BNWL-2138
UC-70
Waste Management

FLUIDIZED BED CALCINATION EXPERIENCE
WITH SIMULATED COMMERCIAL HIGH-LEVEL
NUCLEAR WASTE

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November 1976

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ABSTRACT

Development and testing of a pilot-scale fluidized bed calciner (1-2 MTU/day) are described. Simulated high-level liquid waste compositions representing those most likely to be generated by commercial nuclear fuel reprocessors were calcined prior to conversion to borosilicate glass forms. A new, much improved operating technique, continuous inert-bed operation (CIB), is described.

ACKNOWLEDGMENTS

The author is indebted to F. E. Haun for his operational assistance and preparatory work related to this process operation and also to H. H. Irby for his assistance during design and installation.

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SUMMARY

Calcination of simulated high-level nuclear wastes representative of those to be generated by commercial fuel reprocessors has been tested in a fluidized bed calciner using a new operating technique. An inert material is added to the calciner continuously during operation. The addition of this material improves the operation in many respects: particle size control is not required; a low inventory of fission products is maintained in the bed; coupling to a melter is improved; high sodium-bearing wastes can be calcined; and high feed rates are possible.

This type of operation is used as the drying step prior to mixing the wastes with a frit and melting them to a borosilicate glass form, the most likely form for storage of high-level wastes.

The calciner is heated by in-bed combustion and uses sintered metal filters for primary off-gas cleanup. A simplified atomizing nozzle has been used for introducing feed to the calciner. It consists of concentric tubes and is relatively maintenance free. A wide range of feed chemical compositions has been tested, including wastes with sodium concentrations near 1M.

INTRODUCTION

A pilot-scale fluidized bed calciner has been installed and operated at Battelle, Pacific Northwest Laboratory (PNL) since late CY-1974. The work was performed by the Chemical Technology Department's Nuclear Waste Processing Section as part of the Waste Fixation Program. This work is to provide data for process and equipment development in the conversion of simulated high-level liquid commercial nuclear waste to a solid. A calcine product is produced and can be fed directly or indirectly to a melting system for vitrification.

PNL's choice to investigate and develop a vitrified product as a candidate final waste form opened the door for new operating techniques for the calcination step. Several concepts were tried, and significantly improved operating techniques were developed which capitalize on the excellent heat transfer, heat distribution, and solids mixing properties of the fluidized bed. The unconventional operating techniques that have evolved have reduced or eliminated concerns such as fission-product decay heat generation and particle size control which often impede conventional calcination of commercial waste.

The most successful operating concept has been termed the continuous inert bed process (CIB). It was developed from inert bed attrition-elutriation type operation.

PROCESS DESCRIPTION

CALCINATION

The calcination process is based on the decomposition of waste feed solutions (metal nitrates) to various solid oxide compounds (calcine) and nonmetal oxides (off-gas). Figure 1 and Table 1 show a flowsheet and material balance.

Various feed solutions are used representing different reprocessing techniques. Table 2 lists the general composition of some of these solutions. Table 3 lists some of the reactions taking place during calcination.

To operate in the continuous inert bed manner, the bed section of the vessel is filled with a granular inert material-- SiO_2 (quartz sand). This material is cheap, durable, and insensitive to extreme temperature changes. Furthermore, it can be incorporated into accepted glass forms chosen as final products without increasing volume.

A particle size range of about 28 to 65 Tyler mesh is typical. A bed charge of ~15 kg is initially required. Air inflow at a 1 ft/sec superficial velocity is required to fluidize the bed.

Process heat is supplied by the combustion of pure oxygen and kerosene directly in the reaction chamber (bed). Prior to autoignition of the fuel, external heating is needed to heat the bed to ~375°C. A propane heater in the fluidizing air line has been used for rapid heating. When the desired preheat temperature is reached, oxygen and kerosene are metered to the vessel along with nitric acid or feed. Ignition is instantaneous.

Feed solution being calcined either coats the bed, is spray dried, or coats and wears away because of colliding with other particles. The precise mechanism is not quantified. It can be influenced by changing process variables such as temperature, feed composition, atomizing characteristics, or jet grinding.

At or near the time feed is introduced, addition of inert bed material is started from the storage hopper to the reaction chamber. The rate of

FIGURE 1. Fluidized Bed Calciner and Off-Gas System

TABLE 1. Fluidized Bed Calciner Material Balance

	1 ^(a)	2	3	4	5	6	7	8	9	10	11	12	13	14
	FLUIDIZING AIR	PLENUM	LOWER BED	UPPER BED	DISENGAGING SPACE	FUEL	FUEL ATOMIZING OXYGEN	FEED	ATOMIZING AIR	INERT BED MATERIAL	FILTER VESSEL	BLOW BACK AIR	FILTERED OFF-GAS	CALCINE PRODUCED
TEMPERATURE °C	20	360	550	550	475	24	23	25	20	360	100	360		
PRESSURE psig	50	0.2	-0.2	-0.3	-0.4	80	80	5	90	-0.43	80	-0.9		
LIQUID RATE $\frac{\text{L}}{\text{hr}}$					4.5		25							
GAS RATE scfm	6.0		6.0				4.4		4.5			37		
GAS RATE acfm	1.46						0.74		0.68			91		
VELOCITY ft/sec			1.0	6.0	3.0									
SOLIDS RATE $\frac{\text{kg}}{\text{hr}}$									1.11				4.47	

a. Refer to Figure 1.

