QUARTERLY PROGRESS REPORT
STUDIES ON MANAGEMENT
OF SELECTED WASTES
APRIL THROUGH JUNE 1974

Battelle

Pacific Northwest Laboratories
Richland, Washington 99352

JULY 1974

Prepared for the U.S. Atomic Energy
Commission under Contract AT(45-1):1830

BNWL-1843

NOTICE

The report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
U.S. ATOMIC ENERGY COMMISSION
Under Contract AT(45-1)-1830

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$4.00; Microfiche \$1.45

3 3679 00062 1732

BNWL-1843
UC-70
Waste Disposal
and Processing

QUARTERLY PROGRESS REPORT
STUDIES ON MANAGEMENT OF SELECTED WASTES
April through June 1974

Compiled by
K. J. Schneider
Nuclear Waste Technology Department

July 1974

BATTELLE
PACIFIC NORTHWEST LABORATORIES
RICHLAND, WASHINGTON 99352

FOREWORD

This is the third quarterly progress report for studies on management of nonhigh-level wastes being performed by Battelle-Northwest at the AEC's Pacific Northwest Laboratory.

Studies included in this report are:

- Decontamination and densification of chop-leach cladding residues,
- Waste treatment and handling processes, and
- Tritium separation and fixation.

The previous report in this series was BNWL-1825, January through March 1974. At present it is planned that future quarterly progress reporting will be integrated with other waste management studies being performed at the Pacific Northwest Laboratory.

CONTENTS

FOREWORD	iii
LIST OF TABLES	vii
LIST OF FIGURES	vii
SUMMARY	1
DECONTAMINATION AND DENSIFICATION OF CHOP-LEACH CLADDING RESIDUES	2
PROCESS SELECTION	2
ZIRCALOY-STAINLESS STEEL ALLOY EVALUATION	4
WASTE TREATMENT AND HANDLING PROCESSES	6
PROGRAM MANAGEMENT	6
BENCH-SCALE RESEARCH AND DEVELOPMENT	6
EXPERIMENTAL FACILITY DESIGN	17
TRITIUM SEPARATION AND FIXATION	25
AQUEOUS PHASE STUDIES	25
MOLECULAR EXCITATION	26
DISTRIBUTION	Distr-1

LIST OF TABLES

1	Summary of Yields from Pyrolysis at 700° C	8
2	Gas Compositions for Pyrolysis at 700° C of Different Waste Components of Different Sizes	9
3	Gas Compositions for Pyrolysis of PVC (-1/4 + 14 mesh) With and Without Fluxes at 700° C	9
4	Effect of Temperature on Pyrolysis Yields	11
5	Results with Simulated Feed	11
6	Gas Compositions with Simulated Feed	12
7	Manufacturers Contacted	19
8	Preliminary Design Criteria for a Low-Level Waste Facility	20

LIST OF FIGURES

1	Alpha Waste Processing with Tar Destruction by Indirect Heating	13
2	Alpha Waste Process with Tar Destruction by Partial Combustion of Product Gas	14
3	Cocurrent Flow Alpha Waste Process	15
4	Flow Diagram of Experimental Pyrolysis Facility	22

SUMMARY

DECONTAMINATION AND DENSIFICATION OF CHOP-LEACH CLADDING RESIDUES

The production of "typically" corroded test material for cladding hull decontamination process development was initiated. Examination of test materials showed expected results, and autoclaving is continuing.

WASTE TREATMENT AND HANDLING PROCESSES

The experimental work on pyrolysis of components present in alpha waste was completed during this reporting period. Use of sodium hydroxide as a fluxing agent was found to influence significantly the yields obtained during pyrolysis of polyvinyl chloride. The effectiveness of caustic fluxes for retention of chloride was demonstrated. No significant incentive for close control of the feed size is apparent from experimental results with different feed sizes.

The preliminary general design criteria and a preliminary flow diagram for the facility were completed.

TRITIUM SEPARATION AND FIXATION

Experiments were performed to test the effect of aqueous soluble salts on the isotope effect during the extraction of water. Distillation data were also determined. Both measurements indicated lack of appreciable effect.

Refinements have been made in the calculations of the vibration-rotation bands of the excited water molecule. The data indicate that more fundamental spectroscopic measurements are needed for water molecules. Prospects for separation of hydrogen isotopes by laser excitation remain very good.

DECONTAMINATION AND DENSIFICATION OF
CHOP-LEACH CLADDING RESIDUES

R. L. Dillon and R. S. Kemper

Fuel element cladding residues from the chop-leach head end process constitute a low density, high surface area metallic waste with a substantial actinide element contamination. The objective of this study is to determine the feasibility of and to develop methods for removal of long half-life transuranics from the cladding residues and for consolidation of the zirconium and stainless steel residues. The study involves:

- 1. Selection and laboratory testing of methods for transuranic removal by
 - a) aqueous reagents*
 - b) molten salt reagents*
 - c) fluxing during melting.**
- 2. Consolidation of the fuel element hulls by melting and casting Zircaloy, stainless steel, Inconel or alloys of the three.*
- 3. Testing and evaluating the consolidated fuel hulls for long-term waste management.*
- 4. Absorption and fixation of tritium into the waste ingots.*
- 5. Consolidation of transuranics removed.*

PROCESS SELECTION - B. Griggs

The review and selection of potential processes for decontamination and melting of chop-leach cladding residues have been completed and discussed in previous publications.^(1,2) Briefly stated the process selected for development consists of: (1) a gas phase treatment of cladding hulls by hydrogen fluoride or other gaseous fluorides to render the corrosion product oxide soluble in dilute aqueous fluoride solutions, (2) oxide removal and light etching in dilute aqueous fluoride solutions (nitric-hydrofluoric acid or oxalic-hydrofluoric acid-hydrogen peroxide solutions), (3) melting of the hulls into an eutectic stainless steel-Zircaloy alloy

by induction heating in graphite crucibles with and without a flux or solid absorbent. If the metal is to be reused for reactor applications, a more conventional cold wall crucible and arc melting of the segregated stainless steel, Inconel, and zirconium alloys would be required.

