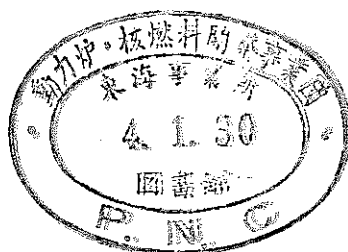


Developments in the Treatment of Solid Alpha-Bearing Wastes at the PNC Plutonium Fuel Facilities

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DEVELOPMENTS IN THE TREATMENT OF SOLID ALPHA-BEARING WASTES
AT THE PNC PLUTONIUM FUEL FACILITIES

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Abstract

DEVELOPMENTS IN THE TREATMENT OF SOLID ALPHA-BEARING WASTES
AT THE PNC PLUTONIUM FUEL FACILITIES

Some results of experiments done in PNC are presented on volume reduction technics for alpha-bearing wastes.

A pilot wood milling machine automatically mills the plywood frames of nipple connected HEPA filters, which result in fine sized wooden chips, two nipples and the filter components. The filter components are melted in an induction furnace to be homogeneous solids. These methods and incineration of wooden chips reduce the stored volume of HEPA filters to 1/50~1/100.

PVC and neoprene rubber are decomposed in concentrated sulfuric acid, followed by oxidation with nitric acid. The acid digestion process generates chlorine-rich gas, from which only chlorine is selectively absorbed in water.

An alpha-bearing vessel and a glovebox are cut at their installed places without spread of plutonium contamination outside the greenhouses.

1. INTRODUCTION

Power Reactor and Nuclear Fuel Development Corporation (PNC) has two plutonium fuel facilities at Tokai Works, which are Plutonium Fuel Development Facility (PFDF) and Plutonium Fuel Fabrication Facility (PFFF). The operation of the facilities has resulted in the accumulation of large quantity of solid alpha-bearing wastes, almost of which has been stored in depots except combustibles. As alpha-bearing wastes should be safely isolated from human environment for thousands of years, methods are being developed to reduce the volume of the wastes and to stabilize them for permanent storage or disposal. A summary report on the management of alpha-bearing wastes at the PNC plutonium fuel facilities was published in the past.[1]

As shown in Fig. 1, the typical waste distribution at the PNC plutonium fuel facilities are 40% of PVC and neoprene rubber, 26% of HEPA filters, 19% of papers, 9% of large equipment and 6% of metals and glasses. A conceptual flowsheet for future waste treatment is shown in Fig. 2. Alpha-bearing wastes will be classified to four categories, which are paper, PVC and neoprene rubber, HEPA filters, and large equipment and non-combustibles.

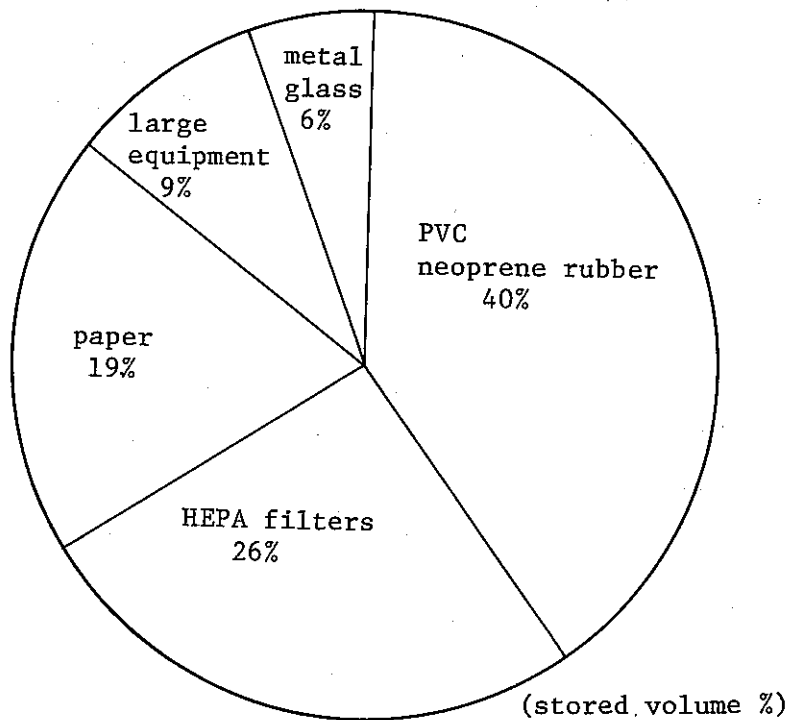


Fig. 1 Typical waste distribution at the PNC plutonium fuel facilities

- Combustible wastes such as paper, PVC and neoprene rubber will be acid digested and/or incinerated.
- HEPA filters will be milled to wooden chips and filter components.
- Wooden chips will be treated together with combustibles and filter components will be melted to freezed solids.
- Non-combustible wastes will be incorporated or melted to solids.
- These solidified wastes will be packaged and stored.

This paper describes the results of the volume reduction experiments for HEPA filters, PVC and neoprene rubber and glovebox.