TABLE 2. Composition Ranges of Representative
High-Level Radioactive Wastes, as
Solution(a)

Concentration M @ 378 g/MTU

Inerts

HNO ₃	1 - 7
Na	0.01 - 1.2
Fe	0.05 - 0.19
Cr	0.01 - 0.045
Ni	0.005 - 0.02
PO ₄	0.025 - 0.24
Gd	0 - 0.15

Fission Products

Rb	0.010
Sr	0.027
Y	0.014
Zr	0.106
Mo	0.095
Tc	0.022
Ru	0.059
Rh	0.010
Pd	0.032
Ag	0.002
Cd	0.002
Te	0.012
Cs	0.054
Ba	0.027
La	0.024
Ce	0.051
Pr	0.023
Nd	0.071
Pm	0.0019
Sm	0.014
Eu	0.003
Gd	0.002

Actinides

U	0.01 - 0.05
Np	0.009
Pu	0.0001 - 0.002
Am	0.002
Cm	0.0004

a. 3.3% Enriched, 33,000 MWd, 30 MW

TABLE 3. Oxides Formed from Calcination Reactions

HNO_3	$\rightarrow$	N_2	$+$	H_2O	$+$	O_2	$+$	NO_x
$\text{Fe}(\text{NO}_3)_3$	$\rightarrow$	Fe_2O_3	$+$	NO_x				
$\text{Cr}(\text{NO}_3)_3$	$\rightarrow$	Cr_2O_3	$+$	NO_x				
$\text{Ni}(\text{NO}_3)_2$	$\rightarrow$	NiO	$+$	NO_x				
H_3PO_4	$\rightarrow$	P_2O_5	$+$	H_2O				
MoO_3	$\rightarrow$	MoO_3						
$\text{Sr}(\text{NO}_3)_2$	$\rightarrow$	SrO	$+$	NO_x				
$\text{Ba}(\text{NO}_3)_2$	$\rightarrow$	BaO	$+$	NO_x				
CsNO_3	$\rightarrow$	Cs_2O	$+$	NO_x				
KNO_3	$\rightarrow$	K_2O	$+$	NO_x				
$\text{Zr}(\text{NO}_3)_2$	$\rightarrow$	ZrO_2	$+$	NO_x				
$\text{Co}(\text{NO}_3)_2$	$\rightarrow$	Co_3O_4	$+$	NO_x				
TeO_2	$\rightarrow$	TeO_2						
AgNO_3	$\rightarrow$	Ag_2O	$+$	NO_x				
$\text{Cd}(\text{NO}_3)_2$	$\rightarrow$	CdO	$+$	NO_x				
$\text{RENO}_3 \text{ Mix}^{(a)}$	$\rightarrow$	$(\text{RE})_2\text{O}_3$	$+$	NO_x				
NaNO_3	$\rightarrow$	Na_2O	$+$	NO_x	$+$	NaNO_3		
$\text{Gd}(\text{NO}_3)_3$	$\rightarrow$	Gd_2O_3	$+$	NO_x				
$\text{Ce}(\text{NO}_3)_3$	$\rightarrow$	Ce_2O_3	$+$	NO_x				
$\text{Nd}(\text{NO}_3)_3$	$\rightarrow$	Nd_2O_3	$+$	NO_x				

a. Rare earths

addition and whether it is continuous or semi-continuous depends on the specific run plan. As a lower limit, to maintain proper bed level the rate of addition needs to be equal to the bed material worn down and elutriated. An upper limit would be dependent on the next processing step. For example, when vitrifying, the inert rate would be equivalent to that needed for subsequent glass making. This is roughly equal to the weight of calcine being generated.

The constantly increasing bed level is controlled by periodically opening a valve in the overflow pipe. Constant bed level control could be maintained by continuous overflow through a properly sized pipe; however, for the pilot-plant unit the valve was desirable.

Off-gas passes from the calcining vessel to the adjacent filter vessel. The gas goes through a cyclone section and sintered metal filters before entering the wet clean-up system. The cyclone is being used to reduce the solids loading to the sintered-metal filters. The cyclone is not required but is being tested as part of the equipment development program.

A seal pot connected to the calciner acts as a safety relief device in case of pressurization.

The properties of the solid produced depend on the waste feed composition and operating conditions. Typical property ranges are listed in Table 4. Table 5 shows typical off-gas composition.

GAS DISTRIBUTION IN THE FLUIDIZED BED

The gas velocity in the middle and upper portions of the fluidized bed is much higher than that needed for fluidization. This is due to the additional gas from combustion, atomizing air, and feed evaporation. The degree of elutriation achieved can be designed into the process by the disengaging space configuration and overflow characteristics. With the CIB process, when a valve is used in the overflow, all gas goes up through the disengaging vessel and to the gas-particulate separator vessel. When the overflow valve is opened, most of the gas will take the path of least resistance

TABLE 4. Typical Properties of Calcine Product^(a)

Bulk Density, g/cc	2.0-2.4
Particle Density, g/cc	4.0
Attrition Index	60-70
Average Particle Size, mm	0.15-0.30
Size Distribution (approximate)	+200 mesh-66%, -200 mesh-34%
X-Ray Pattern	Amorphous
NO ₃ ⁻ , wt%	0.3-4.0 (Temperature dependent)
Total Volatiles, wt%	0.7-7.0
Thermal Conductivity ⁽¹⁾ kW/m°C	@ 40°C = 0.18 @ 600°C = 0.33

a. Bed and fines can vary considerably, depending on feed, operating conditions, etc.