The gas phase fluoride treatment of the autoclaved Zircaloy to make the corrosion product films readily removable by aqueous decontaminants and the melt decontamination of zirconium alloys are the process steps requiring immediate development. The oxidized metal surfaces on which the gas phase conditioning process will be demonstrated are being produced by autoclaving Zircaloy-2 tubing, Inconel 718, and 304 stainless steel strip at 360°C in high purity water. The autoclaving time already exceeds 1600 hours running time with Zircaloy-2 weight gains between 33 and 40 mg/dm². Other treatments to produce "typical" corrosion product films will be compared with this autoclave process to develop a shorter treatment process for "typical" test material.

The necessary decontamination of the molten alloys is dependent on the radioactivities species left in the alloy after surface decontamination. The analysis of reactor exposed fuel cladding to determine the kind, amount, and location of radioactive contamination in the fuel hulls will indicate the validity of calculated values.^(1,2) Activities arise from impurities and alloying agents and define the magnitude of melt decontamination that will be necessary. Funding restrictions have delayed further experimental work until FY-75.

Plans for Next Period

The analyses of the exposed reactor tubing and gas phase pretreatment of corroded Zircaloy will proceed. The distribution of transuranic elements between molten zirconium alloys and flux will be examined together with miniscale tests of the proposed process.

ZIRCALOY-STAINLESS STEEL ALLOY EVALUATION - R. G. Nelson

No laboratory work was performed during this quarter.

Plans for Next Period

Melt stock, crucibles, molds and other materials will be procured. The melting furnace will be prepared for Zircaloy-stainless steel alloy melting. Crucible charges will be prepared and melting will be initiated. The proper melting cycles will be determined for the Zircaloy-10, 15 and 20 wt/% Inconel 718 + 304 stainless steel compositions using chopped Zircaloy-2, Inconel, and stainless steel sheet. The heats will be melted in graphite and in other crucible materials in a vacuum induction furnace. Ten to 30 pound heats will be made to examine crucible reaction, melting characteristics, physical, chemical and corrosion properties of the alloys.

References

1. B. Griggs, Feasibility Studies for Decontamination and Densification of Chop-Leach Cladding Residues, USAEC Report BNWL-1820, in publishing.
2. K. J. Schneider, editor, Quarterly Progress Report - Studies on Management of Selected Wastes - January through March 1974, USAEC Report BNWL-1825, April 1974.

WASTE TREATMENT AND HANDLING PROCESSES

V. L. Hammond, L. K. Mudge,
G. L. Roberts, R. A. Walter,
and R. G. Sullivan

The principal objective of this program is to evaluate current practice and to develop alternative processes for safe and economical volume reduction of low-level contaminated solid wastes (hereafter called alpha wastes) from 10- to 50-fold as a precursor to long-term storage and/or disposal. This objective is being pursued via 1) a phased program of bench-scale research activities leading to and supporting experimental-facility development activities and 2) by systematic and continuing analytical studies to assess developments in "current practice" for alternative candidate techniques for processing alpha wastes prior to long-term storage and/or disposal.

The PNL experimental program will initially emphasize pyrolysis as a means for reducing the volume (and weight) of combustible solid wastes. Also anticipated are significant advantages obtainable by combining pyrolysis with incineration and/or molten salt treatment methods.

PROGRAM MANAGEMENT - V. L. Hammond

Work on the bench-scale studies and the experimental design tasks was directed towards developing information for the annual report to be issued in August 1974. Details of this quarter's progress are discussed in the following sections.

BENCH-SCALE RESEARCH AND DEVELOPMENT - L. K. Mudge and G. L. Roberts

Studies were completed to evaluate the effect of feed size, the addition of fluxing agents, and temperature on pyrolysis of different alpha waste-feed components. Results on volume reduction, yields, gas compositions and char residue stability were reported in previous quarterly reports. Further discussion on the effect of feed size and fluxes is presented in this quarterly report.

Results obtained on pyrolysis of different alpha waste components are presented in Table 1. Based on material balances, generally about 80% of

the feed material is accounted for in the product streams except in some of the runs with polyvinyl chloride (PVC) where the overall accountability is less than 70%. Several factors contribute to the apparent loss of material: 1) since the surface area of the off-gas lines and condenser is quite large, removal of tars from these surfaces for weighing is extremely difficult; 2) some of the condensate is collected in the caustic scrubber solution and wet-test meter, making determination of the weight of condensate extremely difficult; 3) the caustic scrubber appears to be somewhat inefficient for HCl removal, especially in Run 3, where HCl should account for 58% of the weight; however, in Run 5 with tygon, HCl should account for only 25% of the weight; 4) unknowns detected by the chromatographs, are present in the off-gas and are assumed to have a molecular weight of 58 when the average molecular weight of the off-gas is calculated. Items 1 through 3 are suspected to be the major contributors to the material imbalance, especially in Runs 3 and 5 where extra care to account for these factors was not exercised. Unknowns in the gas phase should not affect the overall balance more than 5%. The weight of residue in the reactor can be determined without much difficulty and is accurately known.

Despite the low material balances, the effect of feed size and the addition of fluxes can be ascertained by examination of Table 1 and Tables 2 and 3, which present average gas composition. For the three different sizes of PVC used in Runs 3, 11, and 13 no significant effect on gas composition (Table 2) or on material distribution (Table 1) is apparent, although slightly more entrainment of material may have occurred in Run 11 with the smallest material size. The same observation can be made with the use of two sizes of polyethylene in Runs 6 and 12, except that significantly more methane and fewer unknown gases were produced from the larger size feed. A slower release of high molecular weight gases (unknowns) from the larger size feed than from the smaller size feed could result in a longer residence time in the reactor for the high molecular weight material, and thus more efficient thermal cracking. No significant incentive for close control of the feed size is apparent from the results of the experiments with different feed sizes.

