desorbed iodine. Decontamination factors of  $10^3$  or better are obtainable depending upon the adsorbent depth. (22)

Final particulate filtration is used to prevent any particle or entrained droplets from leaving the system. High efficiency particulate filters which provide particulate DFs of  $10^3$  per stage are used.

Special Problems and R&D Requirements

There are some special areas where problems exist and where further R&D is warranted. The questions of mercury and carbon-14 control are examples of necessary R&D. Since mercury is highly volatile, most mercury in the feed to the calciner-melter system will pass through into the off-gas. Thus, the off-gas system may have to collect and contain the mercury. Carbon-14 has a long half-life (5700 yr) and may have to be controlled.

More R&D is needed in the area of the use and disposal of fission product adsorbers. Can the adsorbers be regenerated successfully? What should be done with the desorbed fission products to prevent revolatilization? Can the adsorbers be successfully placed in the glass with the fission products?

Many of the problem areas will be best researched in an operating situation. None of the problems appear insurmountable and, with the many routes possible in an off-gas train, most problem situations can be overcome.

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DISCUSSION

BURCHSTED: Is there a possibility of trapping the mercury upon activated carbon that has been properly impregnated?

HANSON: There is a possibility, but we're afraid of having nitrogen oxides passing through our scrubbing system which might cause problems with the charcoal.

FIRST: In connection with nitrogen oxide removal by scrubbing with water, our experiences are very unfavorable. One seldom gets more than about 35 to 45 per cent with water scrubbing at ambient temperatures and ambient pressures. How do you intend to cope with this?

HANSON: We hope to pick up a little bit of efficiency by cooling our scrub stream. Initially, we will be using water. After we are operating, we will be using a weak acid to scrub.

VAN BRUNT: You showed a DF of around  $10^{11}$ . I was wondering about this as it is rather different from the  $10^3$  DF shown for the adsorber.

HANSON: Yes, there is a difference. The DF of  $10^3$  is for the adsorber and the  $10^{11}$  is for the entire system.

VAN BRUNT: What kind of DF's do you expect from the absorber?

HANSON: A DF of  $10^3$  is expected. This can be varied by bed depth, i.e., absorbent depth.

VAN BRUNT: Even with high temperatures?

HANSON: There will be temperature effects, so that the bed temperature will have to be controlled to maintain it within a certain range. By the time we get to the absorbent beds, the gas will be close to ambient temperature.

<sup>85</sup>KR STORAGE BY ZEOLITE ENCAPSULATION\*

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Abstract

This paper describes the technology of <sup>85</sup>Kr storage by zeolite encapsulation. The process of encapsulation takes place at high temperatures and pressures, and involves the activated diffusion of krypton into zeolite cages. Experimental results for krypton encapsulation in various zeolites are reviewed and discussed. Activated diffusion parameters determined by measuring krypton leakage rates from zeolites at high temperatures and low pressures are used to estimate leakage rates of <sup>85</sup>Kr during long-term storage. The potential safety benefits are determined for krypton-85 storage by encapsulation in sodalite. Requirements for pilot-scale and process-scale development are discussed briefly.

I. Introduction

Of the noble gases formed by nuclear fission (krypton and xenon), only krypton-85 (<sup>85</sup>Kr) has a half-life sufficiently long to be present at the time of fuel reprocessing. Most of the <sup>85</sup>Kr in the fuel is released during shearing and dissolution and is removed by the off-gas stream at low concentrations. While the technology exists for dispersal of <sup>85</sup>Kr to the atmosphere, methods have been proposed for its collection and storage to avoid potential local hazards and long-term global build-up<sup>(1)</sup>.

Annual requirements for storing <sup>85</sup>Kr (using methods which are applicable to commercial-scale fuel reprocessing) are presented in Table I<sup>(2,3)</sup>. The production of <sup>85</sup>Kr from a 1500 tonne/yr reprocessing plant is assumed\*\* to be 9.81 MCi/yr<sup>(4)</sup>. Pressurized cylinders<sup>(3)</sup> and zeolite encapsulation are compared in Table I. Krypton is assumed to have a relatively pure composition; if impurities such as xenon are present, increased storage positions will be needed in the storage facility. Storage in pressurized cylinders is considered to be available technology. Although storage by zeolite encapsulation will require further development before a production-scale system can be constructed and operated<sup>(1)</sup>, there are potential additional safety benefits in zeolite encapsulation (see Section IV). A program is under way at the Idaho National Engineering Laboratory (INEL) to develop both storage methods to a conceptual design level for a production-scale system.

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\*Work performed under USERDA Contract E-(10-1)-1375 S-72-1

\*\*Based on a burnup of 25,000 MWd. A burnup of 33,000 MWd would produce 16.8 MCi.

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Table I. Annual  $^{85}\text{Kr}$  storage requirements for a  
1500 tonne/yr reprocessing plant.\*

Storage Method	Pressure		Amount Zeolite, kg	Storage Temperature, °C	Number of 50- $\lambda$ Cylinders
	Atm	Psi			
Pressurized Cylinders	35	500	--	60**	77
	137	2000	--	127**	24
Zeolite Encapsulation <sup>†</sup>	--	--	2800	120 <sup>††</sup>	82

This paper will describe the technology of  $^{85}\text{Kr}$  storage by zeolite encapsulation. A technical description of zeolite encapsulation in general will be presented, and laboratory-scale results will be reviewed and will be used to predict long-term storage behavior of krypton-85 in sodalite and zeolite 3A. A brief discussion of the development required for a process-scale encapsulation system will conclude this paper.