TABLE 5. Typical Off-Gas Composition

<u>Component</u>	<u>Mole %</u>
N ₂	71.0
O ₂	16.0
N ₂ O	0.15
NO + NO ₂ + N ₂ O ₄	0.52
CO ₂	11.3
CH ₄	0.02
CO	1.0

through the overflow, sweeping the bed material with it. Figure 2 shows the gas velocity and volumetric rates at various points in the calciner. It also indicates the source of the gas and the operating pressure in the vessel.

FIGURE 2. Gas Velocity and Distribution in the Fluidized Bed Calciner Heated by In-Bed Combustion

CALCINATION-VITRIFICATION

Calcination and vitrification equipment as envisioned for a commercial reprocessing facility would be operated as a coupled unit. Vitrification could be done using either an in-can melter⁽²⁾ or continuous ceramic melter.⁽³⁾ This was not always practical in the pilot plant. For example, the in-can melting system, a portable unit, has been coupled with a spray calciner, the fluidized bed calciner, and a wiped-film evaporator. Runs have been made with the in-can melter directly coupled using the configuration as shown in Figure 3. All gases generated in the canister are filtered through the calciner's sintered metal filters. Glass-forming material (frit) is added from a feeder to the melter proportionately to the CIB product being generated.

The continuous ceramic melter, however, as being tested at PNL, was not designed as a portable unit. Operation with the continuous ceramic melter has been through an indirect coupling or using no coupling at all. Indirect coupling would be simply feeding previously calcined material to the melter while routing the off-gas through the fluidized bed. Direct coupling would be as shown in Figure 4.

Coupling to either melter is quite simple and has not been considered a design problem.

FIGURE 3. Fluidized Bed Calciner Coupled to the In-Can Melter

FIGURE 4. Fluidized Bed Calciner Coupled to the Continuous Ceramic Melter

EQUIPMENT DESCRIPTION

CALCINER VESSEL

The calciner vessel comprises three sections which, flanged together, give a total height of about 5-1/2 ft (Figure 5). The bottom section (plenum) is made of 3/8-in. type 310 stainless steel (SST) plate. It is 6-3/4 in. square and 7-1/16 in. long. It contains a bed drain, plenum drain, distributor plate, fluidizing air inlet, and pressure tap. The second section (spool piece) is 6-3/4 in. square by 20-1/4 in. long and built of 3/8 in. type 310 SST plate. It contains the product overflow, feed nozzle, fuel nozzle, pressure taps, removable door, and bed drain. The third section (disengaging) is 9-3/4 in. square and 3 ft long. Made of 3/8 in. type 310 SST plate, it contains the off-gas line, seal pot line, bed addition line, thermocouples and pressure taps. All pipes, fittings, and flanges on the vessel are 304L SST.

Distributor Plate

A perforated distributor plate (drilled with one hundred 0.046-in.-dia holes on a 0.707 in. square grid pattern) has been used for most testing. The distributor plate is inclined to facilitate bed draining. Some tests have been started recently with a conical distributor.

Feed Nozzle

Air atomized feed nozzles are used to introduce the waste into the calciner. At first modified commercial nozzles (Spraying Systems Company) were used, typically a 40100 fluid nozzle with a 120 air cap. Later a much simpler tube type nozzle was used consisting of two concentric tubes. See the section on equipment development for details.

Fuel Nozzle

Commercial gas atomized wide-angle internal mix nozzles have been used for the atomization and combustion of oxygen and kerosene. Specific nozzles used were purchased from Spraying Systems Company.

FIGURE 5. Calciner Vessel

Solids Feeder

A slide valve feeder (Figure 6) is used to introduce bed and inert material into the calciner while operating. The sealed hopper prevents in-leakage to the vessel, which operates at a negative pressure. A valve between the hopper and vessel is closed when charging the hopper with new material. An air pulse type of solids feeder with no moving parts has also been used to add materials continuously to the bed.

FILTER-CYCLONE VESSEL

The filter-cyclone vessel consists of three pieces which when flanged together give a total height of 9 ft 6 in. The top piece, a blowback dome, is 20-5/8 in. in diameter by 7-3/16 in. tall. Made of 304L SS, it contains the blowback nozzles for the filters, off-gas outlet, pressure taps, and thermocouples (Figure 7).

FIGURE 6. Slide Valve Solids Feeder

FIGURE 7. Filter Vessel

The filter vessel is 20-5/8 in. in diameter by 33-1/8 in. tall. It is reduced to 12-3/4 in. dia where it connects with the cyclone chamber. It contains ten 18-in. tall by 2-3/4 in.-dia and seven 36-in. tall by 2-3/4-in.-dia sintered metal filters. It is built of 304L SS and has a removable inspection door, thermocouples, and pressure taps.

The cyclone chamber (originally a smaller filter vessel) is constructed from a 12-in.-dia Sch 10S type 304L SS pipe. It contains the tangential gas-inlet duct, gas outlet cone, product overflow line, pressure taps, and thermocouples. The lower portion is reduced to 4-in.-dia pipe angled so as to connect to a melter or receiver (Figure 8).

FIGURE 8. Cyclone Chamber

FEED SYSTEM

Tankage, pumps, and piping used for all pilot-scale equipment in the Engineering Development Laboratory supply feed to the calciner. The solutions are pumped from agitated tanks through a recirculation loop. From this loop a sidestream is withdrawn to the calciner. Magnetic flowmeters and flow control valves regulate the flow. Figure 9 is a schematic diagram of the feed system.