TABLE 1. Summary of Yields from Pyrolysis at 700° C

Run	Waste Component	Yield, Weight %					Total Weight % Yield	Gas Vol. Liter/kg
		Gas	Condensate	Residue	H ₂ S	HCl		
1	Paper and Rags, - 5/8 in. + 1/4 in.	20.2	40	20.1	--	--	80.4	198
2	Neoprene, - 5/8 in. + 1/4 in.	16.9	6	43.6	0.9	12.9	80.2	199
3	PVC, - 5/8 in. + 1/4 in.	11.3	0.7	13.7	--	25.7	51.4	167
4	Latex, - 5/8 in. + 1/4 in.	40.3	42.4	1.5	--	0.3	84.5	338
6	Polyethylene, - 5/8 in. + 1/4 in.	74.6	6.5	0.3	--	--	81.4	634
5	Tygon, - 5/8 in. + 1/4 in.	25.3	2.7	7.3	0.2	29.1	64.6	300
7	PVC, -1/4 in. + 14 Mesh + Stoichiometric Na ₂ CO ₃	15.3	11.4 Tar 4.4 Aq	12.6	--	18.9	62.6	179
8	PVC, - 1/4 in. + 14 Mesh + 100% excess Na ₂ CO ₃	17.8	13.4 Tar 9.2 Aq	6.8	--	7.0	54.2	178
9	PVC, - 1/4 in. + 14 Mesh + Stoichiometric NaOH	11.0	23.0 Tar 9.0 Aq	36.6	--	7.4	87.0	205
10	PVC, - 1/4 in. + 14 Mesh + 100% excess NaOH	10.4	7.5 Tar 39.4 Aq	30.1	--	-0-	87.4	276
11	PVC, - 1/4 in. + 14 Mesh	10.6	11.9	14.1	--	47.5	84.1	165
13	PVC, - 1 in. + 5/8 in.	11.1	5.6	15.2	--	36.6	68.5	185
12	Polyethylene, - 1 in. + 5/8 in.	71.9	14.3	0.6	--	--	86.8	693

TABLE 2. Gas Compositions for Pyrolysis at 700°C of Different Waste Components of Different Sizes

Run	Waste Component	Composition, Volume %								Average Molecular Weight (a)
		H ₂	CO ₂	C ₂ H ₄	C ₂ H ₆	CH ₄	CO	C ₃ H ₈	Unknowns	
6	Polyethylene, -5/8 in. + 1/4 in.	8.9	0.07	35.1	7.1	23.9	--	12.6	12.3	28.7
12	Polyethylene, -1 in. + 5/8 in.	8.4	0.07	34.2	5.9	34.4	--	12.0	5	25.3
3	PVC, -5/8 in. + 1/4 in.	40.3	0.7	12.7	6.1	27.5	2.8	6.4	3.5	16.5
11	PVC, -1/4 in. + 1/4 Mesh	41.8	0.07	13.2	4.0	30.9	0.7	4.3	5	15.7
13	PVC, -1 in. + 5/8 in.	40.2	0.2	15	4.1	35.0	--	3.5	2	14.6

a. Molecular weight of 58 assumed for unknowns.

TABLE 3. Gas Compositions for Pyrolysis of PVC (-1/4 + 1/4 mesh) With and Without Fluxes at 700°C

Run	Flux	Composition, Volume %							Average Molecular Weight (a)	
		H ₂	CO ₂	C ₂ H ₄	C ₂ H ₆	CH ₄	CO	C ₃ H ₈		Unknowns
7	Stoichiometric Na ₂ CO ₃	31.4	9.6	10.9	6.5	25.1	6.1	5.4	5	20.9
8	100% excess Na ₂ CO ₃	25.5	23.7	10.4	4.4	24.4	2.9	3.6	5	24.4
9	Stoichiometric NaOH	57.1	0.8	9.2	4.1	19.6	0.6	3.7	5	13.1
10	100% excess NaOH	72.5	0.9	6.0	2.9	12.1	0.2	2.4	3	9.2
11	--	41.8	0.07	13.2	4.0	30.9	0.7	4.3	5	15.7

a. Molecular weight of 58 assumed for unknowns.

Use of fluxes with PVC significantly affected the gas composition (Table 3) and the material distribution (Table 1). An actual reduction in the amount of residue is noted when Na_2CO_3 is used as the flux in Runs 7 and 8, and, of course, the amount of CO_2 and CO in the product gas increases. This can be explained by examination of the reaction with HCl that occurs:

The molecular weight of the NaCl retained in the residue is less than the molecular weight of the Na_2CO_3 flux. The CO_2 and water both react with products of pyrolysis to produce CO.

The Na_2CO_3 flux was not nearly so effective for chloride retention as was the NaOH flux used in Runs 9 and 10. The use of the NaOH flux significantly influenced the volume of gas generated (Table 1) and the composition of the gas, which was rich in H_2 . The amount of residue also increased significantly (Table 1) with the use of the NaOH flux, as would be expected from the following reaction:

The molecular weight of the NaCl is greater than the NaOH flux, which contributes to the added weight of residue. Water produced by the reaction could react with the char from pyrolysis to produce the large amounts of H_2 , but this is doubtful since CO (which is not present in the product gas) would also be produced. The NaOH must catalyze degradation of PVC in a manner to produce large amounts of H_2 .

Results of pyrolysis experiments at 500°C with polyethylene and PVC feeds are compared to results at 700°C in Table 4. In general, the amount of conversion of the materials to a gaseous product is greater at the higher temperature while the amount of residue and condensate is less. With polyethylene at 500°C, the condensate had the fluidity of a highly viscous grease while at 700°C the condensate appeared to have the fluidity of number 10 oil. Volume reduction is the volume of feed minus the volume of uncompacted residue divided by the volume of feed.