### II. Technical Description

Zeolite materials are crystalline aluminosilicates which contain a regular array of interconnected cages of uniform size<sup>(5)</sup>. For a given zeolite type, the cage dimensions are uniquely deter-

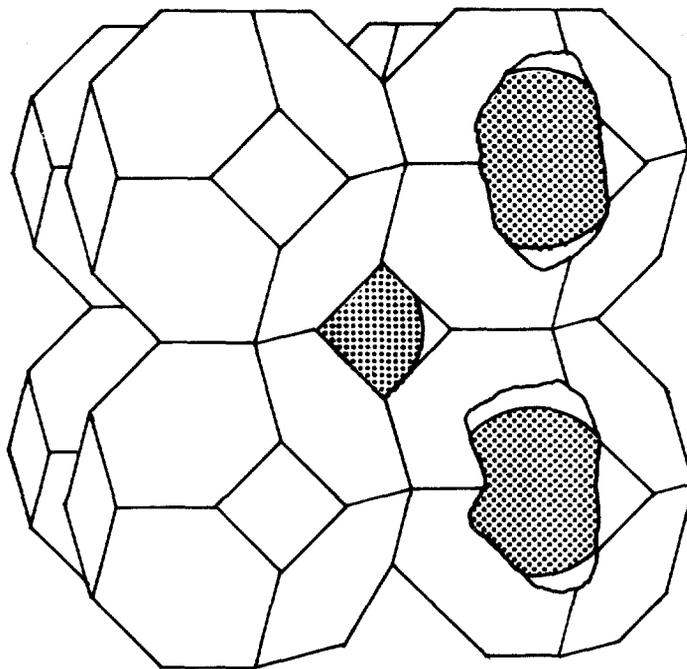


Figure 1. Representation of sodalite cages containing krypton atoms.

\*Annual production : 9.81 MCi of 6%  $^{85}\text{Kr}$  in krypton; based on a burnup of 25,000 MWd.

\*\*Wall temperature

†Assumed loading :  $1.8 \times 10^{-3}$  mole ( $40 \text{ cm}^3$  STP) Kr  $\text{g}^{-1}$  zeolite.

††Mean temperature: center-line temperature is  $150^\circ\text{C}$ . See Section IV.

mined by the structure of the crystal<sup>(5)</sup>. Figure 1 shows the structure of a group of sodalite cages, each containing one atom of krypton. Each sodalite cage consists of a truncated octahedron ( $\sim 6.6$  Å free diameter). Each six-ring face is shared with adjoining sodalite cages to make up the overall crystal structure. The krypton atom shown occupying each cage has a room-temperature gas-kinetic diameter of  $\sim 3.5$  Å. Not shown in Figure 1 are the cations (such as sodium) attached to various locations on the aluminosilicate framework. Cations which partially block cage openings (e.g., the six-ring face in Figure 1) can be exchanged with larger or smaller cationic species to alter the dimensions of the opening. Such a modification can have a strong effect on the diffusion of gas molecules.

The process by which krypton diffuses through such a pore structure is known as activated diffusion, since an activation energy is required for krypton atoms to pass through the 2.3 Å apertures<sup>(5-7)</sup>. At high temperature and pressure (450°C, 1000 atm)<sup>(6)</sup>, there is sufficient energy for krypton to diffuse into the crystalline sodalite cages, while at low temperatures (<150°C) the encapsulated krypton does not have enough energy to diffuse out at appreciable rates. Thus, krypton can be introduced into the cages at conditions corresponding to rapid diffusion and then trapped in sodalite at ambient external pressure, even though each krypton atom experiences a high effective "pressure" inside its cage.

While sodalite appears to be a promising trapping medium, krypton encapsulation should be possible with other zeolites. Zeolites with larger cage diameters may be used if the cage openings are kept narrow by suitable ion exchange. Such zeolites include the potassium, cesium, or rubidium-exchanged forms of zeolite A, chabazite, and erionite. Some data on zeolite 3A (potassium-exchanged A) will be presented in Section III.

### III. Experimental Results

The experimental study is divided into two general areas: encapsulation and leakage measurements. Experimental encapsulation and leakage studies of krypton in sodalite and zeolite 3A, which have been made at the INEL and elsewhere<sup>(5, 6, 8, 9)</sup>, will be reviewed and discussed. Theory will be used in interpreting the experimental data and will allow predictions of long-term storage behavior of  $^{85}\text{Kr}$  (Section IV).

#### Encapsulation

A typical process flowsheet for encapsulating krypton in zeolite is shown in Figure 2. Activated zeolite (with interstitial water removed) is loaded into the pressure vessel and heated to the encapsulation temperature. Krypton is introduced at the encapsulation pressure for a preselected time. The temperature is lowered, and the unencapsulated krypton is recycled to the storage cylinder. The krypton-containing zeolite is then removed for further testing. The laboratory-scale system in use at the INEL was obtained commercially and consists of two diaphragm compressors

connected in series to a 250 cm<sup>3</sup> vessel (A-286 alloy composition) enclosed in a heating blanket. At temperatures below 500°C, the vessel can be pressurized to 2000 atm (30,000 psi). As the temperature is increased from 500 to 650°C, the maximum operating pressure is decreased from 2000 to 1630 atm (24,000 psi), respectively, at the same safety factor. The high pressure system is housed inside a steel barricade for personnel protection from accidental rupture while pressurized.