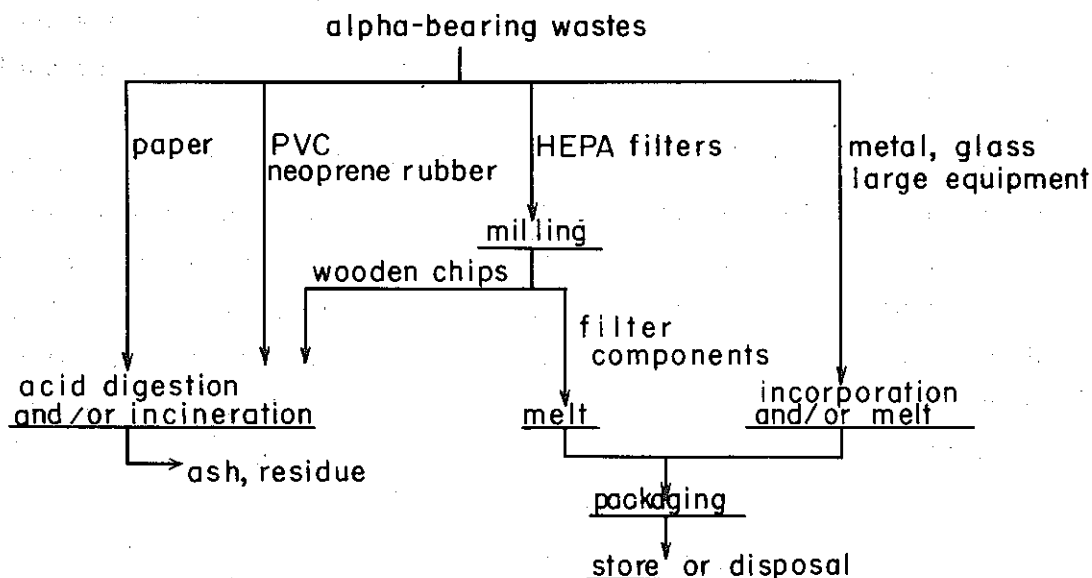


Fig. 2 A conceptual flowsheet for treatment

2. EXPERIMENTS AND RESULTS

2.1 Volume reduction of HEPA filters

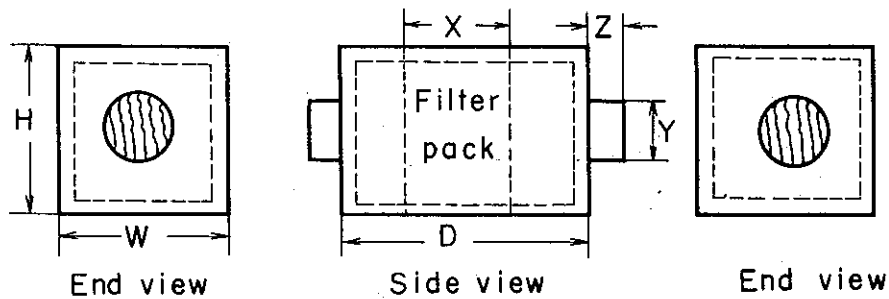
A high efficient air filtration system is essential in plant operations to safeguard personnel and the environment. HEPA filters must be replaced frequently because of pressure drop. At the PNC plutonium fuel facilities, about 300 of nipple connected HEPA filters, shown in Table I, are currently replaced per year and future operations will require use of up to 1,000 filters. These replaced HEPA filters are now stored in depots sealed in PVC bags and/or contained in drums, which amount to 26 volume percent of all solid alpha-bearing wastes at the facilities.

Scouting tests were performed on HEPA filters to evaluate the potential of certain processes for volume reduction and chemical stabilization. Included in these tests were milling of plywood frames, incineration of

milled wooden chips and melting of filter components. In this paper, experimental results of milling and melting are described.

Table 1 Sizes of the HEPA filters used in PNC plutonium fuel facilities

Size	Dimensions (mm)					
	H	W	D	X	Y	Z
C	305	305	457	150	100	38
F	610	610	508	292	300	102



2.1.1 Milling of plywood frames

A pilot wood milling machine was designed and constructed to demonstrate its feasibility. As shown in Fig. 3, the pilot model consisted of a filter feeder, and a milling machine with an end-mill cutter. The function of the model was to separate the filter components and nipples from a HEPA filter by milling the plywood frames. By exchanging chuck and filter support, the pilot model could treat both 610 by 610 by 508-mm and 305 by 305 by 457-mm filter.

For example, a F sized filter was chucked horizontally on the machine and milled in the way as illustrated in Fig. 4.

Circle one and two show that an nipple of the endframe was separated from the filter and let be down. As shown in circle three, the holed out endframe was rotated and milled from the central part to the outer part. Next to milling of the endframe, circle four shows that the filter was advanced in circle A direction for one-fourth of the filter length and fixed in the horizontal position. The downward sideframe was milled in circle B direction in the width of one-fourth of the filter length. Circle five shows the filter rotation for 90 degrees, and four times repetitional operations. Circle six shows that the filter was again advanced in circle A direction and fixed in the same way as the last