TABLE 4. Effect of Temperature on Pyrolysis Yields

<u>Variable</u>	<u>PVC</u>		<u>Polyethylene</u>	
	<u>500°C</u>	<u>700°C</u>	<u>500°C</u>	<u>700°C</u>
Wt% Gas	8.3 ^(a)	10.6 ^(a)	30.7	74.6
Wt% Residue	17.9	14.1	-0-	0.3
Wt% Condensate	19.6	11.9	63.1	6.5
% Volume Reduction	49	62	>99	>99

a. Does not include volatilized HCl.

Experimental and calculated results from pyrolysis at 700°C of a simulated feed (15 wt% latex rubber, 15 wt% neoprene, 20 wt% PVC, 10 wt% tygon, 10 wt% polyethylene, 15 wt% paper, and 15 wt% cloth) are presented in Table 5. Calculated results are based on experimental results obtained with individual components combined in proportion to their presence in the simulated feed. Experimental results differ significantly from the calculated results only in the amount of condensate obtained.

TABLE 5. Results with Simulated Feed

<u>Variable</u>	<u>Calculated</u>	<u>Experimental</u>
Wt%, Gas	26.9 ^(a)	27.1 ^(a)
Wt%, Residue	17.1	18.5
Wt%, Condensate	24.1	41.9
Volume Reduction, %	52.1	48.4

a. Does not include volatilized HCl.

Material balances with the individual components were poor. The lost material was probably condensate, which is why the amount of condensate predicted for combining the individual components is low. Table 6 shows the gas composition obtained with the simulated feed, and the

composition calculated from results with individual components. Close agreement in calculated and experimental compositions is unlikely because of gas phase interactions.

TABLE 6. Gas Compositions with Simulated Feed

Method of Determination	Volume %							Unknown
	H_2	CO_2	C_2H_4	C_2H_6	CH_4	CO	C_3H_8	
Calculated	20.0	7.8	16.2	5.0	25.6	9.8	6.6	9
Experimental	24.0	4.4	12.4	5.5	20.6	9.0	6.1	18

An experiment was conducted in which simulated alpha waste of composition given above was gasified with air. Char from pyrolysis of simulated feed at 700°C was added to the reactor and was heated to 500°C. Air was then admitted at rates varying from 1 liter/min to 2 liter/min and the power to the heater interrupted. After burning the char for about 1 hour, simulated feed was added to the reactor in 50 gram batches at intervals of approximately 20 minutes. The gas generated was monitored continuously for CO concentration. An increase in the CO concentration after tamping the bed with the ram indicated that the ram was effective for channeling of air through the bed of waste. A total of 250 grams of feed was processed, and about 89 grams of a thick, viscous condensate was obtained. A volume reduction of 95% was obtained. Average processing rates were about 0.8 kg/hr m² at an air flow of 2 liter/min. Longer runs (at least 6 hr) would be required to firmly establish the processing rate for each airflow rate.

Processes for alpha waste employing gasification have the advantage that less effluent gas must be treated than with conventional incineration. Gas volume is less than 10% of the amount generated in conventional incineration. Tars formed in the process can be either removed or destroyed. Schematic flow diagrams for several processes employing tar destruction are shown in Figures 1 to 3. In addition, tar scrubbing with water or an oil solvent could also be used but would result in the generation of an undesirable waste stream.

FIGURE 1. Alpha Waste Processing with Tar Destruction by Indirect Heating

FIGURE 2. Alpha Waste Process with Tar Destruction by Partial Combustion of Product Gas

FIGURE 3. Cocurrent Flow Alpha Waste Process

Figure 1 represents destruction of tars by heating the exit gases indirectly to about 800°C to crack tars and oils. Heating of the gases is accomplished by burning a portion of the cleaned gas in the heat exchanger. Gases are cooled before filtering in a cyclone separator and a scrubbing tower. The cleaned gases not used for heating of the exit gas in the heat exchanger are incinerated before release to the atmosphere. Aqueous scrubbing may not be necessary if halides can be released from the system.

Figure 2 shows the same scheme for tar destruction as Figure 1, with the exception that heating of the gases is accomplished by burning a portion of the gases directly with O_2 . Such a scheme results in about a 9% increase in the volume of the gases if pure O_2 is used. The volume of gas that must be treated is still less than 12% of the volume that must be treated in processes employing conventional incineration. Destruction of tars by partial combustion of the product gases is practiced commercially in the Winkler process for coal gasification.

Cocurrent flow of air and waste material, as shown in Figure 3, results in complete destruction of tars since the gases pass through the hot ash zone before they exit the gasification reactor. The volume of gas generated by the process will be about the same as the volume generated by the process shown in Figure 2.

Use of fluxes for chloride retention would increase the amount of residue that must be handled for actinide recovery or for final disposition. The effect of the use of fluxes on final disposal and actinide recovery must be investigated before such use can be recommended. Therefore, a flow scheme employing fluxes was not considered at this time. The flow schemes shown in Figures 1 through 3 represent systems that could be used for effective processing of alpha waste to reduce their volume for final storage or actinide recovery. These schemes will be evaluated in greater detail later in the program.

EXPERIMENTAL FACILITY DESIGN - R. A. Walter and R. G. Sullivan

Work on the conceptual design of a low-level waste facility involved gathering of general process requirements. Establishment of these requirements can in part be based on previous experience gained from similar processes. A number of incineration and pyrolysis processes were investigated to determine the success of comparable hardware. Some of these processes include:

- Nuclear Waste Incineration System, General Electric Co.
- Contaminated Waste Recovery Facility, Atlantic Richfield Hanford Co.
- Garrett Pyrolysis Process, Garrett Research & Development Co., Inc.
- Rocky Flats Incinerator, USAEC
- Harvard University Air Cleaning Laboratory
- Radioactive Waste Incinerator, US Army Nuclear Defense Laboratory
- Wellmann-Galusha Gasifier (coal gasification), McDowell-Wellmann Co.
- SASOL Lurgi Pressurized Gasifier (coal gasification), South African Coal, Oil, and Gas Corporation.