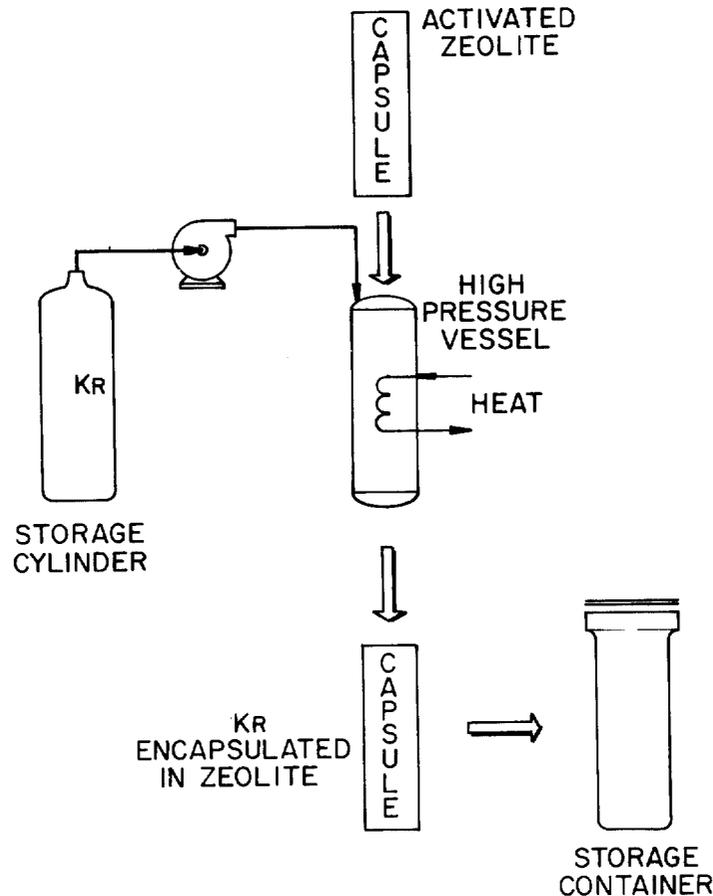


Figure 2. Process for high pressure encapsulation of Kr in zeolite.

We have determined loading densities for argon and krypton in sodalite and zeolite 3A. Representative values are shown in Table II.

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Table II. Argon and krypton loaded on zeolite samples.

Gas	Experimental Conditions			Amount Encapsulated, cm <sup>3</sup> STP g <sup>-1</sup> Solid	
	T, °C	P, psi	Time, hr	Sodalite*	Zeolite 3A
Ar	355	10,500	4	32-34	47
Ar	355	28,000	4	38-46	68
Kr	355	28,000	4	10-12	49
Kr	390	28,000	4	18-22	53
Kr	430	26,000	4	25-27	49

The encapsulation of larger amounts of argon than krypton at the same conditions is due to the lower activation energy of diffusion for argon (27 kcal mole<sup>-1</sup> in sodalite). (The activation energy for krypton in sodalite is 38 kcal mole<sup>-1</sup>.) Argon is  $\sim 0.1$  Å smaller than krypton, thus lowering the energy barrier for diffusion. As the temperature is raised, more krypton can be encapsulated. Values near 25 cm<sup>3</sup> g<sup>-1</sup> are considered to be practical for long-term storage of <sup>85</sup>Kr. If krypton is not readily available, experiments with argon may be used (with a correction factor) to simulate krypton behavior.

Basic sodalite normally contains some intercalated NaOH<sup>(10)</sup>. Thus the unit cell composition of an ideal sodalite hydrate, Na<sub>6</sub>(Al<sub>6</sub> Si<sub>6</sub> O<sub>24</sub>) · 8H<sub>2</sub>O becomes Na<sub>6</sub>(Al<sub>6</sub> Si<sub>6</sub> O<sub>24</sub>) x NaOH · (8-2x)H<sub>2</sub>O, since each NaOH replaces 2 H<sub>2</sub>O molecules<sup>(11)</sup>. The results shown in Table II were obtained using sodalite which had been extracted to remove most of the intercalated NaOH. When samples containing up to  $\sim 5$  weight per cent were encapsulated,  $\sim 30$ -40% reduction in loading densities were observed for a given temperature and pressure (at 4 hr).

A series of krypton encapsulation experiments using sodalite and other zeolites is in progress and will determine the encapsulation behavior in the experimental space : 390-430°C; 20,000-26,000 psi; and 1-4 hr. The results will be used to establish a model for the encapsulation process which can be used to optimize the loadings for given experimental constraints.

Figure 3 presents data obtained by Vaughan for typical isotherms of krypton encapsulated in sodalite<sup>(9)</sup>. A sorption isotherm obtained by Sesny for argon in zeolite 3A at 5000-45,000 psi and 350°C gives a maximum loading of  $\sim 77$  cc/g<sup>(8)</sup>. The values shown in Table II are consistent with the above.