FIGURE 9. Calciner Feed System Piping

FUEL SYSTEM

The fuel system for the in-bed combustion consists of an oxygen system, a kerosene system, and associated equipment and piping to deliver the two streams to the calciner vessel.

Liquid oxygen is received in portable cylinders and connected to a vaporizer manifold. A pressure regulator and coil on the container keep oxygen withdrawal at the desired flow and pressure. The vaporizer and cylinders are located outside the building.

Kerosene is stored outside the 324 Building in a 280-gal storage tank. It is pumped to a smaller feed pot inside the building. The kerosene is fed to the atomizing nozzle through a Sundstrand pump. The oxygen and

kerosene are combined in an internal mix nozzle manufactured by Spraying Systems Company. A 2850 liquid nozzle is used with a 140-6-52-70° wide-angle cap. Both the oxygen and the kerosene lines are purged with air and have check valves to prevent any back mixing. Figure 10 is a schematic drawing of the piping.

OFF-GAS SYSTEM

The existing off-gas cleanup system in the 324 Building, consisting of a condenser and scrubber used for the existing spray calciner and wiped film evaporator systems, was also used for the fluidized bed calciner. (See Figure 1.)

FIGURE 10. Calciner Combustion System Piping

FLUIDIZING AIR PREHEATER

The fluidizing air is heated prior to entering the calcine vessel. The heater is a 240-V, three-phase, 9000-W unit with an Incoloy sheath element. A maximum air temperature of 400°C is attained.

Figures 11 and 12 are photographs of the equipment during two stages of testing. The initial calciner design without any insulation is shown in Figure 11; Figure 12 shows the calciner with a modified filter vessel.

FIGURE 11. Fluidized Bed Calciner Initial Design

FIGURE 12. Fluidized Bed Calciner Modified Design

TESTING RESULTS

EQUIPMENT TESTS

Feed Nozzle

Feed nozzle development has aimed at creating simpler, more efficient nozzles. Because the calciner was originally designed as a prototype for remote operation, the first nozzles had remote connectors and fittings. The nozzles were equipped with a cleanout needle actuated by an air cylinder. Two methods of sealing the cleanout needle were tried, first using a bellows and second an oversized cleanout needle shaft with a packing gland. Both designs worked well through the limited testing.

The nozzle first designed was costly to make; hence a simpler version using a manual cleanout needle was designed. This nozzle worked satisfactorily. This and the previous nozzle had small liquid orifices (40-60 mill dia) and required strainers upstream to remove large foreign particles sometimes present in the feed. To avoid this need, a much larger nozzle was tried, comprising two concentric tubes with the inner tube recessed. No cleanout needle has been required with this nozzle. Atomizing air rates have been equivalent to or lower than that required for previous nozzles, indicating that quality atomization is unneeded. This nozzle is oriented to spray at a declining angle into the bed, near the combustion nozzle. Previously used nozzles were located to spray horizontally across the bed. At high feed rates and air rates the adjacent wall showed signs of feed impingement. Figures 13 through 16 show the nozzles described. Table 6 summarizes nozzle operating conditions.

One run with a single-fluid nozzle was attempted. The advantages of this would be 1) less off-gas, 2) fewer control parameters, and 3) simpler operation. The less attractive features are that it 1) requires a positive-pressure feed system, 2) has a smaller orifice than a two-fluid nozzle, and 3) may run hotter than a two-fluid nozzle. The attempt to use a nozzle as shown in Figure 17 failed because the orifice plugged and the cleanout needle did not clear it. It is thought, however, that this design might work on a larger scale. Spray patterns of two nozzles are shown in Figure 18.

FIGURE 13. Feed Nozzle Using Cleanout Needle with Air Piston

FIGURE 14. Feed Nozzle Using Manual Cleanout Needle

FIGURE 15. Tube Type Nozzle

Fuel Nozzle

The fuel nozzle (Figures 19 and 20), used to atomize kerosene and oxygen so that efficient combustion can occur in the bed, is designed like the initial feed nozzle. It uses an internal-mix, wide-angle gas cap. All-welded construction is essential to prevent any combining of fuel and O_2 prior to the mixing cap. Screwed fittings have been allowed for the gas cap, but metallic gaskets are used and leak tests are made to assure proper fit.

The gas cap and liquid nozzle are made of 316 stainless steel. Though the commercial nozzle parts were not designed for use as a combustion nozzle, they have worked well in the equipment tests. Larger calciner units may well use the commercially designed fuel-oxygen combustion nozzles available in larger sizes. The fuel nozzle is located in the lower portion of the bed below the feed nozzle. Table 7 lists the nozzle operating conditions.

Propane Nozzle

A propane-air nozzle (Figure 21) has been used for initial heating of the bed chamber to the autoignition point of the kerosene-oxygen fuel. This nozzle reduces startup time significantly more than do external bed heaters. At first externally mounted resistance heaters were used along with heated fluidizing air to preheat the bed. This required several hours to reach the ignition point of 375°C . The propane torch, located upstream of the plenum, reduced this time to about one hour. This nozzle has been used both directly mounted to the bed and in the fluidizing air line prior to the plenum.