Several observations were made from the study of these processes:

- The incoming solid waste requires close inspection to remove as much tramp metal as possible.
- The average size of waste fed into a reactor can be 2 to 4 inches for a batch feed process, but should be 1 inch or less for a continuous feed process.
- Horsepower requirements for shredding of the solid waste will be in the range of 0.8 to 1.5 hp-min/lb.
- The feed hopper for the reactor will most likely be sealed at its inlet to prevent air leakage into the process.
- Careful design of the valving used at the ash removal area of the reactor will be necessary to prevent excessive leakage and wear. Numerous processes have experienced problems in this area.

- Condensates and the larger particulates can most likely be removed from the off-gas stream with one piece of equipment.
- A centrifugal scrubber usually eliminates the necessity of an electrostatic scrubber in a process of this type.
- A fairly constant gas flow rate is required in a centrifugal scrubber to maintain consistent, efficient removal of particulates in the off-gas stream.
- A negative-pressure airflow system is preferable to a positive-pressure system.
- Allowance for expansion of the reactor due to temperature changes is essential.

In addition to the study made of available information on incineration, pyrolysis and coal gasification processes, numerous hardware manufacturers were contacted to determine what equipment was available for possible use in this facility. A list of these manufacturers is shown in Table 7. Discussions with these companies and others are continuing at the time of this report. On the basis of the process studies and the manufacturer's information, a preliminary list of design criteria was developed (Table 8).

A general process illustration is shown in Figure 4. The solid waste will be brought into the facility in boxes. These boxes will be emptied and the waste inspected on an open conveyor belt (in a hood). Through hand inspection and magnetic metal detection, most metal and other undesirable materials can be removed. The waste and containers will then be shredded to the proper size and transferred to a feed hopper. As stated earlier, the waste will most likely pass through a valve enroute to the hopper. The waste is transferred from the hopper to the reactor by a screw conveyor. In the reactor, the waste will first be distributed and then compacted by a rotating and oscillating mechanical device.

TABLE 7. Manufacturers Contacted

<u>Product</u>	<u>Manufacturer</u>
Shredders, Choppers	Rietz Manufacturing Co., Santa Rosa, Ca. Star Machinery, Seattle, Wa. Williams Crusher & Grinder, St. Louis, Mo. American Pulverizer Co., St. Louis, Mo.
Cyclone Separators	Joy Manufacturing Co., Seattle, Wa. J. A. Courtney Co., Portland, Or. Manning Packing & Supply, Portland, Or.
Air Lock Valves	Joy Manufacturing Co., Seattle, Wa.
Hoppers, Feeders, Conveyors	J. O. Roisum Co., Inc., Boise, Id. United Conveyor Corp., Chicago, Il. Syntron, Homer City, Pa. Meyer Machine Co., San Antonio, Tx. Link-Belt Co., Seattle, Wa. Kalamazoo Conveyor Co., Kalamazoo, Mi.
Absolute Filters	Joy Manufacturing Co., Seattle, Wa.
High Temperature Seals	Borg-Warner, Seattle, Wa.
Gas Burners	Johnson Appliance Co., Cedar Rapids, Ia.
Refractories	Babcock & Wilcox, Seattle, Wa.
Glass Lined Pipe	Ceramic Coating Co., Newport, Ky.

TABLE 8. Preliminary Design Criteria for a Low-Level Waste Facility

General Facility:

1. The capital cost of the facility should be reasonable.
2. The process utilized for the volume reduction of waste is one of pyrolysis/incineration. With minimal modifications, it would be advantageous for the hardware used for the process to be adaptable to the use of molten salts for ash removal.
3. The operation of the facility should be as automatic as is feasible.
4. Switching performed during operation of the facility will be interlocked to minimize operator error.
5. The facility must be adaptable to glove-box operation.
6. Potential problems due to corrosion in the vessel or in the off-gas treatment equipment will be addressed.
7. An inventory of radioactive materials will be kept at all necessary points in the process.
8. The mass flow rate of waste will be from 25 to 100 pounds per hour.
9. Overall airflow for the system will be from the surrounding area to a glove box and from this glove box into the process.
10. The airflow rate through the facility should be as constant as possible to insure acceptable and consistent operation of the cyclone separator.
11. The system will be designed to prevent generation of any secondary waste.

Feed System:

1. The unprepared waste must be thoroughly inspected by hand and by metal detection equipment to insure the removal of tramp metal and other noncombustibles.
2. The metal detection equipment should have a magnetic field of about 5000 gauss.
3. The waste will be shredded or chopped to a size of 1 to 4 inches.
4. The shredder or chopper selected must be capable of accepting some small amount of tramp metal.

Reactor Vessel:

1. The process will be carried out in a single, vertical vessel 1 to 2 ft in diameter and 4 to 8 ft in working length.
2. At least a portion of the inside walls of the vessel will be lined with two layers of cast refractory.
3. The vessel will be designed with sufficient expansion joints to prevent failure due to changes in temperature.
4. The process will take place at near atmospheric pressure and at temperatures ranging from 100 to 1400°C.
5. The reactor will operate under negative pressure. All openings into the reactor will be gasketed with high-temperature seal materials.
6. Provisions should be made for insertion of any fluxing agents used in the process.
7. The vessel will be constructed to allow for ease of inspection and maintenance.
8. Points for potential buildup of radioactivity in the walls of the reactor vessel will be minimized.
9. The overall volume reduction of the solids in this process will be from 10- to 50-fold.
10. The top level of waste in the reactor vessel should be distributed and compacted.
11. The discharge of ash from the reactor vessel should not affect the continuous operation of the facility. The ash discharge system will be removable.
12. The grate in the vessel will be designed to assure a smooth and uniform ashflow.
13. Means of monitoring the proper mass flow rate of solids and residence time in the vessel should be provided.

Gas Clean-Up:

1. The life of absolute filters used in the process should be reasonably long.
2. The system will be designed to meet criteria for release of exhaust gases to the atmosphere.