The gas kinetic collision diameter at room temperature for krypton is  $\sim 3.5$  Å, and the free diameter of a sodalite cage is  $\sim 6.6$  Å (see Figure 1). If one krypton atom occupies each cage of

\*Intercalated NaOH has been extracted from these samples.

sodalite, the saturation capacity of krypton for ideal sodalites is  $52.6 \text{ cm}^3$  (STP) per anhydrous gram<sup>(6)</sup>. Ideal sodalite may constitute a nearly perfect sorbent in the sense given by Langmuir. Each cage represents an identical site, and all sites are separated through the 6-ring windows in such a way that the guest species should not be able to interact by direct contact (Figure 1). The experimental isotherms in Figure 3 are of a Langmuir form:

$$K = \frac{\theta}{f(1-\theta)} = \frac{v/v_{\text{sat}}}{f(1-v/v_{\text{sat}})} \quad (1)$$

where  $K$  is the equilibrium constant,  $\theta$  (or  $v/v_{\text{sat}}$ ) is the fraction of saturation capacity sorbed ( $v$ , the volume sorbed in  $\text{cm}^3$  at STP per anhydrous gram and  $v_{\text{sat}}$ , the saturation capacity), and  $f$  is the fugacity. When  $f/v$  is plotted versus  $f$ , a straight line results with slope  $v_{\text{sat}}$ . The data of Figure 3 were used to evaluate  $v_{\text{sat}}$  as

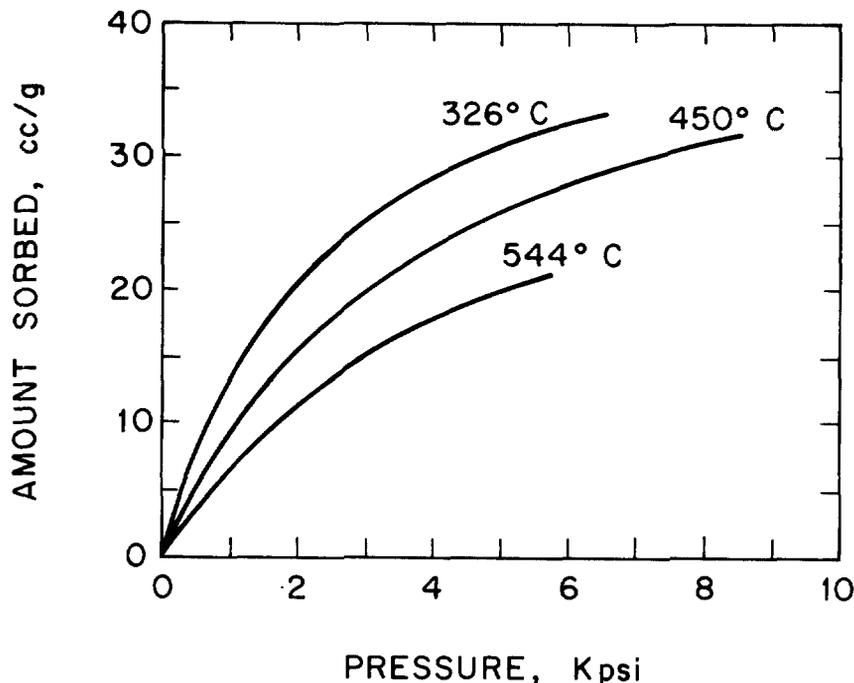


Figure 3. Isotherms of Kr sorbed on extracted sodalite (S2)<sup>(9)</sup>.

equal to  $\sim 45 \text{ cm}^3 \text{ g}^{-1}$ , in reasonable agreement with the ideal case<sup>(6)</sup>. The results shown in Figure 3 were obtained using sodalite (sample S2) which had most of the intercalated NaOH removed by extraction. Sodalite (sample S1) containing NaOH in three times the amount of S2 was also studied<sup>(6)</sup>. The equilibrium saturation capacities did not change, indicating that krypton could occupy a cage containing sodium hydroxide.

Diffusion Measurements

After krypton has been encapsulated in a zeolite, measurements of its diffusion from the solid at high temperatures can be used to estimate  $^{85}\text{Kr}$  leakage under long-term storage conditions. Experimental and theoretical methods of determining the diffusivity of gases in zeolites from leakage measurements will be described in this section, while prediction of krypton-85 leakage will be shown in the following section.

A typical process flowsheet for measuring leakage rates at three different temperatures of krypton encapsulated in a zeolite is shown in Figure 4. The solid sample is placed in each of three sample tubes, and the system is evacuated. After isolating the samples from the vacuum, the sample tubes are heated to temperatures  $T_1$ ,  $T_2$ , and  $T_3$ . Measurements can be made of the amount of gas released as a function of time for each tube in turn using the pressure gauge and/or the mass spectrometer. The results of the measurements obtained by Vaughan<sup>(9)</sup> for krypton in extracted sodalite (S2) are shown in Figure 5, where  $Q_t$  and  $Q_\infty$  are the amounts of gas released up to times  $t$  and infinity, respectively. Because of the initial temperature rise from room temperature to a higher constant temperature, the curves of the amount desorbed vs time are sigmoid in shape. The theory and method of analysis of the curves has been given elsewhere<sup>(7,12)</sup>, and only the directly applicable portion of the theory will be described. For fractional leakage ( $Q_t/Q_\infty$ ) less than  $\sim 0.3$ ,  $D$  (the diffusivity) at the final steady temperature,  $T$ , is given by:

$$D = \frac{\pi r_0^2}{36} \frac{d(Q_t/Q_\infty)^2}{dt} \quad (2)$$

where  $r_0$  is an average diffusion path length and is related to the size of the zeolite crystals. Thus, the square root of  $D$  can be obtained from the data in Figure 5 using equation (2).