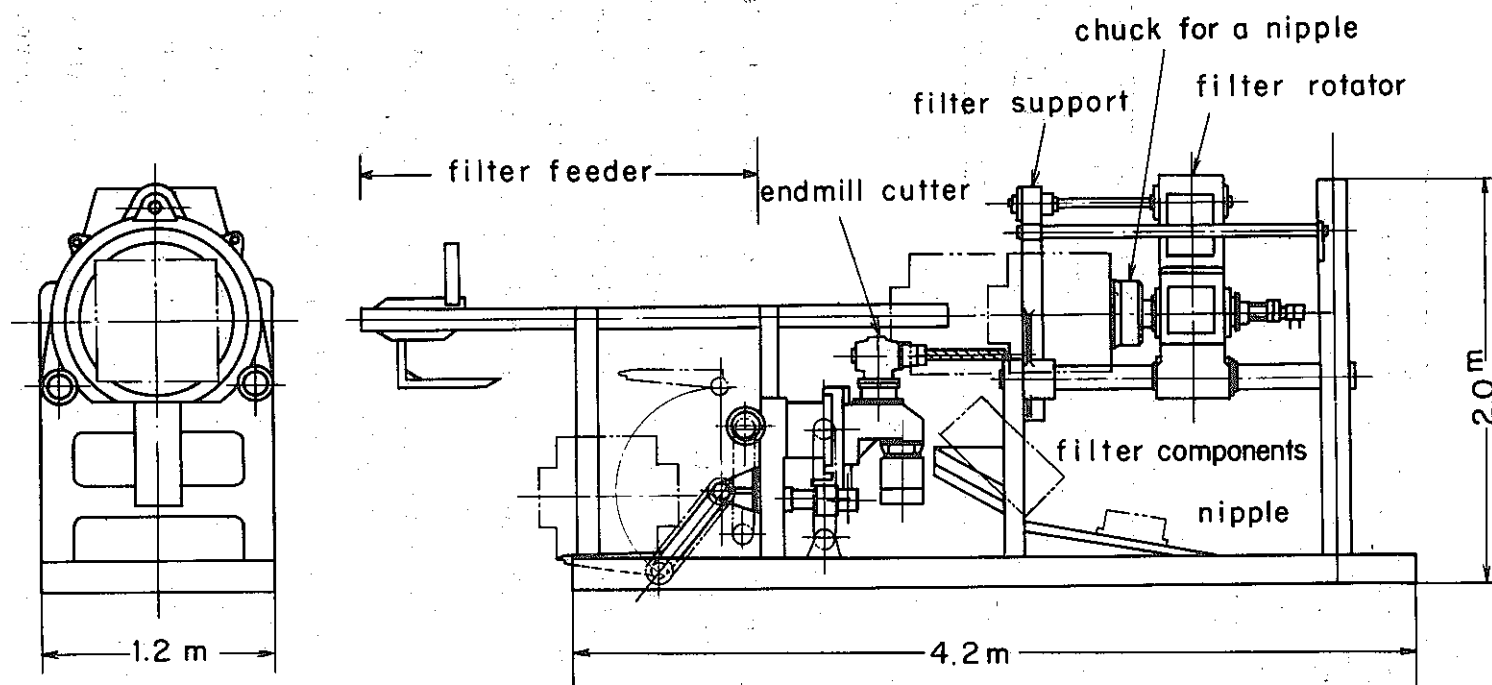


Fig. 3 A pilot wood milling machine for HEPA filter

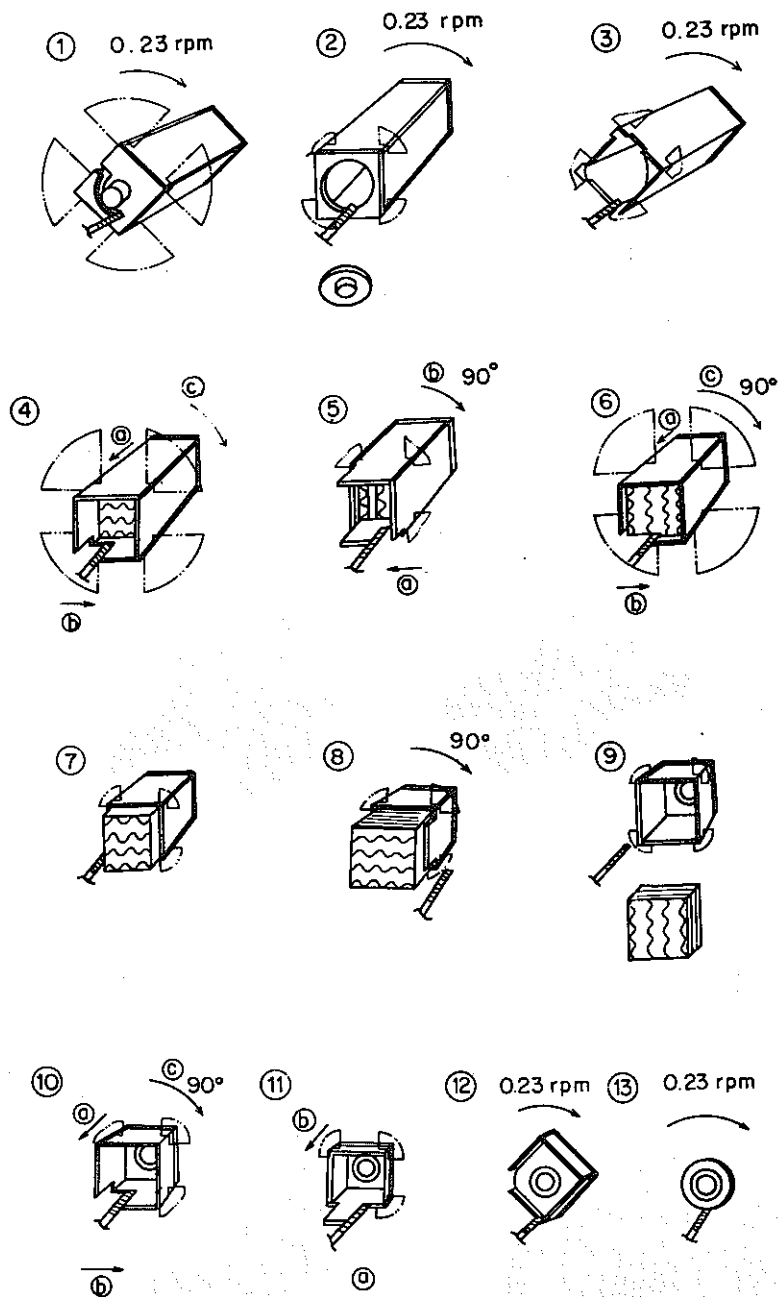
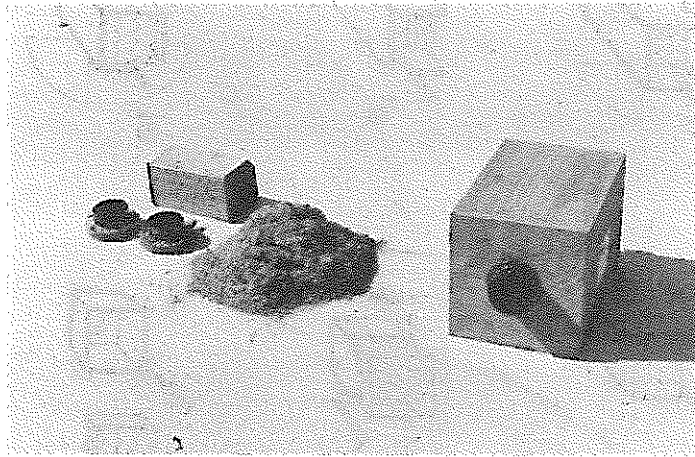


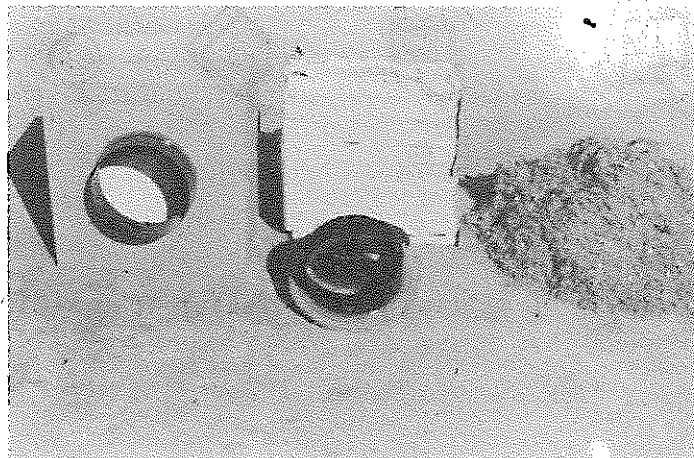
Fig. 4 Procedure of milling a HEPA filter (610 × 610 × 508-mm)

operations. As shown in circle seven to eleven, the four times operations were repeated four times until the sideframes were milled over. Circle twelve and thirteen show that only another endframe of the filter was left on the machine. The endframe was rotated and milled from the outer part and resulted in only a nipple.

With the current system, a HEPA filter on the milling machine was automatically milled from one endframe to four sideframes to another endframe, and resulted in fine sized wooden chips, two nipples and the filter components. Two kinds of HEPA filters and their milled parts are shown in Fig. 5.



305 x 305 x 457 mm filter



610 x 610 x 508 mm filter

Fig. 5 Milled HEPA filters

These experimental operations required about an hour for a C sized filter and less than two hours for a F sized filter. Longer endmill cutter and faster feed rate of cutter could more quickly mill over HEPA filters.

2.1.2 Melting of filter components

Melting experiments were conducted on filter components made of asbestos separators and glassfiber cloth. The power supply for a coreless electric induction furnace is 800 volts AC at 4,000 hertz and a current of approximately 300 amperes. Three graphite crucibles were made for melting the filter components. Each had its own tapping nozzle of 10, 14 and 16 millimeters inner diameter, respectively, in order to decide the most appropriate diameter for tapping. Inner diameter and thickness of the crucible were 200 millimeters and 30, respectively. As shown in Fig. 6, a graphite crucible was contained in a chamber to be in an inert atmosphere. The crucible heated itself by means of two separate induction heating coils. One was for melting zone and another was for tapping nozzle. The latter coil was used only for tapping.