FIGURE 4. Flow Diagram of Experimental Pyrolysis Facility

The products from the pyrolysis/incineration process will be the ash and the off-gas. The ash will pass through an eccentrically rotating valve into an ash container. The off-gas stream will first pass through a gas cleanup system to remove the condensates and the particulates. Methods for handling the particulates and condensate will be developed after the particulates and condensates have been defined in the experimental program. The remaining gas will pass from the cleanup system to the absolute filters. The gas stream will then be mixed with excess air and combusted in a secondary burner which exhausts to the atmosphere.

The conceptual design of the pyrolysis reactor was completed during the report period. Based upon approximate material flow rates, the working size of the reactor was estimated to be 18 to 20 inches inside diameter and 96 inches long. The inlet feed mechanism for the solid waste was chosen to be a properly sized (about 1 foot in diameter) screw feeder. This selection is not final; both a hopper-feeder and a mechanical ram will be investigated as alternatives. Distributor and compactor mechanisms were conceptually designed to handle the waste immediately after the waste is fed into the reactor. The controls for the distributing and compacting mechanisms will be designed to operate independently. These mechanisms distribute and compact the waste to insure a uniform density which will prevent channeling of the air as it flows upward through the reactor.

The reactor itself will be lined with two layers of refractory in the working zones. The inside layer will be designed for service up to 1800°C, and the outer layer to 1000°C. The walls of the reactor are fitted with an appropriate number of parts for instrumenting the reactor.

At the lower end of the reactor, an ash-discharge air-inlet system has been conceptually designed. The grate used in this application will rotate continuously. The grate will contain openings to allow upward airflow and downward ashflow. The larger ash particles will be ground against the sides of the grate and subsequently discharged around the

sides of the rotating grate. These "clinkers" will be ground up against a metal surface which must be easily replaceable because of the anticipated wear from the highly abrasive ash. The rotating grate will be operated through a set of bevel gears driven external to the reactor.

The ash will be collected below the grate in a hopper with a steep angle to prevent bridging. The ash will subsequently be discharged through a rotary air-lock valve. A slide valve will be provided between the hopper and the air-lock valve to facilitate maintenance of the valve without stopping the pyrolysis process.

An engineering drawing of the pyrolysis reactor just described is currently being prepared.

Plans for Next Period

An interim report covering the activities in the program will be prepared. Process development activities continue.

TRITIUM SEPARATION AND FIXATION

L. L. Burger, R. D. Scheele,
and J. R. Morrey

The objectives of this program are to identify potential tritium separations methods and methods of fixing the tritium in forms suitable for storage.

The separations program aims to evaluate solvent extraction, molecular excitation, and other techniques that appear attractive. A secondary task is to implement the identification of potential separations methods by calculating separative work and costs in terms of separation parameters.

The fixation study will define the problem in terms of concentrations and amounts of tritiated water wastes and examine methods of immobilizing HTO for permanent storage.

AQUEOUS PHASE STUDIES - R. D. Scheele, L. L. Burger

Previous results from the attempts to utilize differences in hydrogen bonding between isotopic hydrogen species in water and water saturated organic solvents showed negligible isotopic separation effects. Work was carried out first with D₂O-H₂O mixtures, then with HTO-H₂O mixtures.

The relative volatilities of HTO and HDO with respect to H₂O are calculated to be:⁽¹⁾

<u>t°C</u>	<u>HTO/H₂O</u>	<u>HDO/H₂O</u>
25	0.913	0.930
50	0.934	0.950

A thermodynamically "ideal" solvent would then presumably extract the species in these ratios. At the other extreme one would hope that highly polar solvents would differentiate on the basis of differing hydrogen bond strengths and differing degrees of structure in the liquid water phase. In each case the forces in the aqueous phase appeared to be roughly balanced by similar ones in the organic phase.

As a final attempt to utilize structural differences, several attempts were made to:

1. Extract species other than water (such as HNO_2 , which forms very strong bonds with molecules like tributyl phosphate).
2. Add salts to water which are known to have marked structure making or structure breaking characteristics.

Numerous data exist which suggest differences in isotopic behavior, e.g., in hydrogen bond lengths in hydrates⁽²⁾ or differing mole fractions of nonbonded, singly bonded or doubly bonded H_2O molecules as a function of salt type.⁽³⁾ In the latter case, one might expect the more highly structured heavy isotopic species to be more affected than H_2O .

First attempts indicated some separation using both extraction with solvents and distillation from salted solutions. It appears that these data were erroneous and probably caused by quenching errors (scintillation counting) due to traces of salts.

D_2O solutions at 3% concentration in water provide a data check. At this concentration the species is nearly all DHO ($\sim 0.09\%$ D_2O) and can be determined by IR spectrophotometry using the 2500 cm^{-1} band. Experiments were carried out with $3M$ HNO_2 solutions and with the salt free water. Distillation of about 10% of the water was carried out at about 30°C . Both gave the same separation α , $\text{DHO}/\text{H}_2\text{O} = 0.93 \pm 0.02$. This is in good agreement with published vapor pressure ratios, which indicate 0.930 at 25°C , and indicates no measurable effect of the sodium nitrite.

Thus it appears that solvent extraction of water has a diminishingly small chance of showing an appreciable isotopic effect.

MOLECULAR EXCITATION - J. R. Morrey, L. L. Burger

The last quarterly report summarized the number of ways which optical excitation might be used to separate hydrogen isotopes. They are broadly

categorized as electronic excitation, vibrational excitation, and combination excitation. We have chosen to concentrate first on multiple vibrational excitation.