For an activated diffusion process:

$$D = D_0 \exp(-E/(RT)) \quad (3)$$

where  $E$  is the activation energy for diffusion and  $D_0$  is a coefficient independent of temperature. If equations (2) and (3) are combined, it is seen that plots of

$$\text{Log}_{10} \left( \frac{d(Q_t/Q_\infty)}{dt^{1/2}} \right) = \frac{1}{2} \log \alpha D \text{ vs } 1/T$$

should be straight lines of slope  $-E/(4.606R)$ , where  $\alpha = (1.3/(\pi r_0^2)) \times 10^5$  and  $R$  is the universal gas constant. Such a plot is shown in Figure 6 for the data of Vaughan<sup>(9)</sup> (with  $D$  in  $\text{cm}^2 \text{sec}^{-1}$ ) obtained using two different sodalite samples, S1 and S2 (S1 contains approximately three times the amount of sodium hydroxide

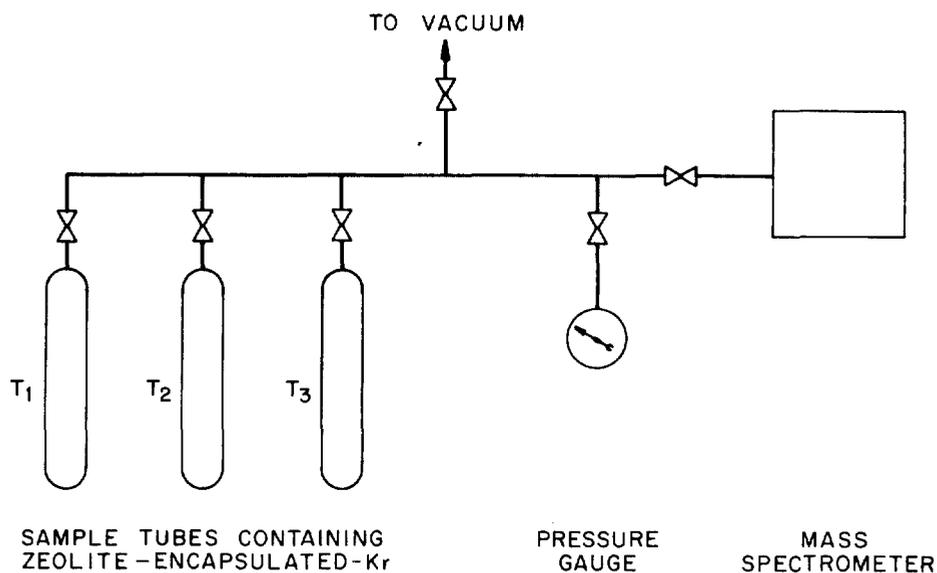


Figure 4. Process for determining rates of leakage of krypton from zeolite.

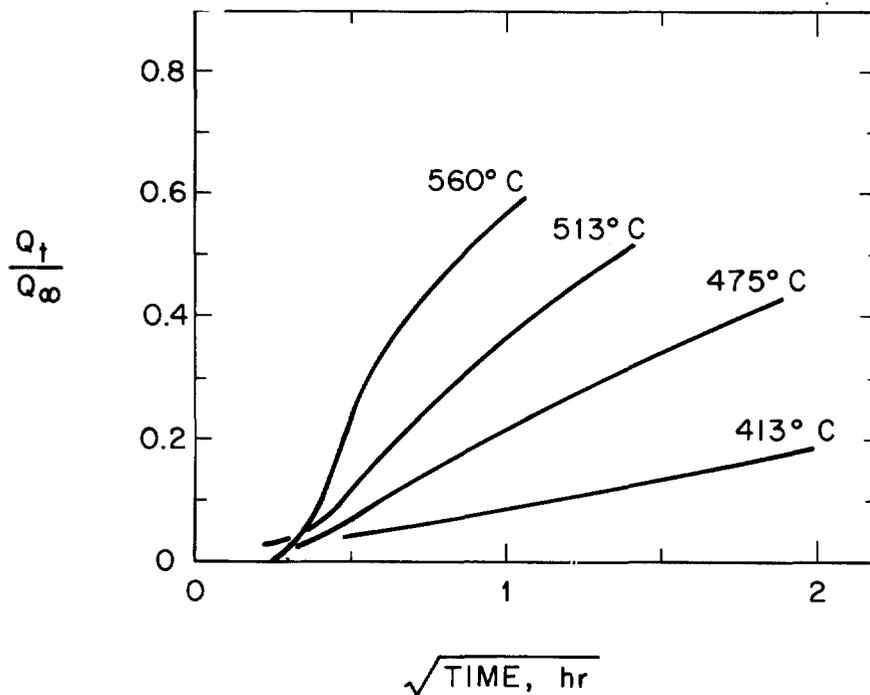


Figure 5. Rate of fractional leakage of krypton from extracted sodalite (S2)<sup>(9)</sup>.