FIGURE 16. Feed Nozzles Tested

TABLE 6. Feed Nozzle Operating Conditions

Nozzle Type →	{ Liquid Nozzle 40100 ^(a) Aircap 120		Liquid Nozzle 60100 Aircap 120	Tube Nozzle
SCFM Atomizing Air	3-6		4-5.3	3-7
Feed, ℓ /hr	10-25		20-41	18-31
NAR	250-690		220-330	200-520
Feed Pump Pressure, psig	18-33		18-22	12-19
Pressure at Nozzle, psig	2-20		4-15	2-8
Air Pressure at Nozzle Tip, psig	40-80		65-90	5-44
Air Supply Pressure, psig	80-100		90	80-90
Temperature Air	Ambient		Ambient	Ambient
Temperature Liquid	Ambient		Ambient	Ambient
Location Above Distributor Plate	9", 13"		8"	7"

a. Manufacturer's designation indicates nozzle dimensions (Spraying Systems Co.)

FIGURE 17. Single-Fluid Nozzle

Commercial Nozzle

Tube Nozzle

FIGURE 18. Spray Pattern Comparison of Commercial Nozzle and Tube Nozzle

FIGURE 19. Fuel Nozzle

FIGURE 20. Photograph of Fuel Nozzle

TABLE 7. Fuel Nozzle Operating Ranges

Nozzle Set Up (a)	Liquid Nozzle: Aircap:	2850 120-6-35-60	2850 140-6-37-60	2850 140-6-52-70
Kerosene Flow, l/hr		1.3-5.0	4-5	4-5
O ₂ Flow, scfm		3.2-5.5	4-5	4.5-6.2
O ₂ /Kerosene Vol. Ratio		1800-3100	1900-2000	1700-2200
O ₂ Temp, °C		23-34°C	22-25	22
Kerosene Temp, °C		23-34	24-27	25
Bed Temp, °C		410-790	575	550
Kerosene Supply Pressure, psig		70-90	77	77
Kerosene Nozzle Pressure, psig		12-60	38-41	6-12
O ₂ Supply Pressure, psig		62-81	82	80
O ₂ Nozzle Pressure, psig		32-72	48-52	24-35
Location Above Distributor		9.5", 6"	6"	6"

a. Manufacture designation, Spraying Systems Co.

FIGURE 21. Propane Nozzle

Direct bed mounting is the most efficient, but plugging of the nozzle by the bed particles can sometimes occur. Minor design and installation changes would correct this, but these were not done.

Sintered Metal Off-Gas Filters

The use of sintered metal filters has been ongoing at Battelle for several years in both fluidized bed and spray calciners. This subject has been treated in a separate report,⁽⁴⁾ in which the reader will find details on sintered metal filters. This section briefly summarizes a portion of that report.

Work at PNL has been oriented mainly toward unconventional calcination techniques such as inert bed operation, attrition/elutriation, etc. This developmental work has created product characteristics in ranges wider than normally experienced when a fixed operating concept is used or conventional calcination is done. Typical characteristics of calcine are shown in Table 8.

The amount and characteristics of fines that reach the sintered metal filters in the fluidized bed calciner can vary over a wide range, depending on how the calciner is operated. Unlike a spray calciner, which generates typically similar sized particles, fluidized bed calcination is a coating process that generates fines by abrasion of bed particles, by external

TABLE 8. Characteristics of Calcine^(a)

Size, mm	Bed	0.15 - 0.50
	Fines	0.04 - 0.15
Density, g/cc		1.5 - 2.5
Nitrate, wt%		0.02 - 10
H ₂ O, wt%		0.06 - 1.2

a. Characteristics of fluidized bed calcine will vary greatly, depending on operating temperature, type of feed, operating conditions, etc.

eroding forces such as jet grinders, and by some spray drying. The amount and nature of these fines can be varied, depending on the needs of the operation.

The initial configuration of the fluidized bed calciner process had the filters adjacent to the calcining vessel (Figure 11). Over 250 hr of operation were completed with this arrangement. Modifications to the system were later made to increase the filtering area. Seven 36-in. by 2-3/4-in. filters were housed in a 12-in. dia Sch 10S type 304L SST pipe used as the filter vessel. Venturi tubes were used with 3/8-in.-dia by 0.12 wall tubing as blowback nozzle. Each nozzle was 3/8 in. above the venturi.

During typical operation all material elutriated from the bed and carried to the filtering vessel was <149 μ . Table 9 shows a typical distribution.

With intentional attrition (by means of jet grinder or high air flow through a nozzle) the size distribution is changed as shown in Table 10. The significant increase is in the -44 μ ($\sim$ 325 mesh) range (Table 10).

TABLE 9. Size Distribution of Material Elutriated to Filters in the Fluidized Bed

Size, μ	wt%
210	0.85
149	0.70
74	13.57
37	59.06
20	14.84
10	10.22
<10	0.76

TABLE 10. Size Distribution of Fluidized Bed Calcine Fines with Intentional Attrition

Size, μ (a)	wt%
+105	10.7
-105 +88	8.4
-88 +74	7.7
-74 +53	9.6
-53 +44	22.6
-44	41.1

a. Sieve opening in microns for equivalent Tyler mesh.

During early operation with all new filters, it was noted that some material passed through the porous media. After a few hours of operation, this was no longer noticed. The material which did pass through was analyzed, and the size distribution is shown in Table 11.

Isokinetic sampling using a cascade impactor during typical runs was used to determine the particulate concentration and size in the off-gas passing through the filters. Table 12 presents the results. The off-gas composition was previously shown in Table 5.