After choosing the excitation scheme, $(000) \rightarrow (210) \rightarrow (024)$ for exciting water molecules to about 50 kilocalories, based on calculated rotational levels of the (210) and (024) vibrational levels, the rotational spectrum of the (210) level was obtained by computer enhanced data acquisition. It did not correspond with the theoretically calculated spectrum. The reasons for the discrepancy have been determined to be (1) insufficient accuracy in calculating the moments of inertia of the vibrational state (210) and (2) the neglect of distortion coefficients for the moments at high J values. We conclude that we cannot calculate moments for high vibrational states to better than 1.5%. This means that an error for rotational level $J = 2$ may be as much as 3.4 cm^{-1} and that the transition $2_{11} \rightarrow 2_{02}^{(a)}$ proposed in our scheme, cannot be determined to better than ± 4.34 wave numbers.

The neglect of distortion coefficients in our theoretical calculations imposes additional uncertainty. These coefficients are well known for the ground vibrational states and could be calculated using data available in the first fundamental excitation levels, but it is doubtful that we can obtain sufficiently accurate distortion coefficients to extrapolate to the excited vibrational levels that are of interest. This leads us to the conclusion that more fundamental spectroscopic measurements are needed for the water molecule.

Of course, the interest is in separating tritium from hydrogen, and therefore the fundamental spectroscopy of the THO molecule also should be obtained in great detail. One could choose simpler molecules to demonstrate the separation of tritium from hydrogen, say, for example, HCl and TCI , but the preconversion of water to other molecules before separating the tritium will require considerable expense and energy. There

a. 2_{11} refers to state J_{KaKc} , etc.

is no reason to believe that a scheme cannot be developed for separation reactions involving tritiated water directly, but more fundamental spectroscopic data are needed.

We are aware of the need for spectroscopic data for water and tritiated water and are seeking sponsor support.

It is well known that energy exchange in collisional processes between water molecules is very efficient, principally because of the high density of vibrational states of the water molecule, allowing for possibilities of collisions with low defect energy. These collisions, which produce energy exchange, are detrimental to isotopic separation processes and must be carefully considered. There are schemes, however, on which we are currently working, which will minimize the difficulty of this effect.

The technology for tunable lasers in the ultraviolet is rapidly being developed. This leads us to continue to examine the possibilities of electronic transitions which would give rise to immediate dissociation, thus obviating the difficulties encountered in collisional processes.

Plans for Next Period

Molecular excitation studies will continue. Attempts will be made to obtain a better fit between observed and calculated spectra. The possibility of using other reactions will be considered.

A work plan for FY 1975 will be prepared. In addition to the laser separation program, the work will include continued survey of other separation techniques, experimental fixation studies, consideration of deep well storage, and a review of reprocessing schemes to maximize, recycle, and control of tritium within the plant.

References

1. W. A. Van Hook, J. Phys. Chem., vol. 72, p. 1234, 1968.
2. K. J. Gallagher, in Hydrogen Bonding, D. Haidzi, Ed., Pergamon Press, 1959.
3. G. R. Choppin and K. Buijs, J. Chem. Phys., vol. 39, p. 2042, 1963.

DISTRIBUTION

<u>No. of Copies</u>		<u>No. of Copies</u>	
	<u>OFFSITE</u>		<u>OFFSITE</u>
	<u>UNITED STATES</u>		
1	<u>AEC Chicago Patent Group</u> A. A. Churm	2	<u>AEC Division of Reactor Research and Development</u> Washington, DC 20545 Assistant Director for Reactor Technology E. E. Sinclair Chief, Fuel Recycle Branch W. H. McVey
2	<u>AEC Directorate of Licensing for Fuels and Materials</u> 4915 St. Elmo Ave. Bethesda, MD 20014 Deputy Director for Fuels and Materials S. H. Smiley Chief, Technical Support Branch for Fuels and Materials R. B. Chitwood	9	<u>AEC Division of Waste Management and Transportation</u> Washington, DC 20545 G. H. Daley J. C. Dempsey W. K. Eister O. P. Gormley A. F. Perge F. K. Pittman R. W. Ramsey R. D. Walton R. A. Wolfe
1	<u>AEC Division of Biomedical and Environmental Research</u> Washington, DC 20545 W. G. Belter		
2	<u>AEC Division of Production and Materials Management</u> Washington, DC 20545 F. P. Baronowski W. L. Lennemann	1	<u>AEC Idaho Operations Office</u> P. O. Box 2108 Idaho Falls, ID 83401 K. K. Kennedy
		2	<u>AEC Oak Ridge Operations Office</u> P. O. Box 2108 Idaho Falls, ID 83401 E. H. Hardison O. T. Turmelle

<u>No. of Copies</u>		<u>No. of Copies</u>	
1	<u>AEC Office of the Commissioners</u> Washington, DC 20545 Tech. Asst. - Com. C. E. Larson W. H. Beach	2	<u>Dow Chemical Company (AEC)</u> Rocky Flats Division P. O. Box 888 Golden, CO 80401 D. L. Ziegler M. A. Thompson
1	<u>AEC Savannah River Operations</u> <u>Office</u> P. O. Box A Aiken, SC 29801 P. D. Fairchild	2	<u>duPont Company, Aiken (AEC)</u> E. I. duPont deNemours & Co. Savannah River Laboratory Aiken, SC 29801
212	<u>AEC Technical Information Center</u>		C. H. Ice A. S. Jennings
3	<u>Allied Chemical Corporation</u> 550-2nd Street Idaho Falls, ID 83401 J. A. Buckham C. M. Slansky B. C. Musgrave	1	<u>duPont Company, Wilmington (AEC)</u> E. I. duPont deNemours & Co. Wilmington, DE 19898 A. A. Johnson
1	<u>Allied-Gulf Nuclear Services</u> P. O. Box 847 Barnwell, SC 29812 A. Schneider	2	<u>Environmental Protection Agency</u> Parklawn Building 5600 Fishers Lane Rockville, MD 20852 C. G. Meyers
3	<u>Argonne National Laboratory</u> 9700 South Cass Avenue Argonne, IL 60439 R. C. Vogel M. J. Steindler/L. E. Trevorow N. M. Levitz	1	<u>Environmental Protection Agency</u> P. O. Box 15027 Las Vegas, NV 89114 B. Mann
2	<u>Brookhaven National Laboratory</u> Upton, Long Island, NY 11973 J. J. Reilly R. H. Wiswall	1	<u>Environmental Protection Agency</u> 5555 Ridge Avenue Cincinnati, OH 45213 R. E. Landreth