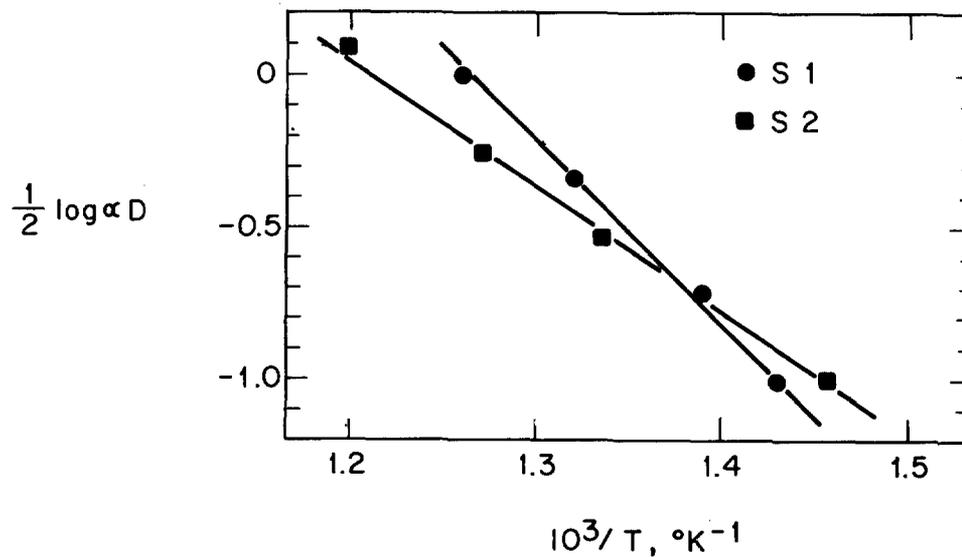


Figure 6. Temperature dependence of diffusion of krypton in extracted sodalite (S2)<sup>(9)</sup>,  $D$  in  $\text{cm}^2 \text{sec}^{-1}$ .

found in S2). Thus it can be seen that sodalite containing more NaOH has a greater activation energy of diffusion. Using experimental values of  $d(Q_t/Q_\infty)/dt^{1/2}$  together with values of  $r_0$  for S1 and S2, Vaughan (6,9) obtains the values of  $D_0$  and  $E$  given in Table III. Values of  $r_0$ ,  $D_0$ , and  $E$  obtained by Walker<sup>(7)</sup> for zeolite 3A are also provided.

Table III. Values of  $E$ ,  $D_0$ , and  $r_0$  for diffusion of krypton in sodalite and zeolite 3A.

Zeolite Sample	$r_0, \text{cm}$	$E, \text{ kcal mole}^{-1}$	$D_0, \text{ cm}^2 \text{sec}^{-1}$	Reference
Sodalite S1	$1.3 \times 10^{-5}$	52	1.1	6
Sodalite S2	$6.1 \times 10^{-6}$	38	$1.1 \times 10^{-5}$	6
Zeolite 3A	$2.0 \times 10^{-4}$	16.4	$6.0 \times 10^{-7}$	7

Using the values of  $E$  and  $D_0$  in equation (3), it is possible to calculate  $D$  at any temperature for the above.

#### IV. Long-Term Storage of $^{85}\text{Kr}$

The laboratory results and theory presented in Section III are used to predict leakage rates of  $^{85}\text{Kr}$  from sodalite and zeolite 3A during long-term storage, and the resulting safety factors over pressurized cylinder storage are shown. The same measurements and calculations can be made for other zeolites in which krypton diffusion obeys equations (2) and (3).

The integrated form of equation (2) can be combined with equation (3) to give equation (4), the fractional leakage (up to  $Q_t/Q_\infty = 0.3$ ) of encapsulated krypton at time  $t$  and temperature  $T$ , once  $D_0$ ,  $E$ , and  $r_0$  have been determined for a given zeolite sample.

$$Q_t/Q_\infty = 6 \left( \frac{D_0 t}{\pi r_0^2} \right)^{1/2} e^{-E/(2RT)} \quad (4)$$

In long-term storage of  $^{85}\text{Kr}$ , the major concern is the leakage of  $^{85}\text{Kr}$  (compared to the original amount stored). Radioactive decay effectively reduces the potential leakage of  $^{85}\text{Kr}$  by a factor of two every 10.73 years. While the amount of total krypton desorbed increases as a function of the square root of time, the amount of  $^{85}\text{Kr}$  which can leak as well as which has leaked is decreasing exponentially. The combined effects are described by equation (5):

$$(Q_t/Q_\infty)_{^{85}\text{Kr}} = 6 \left( \frac{D_0 t}{\pi r_0^2} \right)^{1/2} \exp \left( -\frac{E}{2RT} - \lambda t \right) \quad (5)$$

where  $\lambda$  is the decay constant for  $^{85}\text{Kr}$ . The function described by equation (5) reaches a maximum at a value of  $t=7.7$  years (corresponding to  $1/t=2\lambda$ ). While the time for the maximum possible  $^{85}\text{Kr}$  leakage is fixed, the amount leaked is a function of  $D_0$ ,  $E$ ,  $r_0$ , and  $T$ .