TABLE 11. Particles Passing Through New 65-Micron Filter

Screen Size, μ		Wt%
	+210	5.4
-210	+149	1.7
-149	+74	2.1
-74	+37	15.3
-37	+20	41.4
-20	+10	23.8
-10	+5	10.1
-5		0.2

TABLE 12. Fluidized Bed Calciner Off-Gas Sampling^(a)

Wt% Lost	DF	Mass Concentration mg/scf ^(b)	Aerodynamic Median Diameter, μ
0.008-0.024	10^3 - 10^5	0.004-0.35	2.5-3.8

a. Average Conditions

Pressure Drop, in. H ₂ O	20 - 40
Total acfm	80 - 90
Temperature, °C	300 - 400
Face Velocity ft/min	3.97 ± 0.66
Permeability ft/min, in. H ₂ O	0.14 ± 0.03
Pressure, in. H ₂ O	-2 to -10

b. Noncondensable off-gas

Figure 22 shows the permeability of the filters for the ~300 hr of accumulated operation. The filter permeability was lower initially than expected and is quite a bit lower than that of identical replacement filters. This has not been fully explained; however, some postulations have been made.

Schneider reported in earlier work done at Battelle that the spraying of raw water onto new filters frequently blinds them with a coating that cannot be blown off. This was sometimes done during early shakedown runs. Also the off-gas impinged at high velocity on one filter as it entered the vessel. This filter was noted to respond less to blowback, hence indicating some plugging. To avoid blinding with water, the filters in the modified vessel were precoated with SiO_2 dust prior to introducing any liquids into the system. This was done by fluidizing and abrading a SiO_2 bed without introducing feed.

General operation with the initial set of filters was quite good. It soon became evident that the calciner capacity had increased significantly over its designed rate of 15 liter/hr with the new operating techniques.

FIGURE 22. Permeability Data

In operation at increased capacities, problems such as vacuum availability with existing plant off-gas equipment was a concern. Many runs were made with pressure drops of 30 to 40 in. of water, and frequent blowback (5 to 10 min cycle) was required. Although the filters performed satisfactorily, it was thought that lower differential pressure (ΔP) and much less blowback would be desirable and achievable. The useful life of the filters has been reported by many manufacturers to be lengthened by reducing blowback frequency.

A new filter chamber was designed and installed as described below.

Improved Filter Vessel

The improved filter vessel installation was to accomplish several goals:

- increase filter area to obtain higher calciner feed rates
- run with lower pressure drop <10 to 20 in H_2O and infrequent blowback
- see if precoated filters would behave differently from those initially installed
- use various venturi designs and note any differences in blowback results
- use a cyclone prior to the filters.

The most efficient way of installing an enlarged filter section was to have the housing fabricated and then install it atop the housing from which the previous filters had been removed. See Figures 11-12. This left the original vessel serving no purpose except as a disengaging space. It was decided to modify the vessel to achieve a cyclone effect. This was done by installing a tangential gas inlet and modifying the gas outlet. It was evident that operating conditions would vary so much that the modified design would not result in optimum efficiency. Use of a cyclone with a spray calciner upstream of sintered metal filters had interfered with blowback efficiency. This experience led to some concern; the assumption was that with the cyclone in place only the finest particles reached the filters and formed an especially adherent filter cake. However, it was felt that this would not happen with the fluidized bed since the particles are much larger.

Cyclones have also been used as the major particulate removal system on fluidized beds such as at the waste calcination facility operated by Allied Chemical at the Idaho National Engineering Laboratory, Idaho Falls.

Eighteen sintered metal filters were used in the new vessel. Ten were 18 by 2-3/4-in. dia, and seven were 36 by 2-3/4-in. dia. They were arranged as shown in Figure 23. The blowback nozzles were piped so that two 18-in. filters would operate simultaneously and then one 36-in. filter blown at a time. Frequency, cycle, and duration of blowback were controlled from a specially designed timer panel. Blowback nozzles were the same as previously used.

Runs with the new filter vessel have far exceeded expectations. Although more hours are needed to verify operation, the following data has been accumulated:

- The precoat appeared effective in that the permeability of the filter is much higher than previous permeabilities (see Figure 22).
- Higher calciner feed rates were achieved.
- Pressure drop has been low, and it appears that very infrequent blowback will be required.
- The venturi dimensions tried have little if any noticeable effect on blowback.
- Quantified data on the cyclone efficiency have not been taken. However, observations of the solids loadings on the filters when no blowback is used indicate that the cyclone is removing most of the particles.

Miscellaneous Equipment Tests

Valves in Solids Transport Lines

Equipment design has minimized the number of valves in lines through which calcine or other solids routinely pass. Only two valves are used in the pilot-plant equipment, and these could possibly be eliminated. One valve is in the overflow line and the second in the inert solids addition line. Requirements for valves in this equipment and as extended to

FIGURE 23. Filter Vessel Layout and Venturi Arrangement

radioactive service are severe. The valves must 1) withstand high temperature (500 to 800°C), 2) withstand high radiation, 3) corrode as little as possible in nitrate atmosphere, 4) handle solids flow (full port) and 5) leak little (a small gas leakage can be tolerated). Cylinder valves (316 SS) with modified graphite seats and gaskets have been used successfully. An automatic valve operator is used on the overflow line.