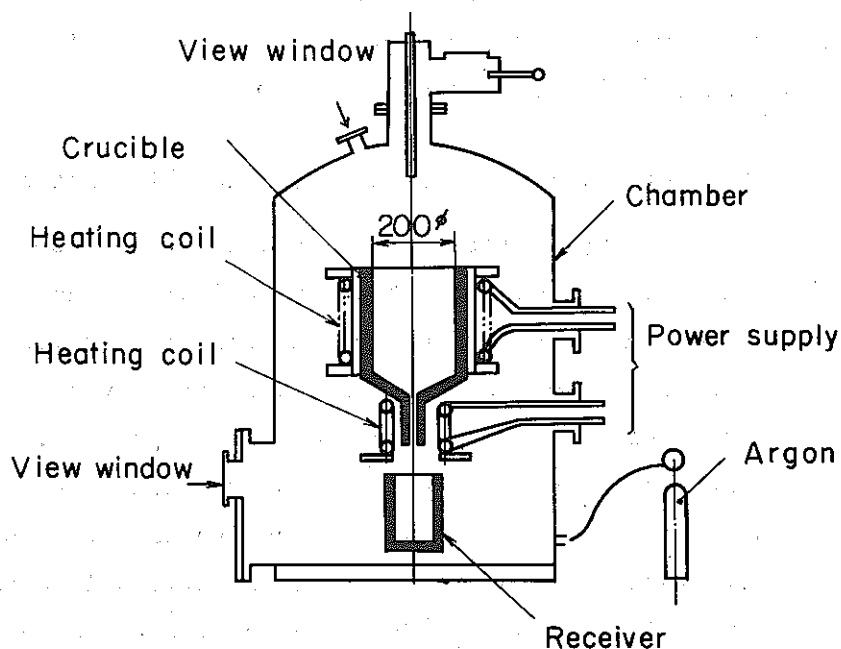


Fig. 6 Experimental melter

In a typical run, 4 kilograms of asbestos and one kilogram of glassfiber cloth were melted together in the crucible at temperatures

between 1,400 centigrade degrees and 1,700, and then the melted materials were tapped through the 16 millimeters of tapping nozzle at 1,400 degrees.

Glassfiber cloth softened at 900 degrees and asbestos separators in the melted glass at 1,400 degrees. The melted materials heated to 1,400 degrees poured intermittently, followed by over 100 seconds of continuous tapping. Freezed solids were shrinkage-cracked when taken out from the receiver.

Melted material, heated up to 1,600 degrees, became homogeneous and tapped continuously during 10 to 60 seconds. The continuous tapping didn't stop by closing the heating coil for tapping nozzle. Freezed solids were not shrinkage-cracked and easily taken out from the receiver. On the other hand, the 14 millimeters of tapping nozzle necessitated longer tapping time and the 10 millimeters of nozzle didn't let the melted material be down.

The melting method reduced the weight of filter components to 67 percent and made freezed solids of which apparent specific gravity was 2.8. X-ray diffraction analyses and polarizing microscopic examinations determined the freezed solids to be forsterite (Mg_2SiO_4). As above mentioned, milling of plywood frames, incineration of chips and melting of filter components could reduce the stored volume of HEPA filters to one-fiftieth or one-hundredths, and stabilize them.

2.2 Acid digestion of chlorine-containing combustible wastes

The ratio of polyvinyl chloride (PVC) and neoprene rubber wastes to the alpha-bearing wastes is 40 percent at the PNC plutonium fuel facilities. These wastes can not be treated with the incinerator installed in the above facilities because of the constructed materials corrosivity. Some preliminary investigations show that acid digestion process, being developed at the Hanford Engineering Development Laboratory, would be one of the most feasible processes to treat these wastes. The process is reported to digest combustible wastes in hot concentrate sulfuric acid containing nitric acid oxidant to form inert residues^[2,3]. Acid digested off-gases of PVC or neoprene rubber contain hydrogen chloride in addition to sulfur dioxide and oxides of nitrogen, which has two problems.

First, as shown in Fig. 7, azeotropic mixture of nitric acid and hydrogen chloride was distilled off at 105 centigrade degrees from the mixed solution of hydrogen chloride, nitric acid, sulfuric acid and water. The

experimental results are indicative of the difficulty to separate hydrogen chloride from nitric acid by distillation.