Using data obtained by Vaughan<sup>(6)</sup> (see Table III) and the value of  $\lambda$  for  $^{85}\text{Kr}$  decay in equation (4), it is possible to calculate the release of original  $^{85}\text{Kr}$  inventory (fractional net leakage of  $^{85}\text{Kr}$ ) as a function of time at a storage temperature of  $150^\circ\text{C}$  in sodalite samples S1 and S2. Figure 7 shows the results of such a calculation. The fractional leakage of all isotopes of krypton at  $150^\circ\text{C}$  and 100 years is  $\sim 6 \times 10^{-4}$  and  $\sim 2 \times 10^{-2}$  for S1 and S2, respectively. The resulting maximum net leakages  $^{85}\text{Kr}$  of 0.3% to 0.01%, if attainable, represent safety factors (based on potential losses from a damaged storage vessel) of 200 to 6000 over pressurized tank storage. Predicted net leakage of ( $^{85}\text{Kr}$ ) from zeolite 3A<sup>(7)</sup> (using data from Table III) was 35% for a storage temperature of  $50^\circ\text{C}$ .

Since the rate of activated diffusion depends on temperature in an exponential manner, the rate of dissipation of  $^{85}\text{Kr}$  radioactive decay heat during storage becomes critical. A heat-transfer model for a 23-cm diameter steel storage cylinder was used to estimate temperature profiles for the cylinder filled with zeolite. At a krypton loading of  $1.8 \times 10^{-3}$  mole ( $40 \text{ cm}^3 \text{ STP}$ )  $\text{g}^{-1}$  of zeolite (equivalent to  $\sim 35$  atm, or  $\sim 500$  psi, storage of gas) and an ambient temperature (convective heat transfer) of  $50^\circ\text{C}$ , the calculated centerline temperature was  $150^\circ\text{C}$ ; the mean temperature was approximately  $120^\circ\text{C}$ . The predicted leakage rates at  $150^\circ\text{C}$  for sodalite shown in Figure 7 can thus be considered conservative for such conditions. Additional cooling or decreased loading density of  $^{85}\text{Kr}$  would be required for encapsulation-storage using zeolite 3A, due to the higher leakage rate.

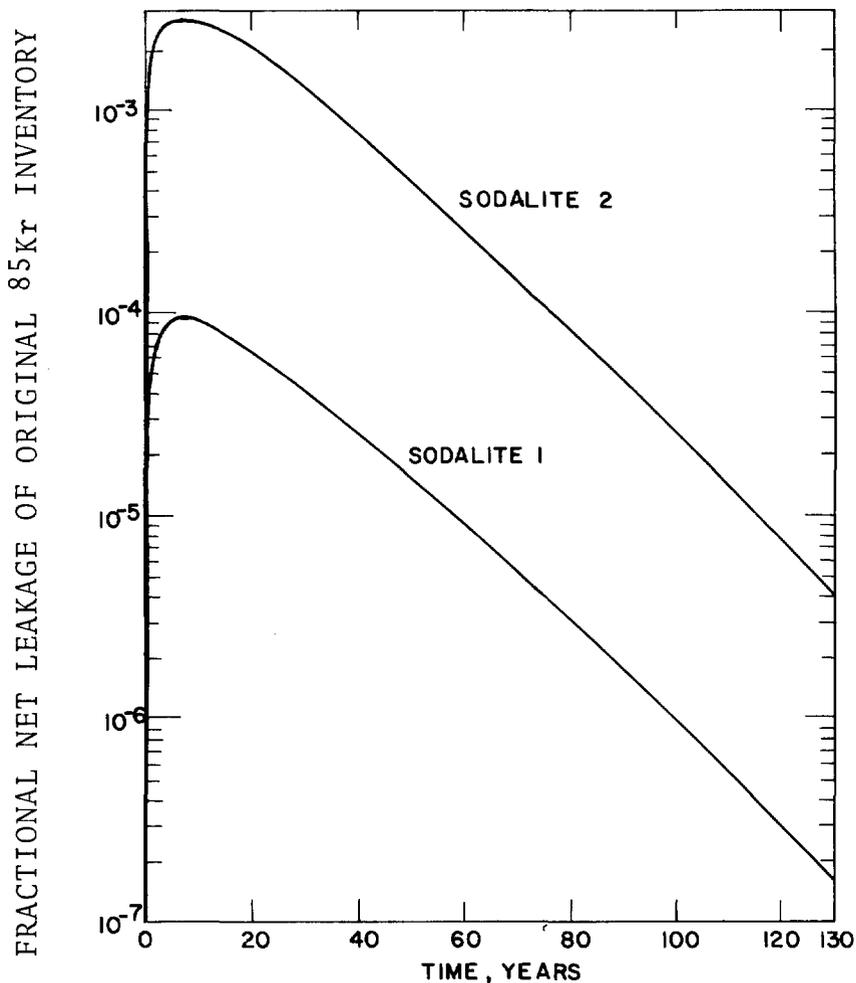


Figure 7. Calculated release of original  $^{85}\text{Kr}$  inventory from sodalite at  $150^{\circ}\text{C}$  as a function of time.

#### V. Program Description

Encapsulation and leakage tests are under way at the INEL using various samples of sodalite and zeolite 3A. New zeolites, including Rb- and Cs-exchanged zeolite A, K-exchanged chabazite and erionite, and a number of different pellet forms of sodalite will be tested as described in Section III. Leakage studies will be used to estimate long-term storage characteristics for the new zeolite forms in the same way as for sodalite and zeolite 3A. Small amounts of the most promising zeolites will be encapsulated with 6%  $^{85}\text{Kr}$  in krypton, and long-term storage tests will be initiated under simulated storage conditions. (Krypton with natural background levels of  $^{85}\text{Kr}$  is being used for all other testing.) Pilot-scale development will include scale-up of the pressure vessel, possibly to a plant-size prototype, combined with developing remote operation and remote materials handling capability. A conceptual design of the production-scale encapsulation and storage facility will be made.