Insulation

A high-temperature insulation WRP-X-AQ felt manufactured by Refractory Products Company has been used to insulate the calciner and filter vessel. The material goes on as a wet blanket and then dries to a rigid form.

Quartz Viewing Window

A quartz viewing window (~2 in. x 6 in.) is occasionally used during calciner operation to observe the bed behavior and combustion characteristics. This window is incorporated into a metal door bolted to the calciner bed section wall. It permits actual visual observation of calciner operation and has worked well at temperatures up to 800°C.

Rotary Valve

To obtain a direct, continuous discharge from the calciner not connected to a melter, a 4-in. rotary valve has been connected to the filter vessel discharge line. The valve works well even at high-temperature operation. Some in-leakage is observed during discharge to an open atmosphere. However, the existing off-gas equipment handles the added load while maintaining suitable vacuum in the calciner. The in-leakage can be eliminated by using a sealed pot to collect discharge from the valve.

Thermocouple Stem

Numerous wall penetrations for thermocouples were initially required to monitor the process. These were eliminated by combining all the thermocouples into a "stem" arrangement which could be inserted through the top of the calciner and protrude through the vessel to the bottom of the bed. This would also facilitate remote replacement.

PROCESS TESTS

The fluidized bed calcination program has tested different waste flowsheets under various operating conditions to evaluate the products and the processes and their application to Battelle's waste vitrification program.

Simulated High-Level Liquid Waste

Actual high-level liquid waste (HLLW) is mainly the raffinate from the first extraction cycle of a Purex process. Other materials may be in the waste, caused by differences in reprocessors' flowsheets, resulting in varied compositions. Simulated HLLW is prepared by using nonradioactive isotopes for many of the elements. Because complete chemical simulation is not practical, substitutes are used. Various HLLW compositions tested in the fluidized bed are shown in Tables 13 and 14. Substituted elements are listed in Table 15.

Run Summaries

Process testing has been ongoing at Battelle since late CY-1974. To date over 300 hr of operation (feed on) have been accumulated in 19 individual runs. Runs 1-4, 6, and 8-11 were operations unrelated to this specific project. Run time has varied between 4-88 hr. Typically runs under 8-hr duration were completed because of manpower and economy.

Run summaries for tests reported here are described in this following section. Table 16 summarizes operating conditions for these runs.

Run 5

Run 5 was a long-duration (88-hr) test using conventional calcination operation (no inert bed addition) on PW-7 feed (Na - 0.01M). Over 90% of the calcine produced was elutriated from the bed to the gas particulate separation vessel. This run showed the need for an improved operating technique such as continuous inert bed addition. It did prove that the equipment design was satisfactory for extended operation. The waste feed contained cesium, and material balances showed that no volatilization was occurring at these temperatures. The product was 4.48 wt% cesium. The tapped bulk density averaged 2.18 g/cc.

**TABLE 13. Compositions of Representative High-Level
Radioactive Wastes, as Solution**

		Concentration, Molarity @ 378 g/MTU					
		PW-4b	PW-7	PW-7a	PW-7b	PW-8	PW-8a
<u>Inerts</u>	HNO ₃	1.0	2.0	2.0	2.0	7.0	2.0
	Na	-	0.01	0.586	0.586	-	1.20
	Fe	0.05	0.10	0.10	0.586	1.32	0.902
	Cr	0.012	0.012	0.012	0.012	0.040	0.040
	Ni	0.005	0.005	0.005	0.005	0.020	0.020
	PO ₄	0.025	0.10	0.236	0.236	0.050	0.050
	Gd	-	0.151	0.151	0.151	-	-
<u>Fission Products</u> (Same for all waste)	Rb			0.010			
	Sr			0.027			
	Y			0.014			
	Zr			0.106			
	Mo			0.095			
	Tc			0.022			
	Ru			0.059			
	Rh			0.010			
	Pd			0.032			
	Ag			0.002			
	Cd			0.002			
	Te			0.012			
	Cs			0.054			
	Ba			0.027			
	La			0.024			
	Ce			0.051			
	Pr			0.023			
	Nd			0.071			
	Pm			0.0019			
	Sm			0.014			
	Eu			0.003			
	Gd			0.002			
<u>Actinides</u>	U	0.011	0.110	0.110	0.110	0.052	0.110
	Np	0.0085	0.0085	0.0085	0.0085	0.0085	0.0085
	Pu	0.0001	0.001	0.001	0.001	0.0005	0.0017
	Am	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018
	Cm	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004

TABLE 14. Compositions of Representative High-Level Radioactive Wastes After Conversion to Calcine