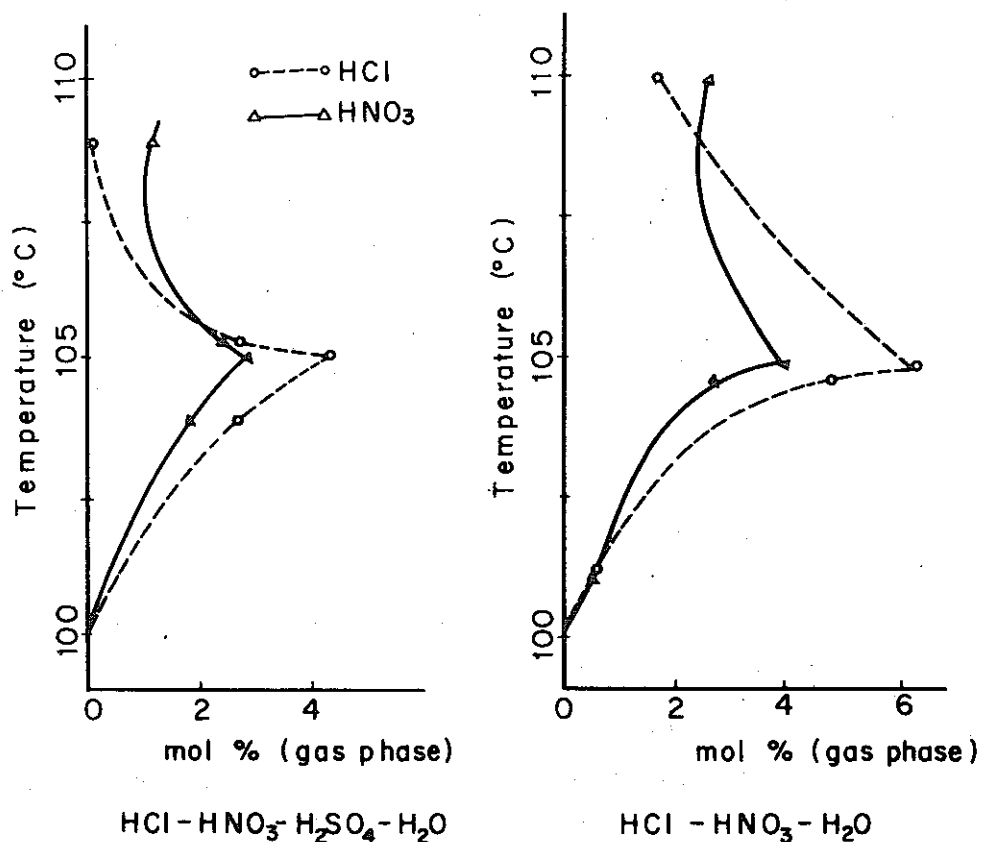


Fig. 7 Distillation curves of HCl and HNO₃

Second, as shown in Table 2, except for number five, dry hydrogen chloride gas was absorbed to nitrosyl chloride in the mixed solution of sulfuric acid, nitric acid and water. Formation of nitrosyl chloride makes it quite difficult to separate hydrogen chloride from nitric acid.

Table 2 Absorption of HCl


No.	(wt %)			Absorption of HCl (g/100g soln)
	H ₂ SO ₄	HNO ₃	H ₂ O	
1	15.8	14.3	69.9	35.5*)
2	29.5	13.3	57.2	20.1*)
3	52.0	11.8	36.2	1.5
4	69.8	10.5	19.7	0.2
5	84.1	9.5	6.4	- **)

*) $\text{HNO}_3 + 3\text{HCl} \rightarrow \boxed{\text{NOCl}} + \text{Cl}_2 + 2\text{H}_2\text{O}$

**) no NOCl

In order to solve the two problems, PVC and neoprene rubber were decomposed in sulfuric acid not containing nitric acid, and after decomposition nitric acid was added.

Table 3 Acid Digestion

PNC	HEDL
Neoprene rubber	All Combustibles
PVC	
1st H_2SO_4	$\text{H}_2\text{SO}_4 - \text{HNO}_3$
2nd HNO_3 addition	Mixed solution
	
Selective recovery of HCl	

2.2.1 Experimental conditions and results

Most experiments were performed on a small scale using all glass equipment. As shown schematically in Fig. 8, a typical setup consisted of a digester and two absorption columns. The digester is a five-neck flask with addition lines of nitric acid and wastes, places for a mixing shaft and a thermocouple, and an off-gas line with de-mister. The gases passed through the de-mister were fed to the two absorption columns.

In a typical run, 100 grams of PVC or neoprene rubber were added into 1,400 grams of concentrated sulfuric acid, which were heated at a temperature rise rate of 3 degrees per minute, and held at temperatures between 250 centigrade degrees and 270 for 30 to 60 minutes. After the decomposition of waste, nitric acid was added till the solution became clear.

Characteristics of gases produced by decomposition of PVC and neoprene rubber were studied in sulfuric acid in order to provide guideline data for off-gas handling. As shown in Fig. 9, the decomposition reaction was very rapid in hot concentrated sulfuric acid with the immediate release of decomposition gases. Neoprene rubber in sulfuric acid generated hydrogen chloride rapidly at 120 degrees, which terminated at 200 degrees. De-chlorination of PVC began at 190 degrees, and increased rapidly at 240 degrees, which terminated at 250 degrees. Both PVC and neoprene rubber generated sulfur dioxide between 150 degrees and 250, which indicate that de-chlorinated wastes were carbonized by sulfuric acid up to 250 degrees.