No. of
Copies

- 1 General Electric Company
175 Curtner Avenue
(M/C 160)
San Jose, CA 95125

R. G. Barnes
- 1 General Electric Company
Vallecitos Nuclear Center
Vallecitos Road
Pleasanton, CA 94566

W. H. Reas
- 1 Gulf Energy and
Environmental Systems
P. O. Box 81608
San Diego, CA 92138

L. H. Brooks
- 2 Los Alamos Scientific
Laboratory (AEC)
P. O. Box 1663
Los Alamos, NM 87544

C. W. Christenson
H. S. Jordon
- 2 Monsanto Research Corporation
Mound Laboratory
P. O. Box 32
Miamisburg, OH 45342

C. J. Kershner
P. Lamberger
- 1 National Lead Company
111 Broadway
New York, NY 10006

Stephen Brown

No. of
Copies

- 1 National Academy of Sciences
Committee of Radioactive
Waste Management
National Research Council
2101 Constitution Avenue
Washington, DC 20418

D. Cyrus Klingsberg, Tech. Sec.
- 2 Nuclear Fuel Services, Inc.
P. O. Box 124
West Valley, NY 14171

Plant Manager

6000 Executive Blvd., Suite 600
Rockville, MD 20852

E. D. North, Director of
Technical Administration
- 1 NYS Atomic and Space
Development Authority
230 Park Ave., Rm. 2425
New York, NY 10017

J. G. Cline, General Manager
- 4 Oak Ridge National Laboratory(AEC)
P. O. Box X
Oak Ridge, TN 37830

Central Research Library,
Document Reference Section
Central Research Library, ORNL
Laboratory Records Dept., ORNL
Laboratory Records Dept.,
ORNL-RC

No. of
Copies

No. of
Copies

5 Union Carbide Corporation (ORNL)
Chemical Technology Division
P. O. Box Y
Oak Ridge, TN 37830

W. E. Clark
D. E. Ferguson
E. H. Kobisk
K. H. Lin
W. C. Ulrich

2 Sandia Laboratories
Albuquerque, NM 87107

A. C. Zuppero
R. L. Hagengruber

FOREIGN

1 EURATOM
Health Physics Division
29, Rue Aldringer
Luxembourg, BELGIUM

Rene Amavis

1 Atomic Energy Research
Establishment
Harwell, Didcot, Berks,
ENGLAND

K. D. B. Johnson

1 United Kingdom Atomic Energy
Authority
Risley
ENGLAND

D. W. Clelland

1 Centre de Marcoule
B. P. 106
30 - Bagnols S/Seze
FRANCE

R. Bonniaud

1 Centre d'Etudes Nucleaires
de Fontenay-aux-Roses
Boite Postale 6
92 - Fontenay-aux-Roses
FRANCE

Y. J. Sousselier

2 Institut für Chemische
Technologie
Kernforschungsanlage
Jülich GmbH
D517 Jülich
Postfach 365
GERMANY

E. R. Merz
K. H. Rattay

1 MGH/GWK/Wiederanfertigung -
Sanlage/WAK
Karlsruhe
GERMANY

W. A. Isse1

1 Nuclear Research Center
Waste Management Dept.
D75 Karlsruhe
Weberstr. 5
GERMANY

H. Krause

2 CNEN
Direttore di Programma
Eurex Del CNEN
Saluggia "Vercelli", ITALY

Giacomo Calleri

Laboratorio di Ingegneria
Sanitaria
Via Anguillarese km 1 + 300
Roma, ITALY

Willy Bocola

<u>No. of Copies</u>		<u>No. of Copies</u>	
2	<u>Bhabha Atomic Research Centre</u> Waste Treatment Division Trombay, Bombay, INDIA N. S. Sunder Rajan K. T. Thomas	9	<u>Atlantic Richfield Hanford Company</u> M. H. Campbell R. E. Isaacson H. P. Shaw A. E. Smith M. J. Szulinski J. H. Warren D. D. Wodrich File Copy
1	<u>India Atomic Energy Establishment</u> Waste Treatment Plant and Decontamination Center Bombay 85, INDIA Victor Amalraj, Plant Superintendent	1	<u>Exxon</u> Richland, WA 99352 S. J. Beard
2	<u>International Atomic Energy Agency</u> Kartner Ring 11 P. O. Box 590 A-1011, Vienna, AUSTRIA	2	<u>United Nuclear Industries, Inc.</u>
1	Dr. H. F. Ramdohr c/o Friedrich Uhde GmbH 46 Durtmund Deggingstr. 10-12 GERMANY <u>ONSITE</u>	1	<u>Westinghouse Hanford Company</u> C. R. Cooley
6	<u>AEC Richland Operations Office</u> O. J. Elgert R. B. Goranson N. T. Karagianes R. D. Fogerson B. J. Melton F. R. Standerfer P. G. Holsted	37	<u>Battelle-Northwest</u> E. L. Alpen L. L. Burger/J. R. Morrey N. E. Carter D. L. Condotta G. M. Dalen R. L. Dillon J. W. Finnigan J. J. Fuquay B. Griggs V. L. Hammond G. Jansen R. S. Kemper/R. G. Nelson M. R. Kreiter D. H. Lester J. L. McElroy L. K. Mudge R. E. Nightingale/R. E. Burns A. M. Platt

BNWL-1843
UC-70

No. of
Copies

Battelle-Northwest (contd)

J. A. Powell
F. P. Roberts
K. J. Schneider (3)
W. H. Swift/D. E. Olesen
P. C. Walkup/G. F. Schiefelbein
W. K. Winegardner
H. H. Van Tuyl/J. L. Ryan
Technical Information (5)
Technical Publications (3)
BNW Patent Office