An estimate of the size and capabilities of a production-scale operation can be made. In a 1500-tonne yr<sup>-1</sup> reprocessing plant, ~9.8 MCi yr<sup>-1</sup> of <sup>85</sup>Kr is produced. If 1.8 x 10<sup>-3</sup> mole (40 std. cm<sup>3</sup>) g<sup>-1</sup> of krypton (with 6% <sup>85</sup>Kr) is encapsulated in a zeolite such as sodalite, ~2,800 kg yr<sup>-1</sup> is required. If 50,000 Ci of <sup>85</sup>Kr is to be encapsulated in one batch, a 20- $\ell$  high-pressure vessel would be necessary. The encapsulation process, including solids transfer operations, must be remotely operated due to the high radiation field. In addition to mechanical shielding of the high pressure process equipment, capability for containing the large amount of radioactive krypton is required in the event of failure of the pressurized system. Technology exists for high pressure, remote operation, and remote handling capabilities, and these will be combined into one operational system. Since relatively large amounts of <sup>85</sup>Kr will be present during the process-scale encapsulation, adequate cooling of radiation-generated heat is required during parts of the process.

Long-term storage criteria will be developed. Stored <sup>85</sup>Kr in zeolite will generate heat, which in turn must be dissipated so that the storage temperature does not increase to the extent that appreciable diffusion of <sup>85</sup>Kr out of the zeolite pores can occur (~150°C in Figure 7 for sodalite). Long-term radiation damage to the zeolite structure will be assessed and minimized. The effect of the <sup>85</sup>Kr decay product, rubidium, will also be determined. (A beneficial effect of rubidium might be to plug up the pores in sodalite.)<sup>(13)</sup> In any handling of zeolite-encapsulated-<sup>85</sup>Kr, dust formation must be prevented or contained.

## VI. Conclusion

Measurements of loading capacity of krypton in sodalite were made at the INEL and elsewhere<sup>(5,6,8,9)</sup>. Kinetics of diffusion of krypton out of sodalite have been determined by Vaughan (6) and can be used to predict leakage of krypton-85 out of sodalite under long-term storage conditions. Based upon these loading and leakage characteristics, the process of encapsulating krypton-85 in sodalite appears to be a feasible storage method. Further developments leading to a conceptual design of a commercial process for krypton-85 encapsulation by zeolites are being pursued at the INEL.

## Acknowledgment

The generous assistance of Dr. D. E. W. Vaughan is gratefully acknowledged.

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DISCUSSION

GRADY: I was wondering what the application of this type of process will be to an industrial reprocessing plant? Is the equipment so large and does it require such high pressures and high temperatures that it's not feasible?

D. A. KNECHT: The estimates of the process scale required in an industrial reprocessing plant are presented in the written text of this paper. Roughly, if 50,000 curies of 6%  $^{85}\text{Kr}$  in krypton are to be encapsulated in one batch (assuming 50,000 curies per day are generated at a 1,500 ton per year reprocessing plant), a 20-liter high pressure vessel would be required. Multiple encapsulation batches using smaller high pressure vessels, i.e., 5 or 10 liters, can meet processing rate requirements. While high pressure technology does exist for such an operation, further work is under way at the INEL to determine the requirements for commercial-scale operations.

CLOSING REMARKS OF SESSION CHAIRMAN:

We've heard eight excellent papers and it's very difficult to summarize them. The incineration processes that have been described represent intensive development to achieve volume reduction in recognition of the requirements of waste management. Significant reduction is achievable in these primary treatments. However, the net reduction factors of these processes will need to be assessed very carefully.

An important consideration will be the cost of waste management versus the cost of direct disposal without treatment. It will be necessary to derive the net cost-benefit of processes and we need data on the process costs, as well as on ERDA's own cost of storage, in order to make valid cost comparisons. Therefore, cost data from incineration systems is extremely important.

The air cleaning of incinerator effluents is a technical challenge that is having major influence on the design selections and, as you can see, several of these incinerators are designed with special combustion features in an attempt to avoid such things as chlorides or particulate carryover in the offgas and the problems that they raise for air cleaning.

Undoubtedly, air cleaning will dominate the design of incineration development for some time and the successful adoption of these units by commercial industry will probably rest on the ability to clean up the effluents from such units efficiently. We've also heard of the air cleaning needs of several other processes, e.g., high level waste treatment and the need for storage for retention of noble gases. These are indeed significant developments, challenging both the government's laboratories and the industry.

I would like to close by saying that many of you who are members of the air cleaning industry probably recognize what is obvious to

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me and that is that we must devise systems that go all the way back to the design of disposable filters and recognize that they will ultimately be a waste material that has to be treated, packaged, and stored. We must, therefore, use the greatest ingenuity in design with this in mind because, indeed, a significant part of waste management occurs at the head end. I've always said that one of the most important persons in waste management is the procurement officer because he's the one who makes all the selections of what finally winds up in the waste bin and has to be managed as waste.