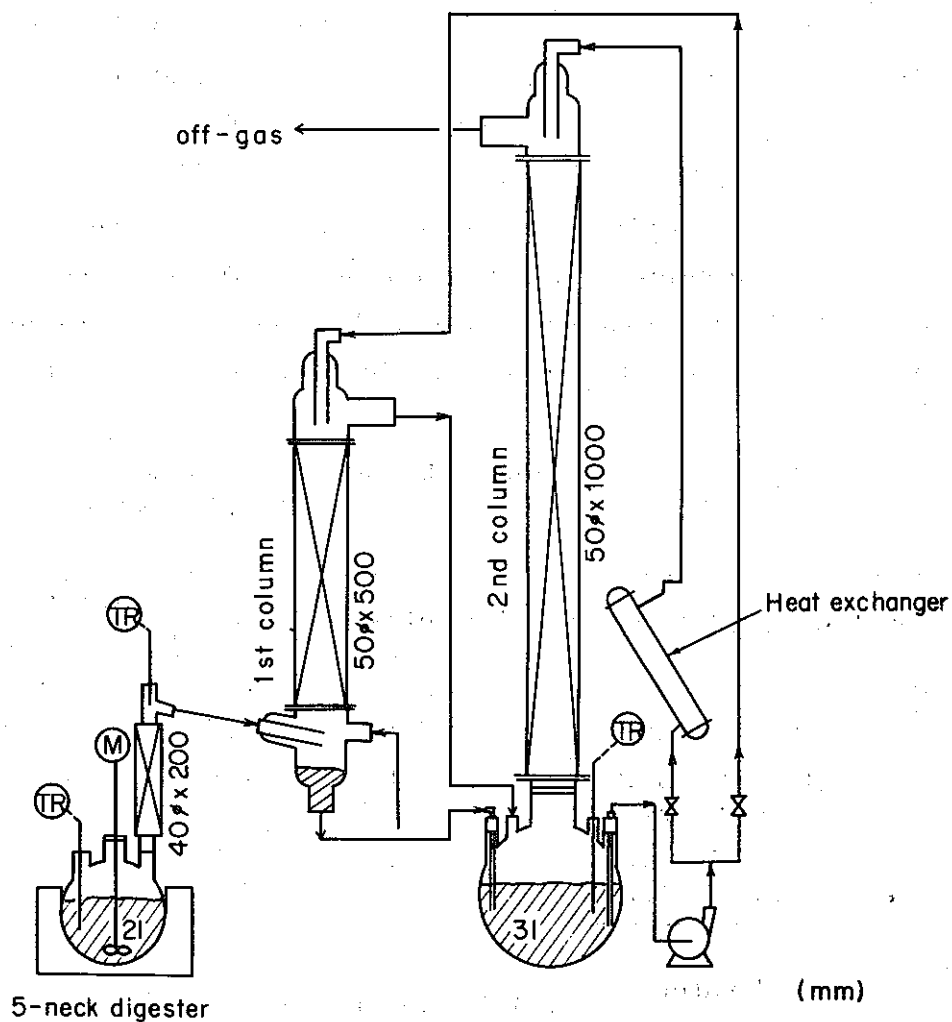


Fig. 8 Schematic of laboratory acid digestion equipment

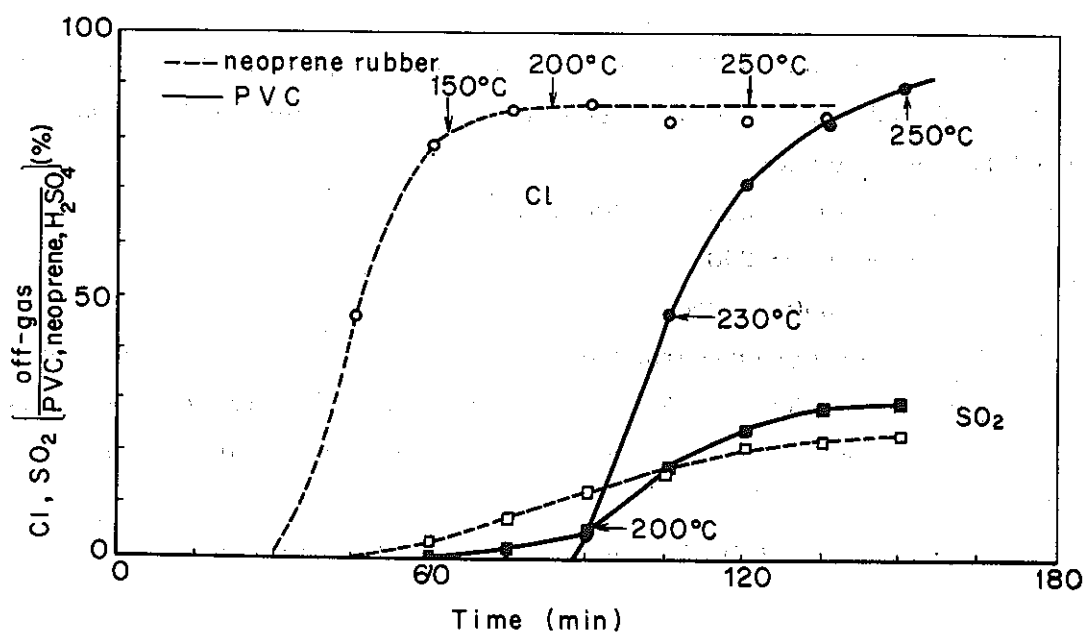


Fig. 9 Decomposition of PVC and neoprene rubber in H₂SO₄

The decomposition gases consisted of hydrogen chloride, sulfur dioxide, carbon dioxide and water vapor. As shown in Table 4, about 90 percent of hydrogen chloride was selectively absorbed in water in the first column, and sulfur dioxide was mainly absorbed to be sulfuric acid in the second column, to which 6 percent hydrogen peroxide solution was circulated. As above mentioned, hydrogen chloride and sulfuric acid could be selectively recovered from the decomposed off-gases. More precise separation of hydrogen chloride from sulfuric acid could be attained by distillation.

Table 4 Absorption of HCl and SO₂ (1 atm)
(g/100g soln)

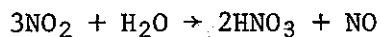
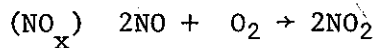
Sample		1st column*	2nd column**	Total	Recovery of chlorine(%)
PVC	Cl	36.4	0.1	36.5	88.6
	H ₂ SO ₄	24.6	373	397.6	
PVC	Cl	37.0	0.1	37.1	90.0
	H ₂ SO ₄	21.2	459	480.2	
Neo-prene	Cl	25.6	0.1	25.7	90.8
	H ₂ SO ₄	15.2	375	390.2	

* 500ml water

** 6% H₂O₂ solution

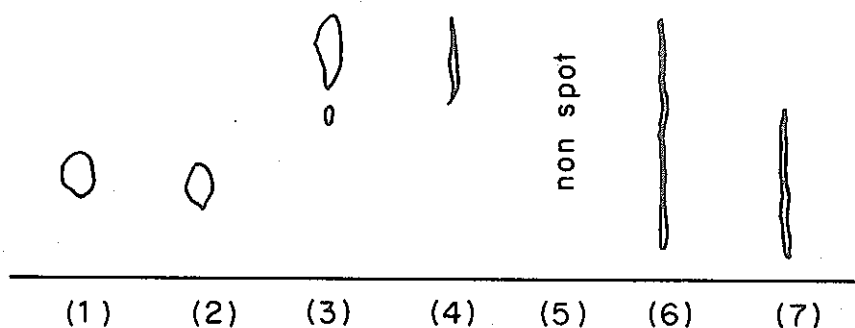
} 30°C (initial temp) ~ 35°C

Sulfur dioxide and oxides of nitrogen were respectively converted to sulfuric acid and nitric acid by the following reactions and can be recycled to the digester.



The thin layer chromatograms of acid solutions digesting PVC and neoprene rubber are shown in Fig. 10, which are indicative that no nitro compounds were formed on acid digestion of these wastes at higher temperature.

Next to these experiments, another group of experiments are now conducted with a 20 liter digester and eight columns.



- (1) 3-nitrophthalic acid
- (2) Phthalic acid
- (3) Acid solution digesting PVC at 260°C
- (4) " PVC at 270°C
- (5) " PVC at 290°C
- (6) " neoprene rubber at 270°C
- (7) " phthalic acid at 270°C

Fig. 10 Thin layer chromatograms

2.3 Dismantling of large equipment

Several experiments were made on dismantling of alpha-bearing gloveboxes and vessels. At the PNC plutonium fuel facilities, gloveboxes had been scrapped in the following conventional steps.

- (1) Bag out of the installed equipment
- (2) Decontamination and painting of the glovebox
- (3) Loading of the glovebox sealed in PVC sheet into a steel container.

These steps necessitated a large space to store them. In order to reduce the space consumption of those large equipment wastes, some dismantling experiments were conducted at their installed places.

2.3.1 Vessel for liquid waste

Polyethylene vessel, which had been used to store alpha-bearing liquid waste for seven years, were dismantled at its installed place. Temporary greenhouse made of PVC sheets was constructed around the 3 m³ of vessel. In the greenhouse, two air-line-suited workers cut the vessel with a portable electromotive saw.

2.3.2 Glovebox

A 3 m³ of glovebox made of stainless steel was cut using plasma cutter in a temporary greenhouse made of PVC sheets, inside of which another greenhouse made of fire-resistant vinylon sheets was constructed. The floor in the greenhouse was covered with PVC sheets and asbestos sheets. In the greenhouse, a worker cut the glovebox collaborating with an assistant and another worker surveyed the alpha-contamination of the greenhouse. The small cut pieces were directly fed into a waste container through a PVC sheet tunnel connected to the greenhouse.

The air passed through an intake prefilter before entering the enclosure or greenhouse. The enclosure was controlled at a negative pressure of 5 ~ 10 mm Water Columns with respect to the process room. The air was exhausted through a prefilter and two HEPA filters by the fan.

Thus, the vessel and glovebox could be cut down without spread of plutonium contamination outside the greenhouse.

3. CONCLUSIONS

- 1) Replaced HEPA filters and chlorine-containing wastes such as PVC and neoprene rubber amount to 66 volume percent of all solid alpha-bearing wastes stored at the PNC plutonium fuel facilities.

HEPA filter was experimentally milled to wooden chips, two nipples and filter components.

Filter components were melted at 1,600 centigrade degrees and freezed to be solids, of which apparent specific gravity was 2.8. The solids were found to be forsterite.

HEPA filters can be volume reduced to one-fiftieth or one-hundredths by milling and incinerating their plywood frames, and melting their components.

- 2) PVC and neoprene rubber were decomposed to carbon in sulfuric acid and oxidized by the addition of nitric acid.

Only chlorine in the vapor from the decomposition process was selectively absorbed in water.

- 3) An alpha-bearing glovebox was cut at the installed place without spread of plutonium contamination outside the greenhouse.

4. Acknowledgement

The authors wish to thank Dr. S. Hirono and his staff of Ningyo Toge Mining Office of PNC for their assistance in the form of determination of the freezed solid to be forsterite, and also thank the staff of Health and Safety Division, who were engaged in the dismantling of large equipment.

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