		Kilograms Oxide /MTU					
		PW-4b	PW-7	PW-7a	PW-7b	PW-8	PW-8a
<u>Inerts</u>	Na ₂ O	-	0.117	6.872	6.872	-	14.057
	Fe ₂ O ₃	1.511	3.022	3.022	17.711	39.895	27.225
	Cr ₂ O ₃	0.345	0.345	0.345	0.345	1.151	1.151
	NiO	0.141	0.141	0.141	0.141	0.566	.566
	P ₂ O ₅	0.672	2.686	6.339	6.339	1.340	1.340
	Al ₂ O ₃	-	-	-	-	-	-
	Gd ₂ O ₃	-	10.360	10.360	10.360	-	-
	Subtotal	2.669	16.671	27.079	41.768	42.952	44.339
<u>Fission Products</u> (Same for all wastes)	Rb ₂ O		0.354				
	SrO		1.059				
	Y ₂ O ₃		0.598				
	ZrO ₂		4.944				
	MoO ₃		5.176				
	Tc ₂ O ₇		1.291				
	RuO ₂		2.972				
	Rh ₂ O ₃		0.480				
	PdO		1.483				
	Ag ₂ O		0.088				
	CdO		0.097				
	TeO ₂		0.725				
	Cs ₂ O		2.880				
	BaO		1.567				
	La ₂ O ₃		1.480				
	CeO ₂		3.323				
	Pr ₆ O ₁₁		1.482				
	Nd ₂ O ₃		4.522				
	Pm ₂ O ₃		0.123				
	Sm ₂ O ₃		0.924				
	Eu ₂ O ₃		0.200				
	Gd ₂ O ₃		0.137				
	Subtotal		35.905				
<u>Actinides</u>	U ₃ O ₈	1.169	11.689	11.689	11.689	5.526	11.689
	NpO ₂	0.865	0.865	0.865	0.865	0.865	.865
	PuO ₂	0.010	0.103	0.103	0.103	0.051	.174
	Am ₂ O ₃	0.181	0.181	0.181	0.181	0.181	.181
	Cm ₂ O ₃	0.040	0.040	0.040	0.040	0.040	.040
	Subtotal	2.265	12.878	12.878	12.878	6.663	12.949
Total		40.8	65.5	75.9	90.6	85.5	93.2

TABLE 15. Representative Chemical Standings Used to Prepare Simulated Nonradioactive High-Level Waste^(a)

<u>Waste Constituent to be Substituted</u>	<u>Reason for Substitution</u>	<u>Substitute Used^(b)</u>
Rb	Expense	K
Y & RE	Expensive to simulate fission product spectrum	Commercially available rare earth mixtures
Tc	No nonradioactive isotope	Mo or Mn
Ru	Expense	Fe
Rh	Expense	Co
Pd	Expense	Ni
Cs ^(c)	Expense	K
U, Np, Pu, Am & Cm	No nonradioactive isotopes	Rare earths

- Inexpensive nonradioactive isotopes are available for all of the fission products not shown.
- Substitutes shown are those which have been used in the Waste Fixation Program at PNL.
- Substituted in some engineering-scale tests only.

Run 7

Run 7 was an attempt at complete attrition-elutriation operation using an Al_2O_3 bed and no inert additives. Successful operation was completed. But this type of operation would be constrained by difficulty in controlling particle growth due to ineffective jet grinding. The inability to find a spherical, attrition-resistant bed contributed to the difficulties.

Run 12

Continuous inert bed operation was initially tested during Run 12. A range of operating conditions was examined: temperatures to 800°C, sodium concentrations to 1M, and five sequential startups and shutdowns using the same bed. This exploratory run demonstrated the versatility of this type of processing.

TABLE 16. Operating Conditions During Calciner Runs

	5	7	12	13	14	15	16	17	18	19
Feed Type	PW-7 0.01M Na 378 ℓ /MTU, Sp.Gr. 1.2 138 g oxide/ ℓ	PW-7 378 ℓ /MTU silica additive	PW-7a (modified with increased Na to 1.0M) 131-174 g oxide/ ℓ	PW-7 concentrated 320 ℓ /MTU	PW-7a-2 398 ℓ /MTU 170 g oxide/ ℓ 0.5M Na	PW-7a-2 0.58M Na 150 g oxide/ ℓ	PW-7a-2 0.64M Na 174 g oxide/ ℓ 1.27 Sp.Gr.	PW-8a 1.0M Na 0.65M Fe 1.34 Sp.Gr. 207 g oxide/ ℓ	PW-7a	PW-7a 1.28 Sp.Gr. 185 g oxide/ ℓ 10% Ru, 100% Cs
Feed Rate, ℓ /hr	17.9	14.5	12-16	20-30	Avg 27-Max 40	20	21.6	20-25	25.9 Avg-35 Max	27.8
Run Time, hr	88	14	19	3.5	6	6.7	6.2	6.5	3.7	13.3
Temperature, $^{\circ}$ C	500-600	500	500-800	500	525-690	500-545	550	575	540	550
Filter Δ P in H ₂ O	25-30	20-32	25-35	1-8'	7-10	6.3-8.4	7-15	8-12	10-15	13-19
Permeability ft/min-in. H ₂ O	0.15-0.17	0.17	0.11-0.12	0.41	0.42	0.4-0.5	0.4-0.2	0.26-0.37	0.25-0.43	0.27
Feed Nozzle	40100 120	Same	Same	Same	60100 120	Tube Nozzle	Tube Nozzle	Tube	Tube	Tube
NAR	300-520	375-620	330-550	350	220-330	500	200-520	320-400	240-425	300
Fuel Nozzle	2850 120-6-35-60	2850 120-6-35-60	2850 120-6-35-60	2850 120-6-35-60	2850 120-6-35-60	2850 120-6-35-60	2850 120-6-35-60	2850 140-6-37-70	2850 140-6-52-70	2850 140-6-52-70
O ₂ ^(a) /Kerosene Ratio	2300	2255	1700-2900	>2000	1830-2200	1800-2260	1600	1800-2000	1700-2300	1940-2130
SCFM (noncondensable)	12.3	12.6	12-19.5	12	20	12-17	12-15	12-14	11-12	15-20
ACFM (total)	63-73	~70	~70	~80-90	121	85	75-95	70-90	66-100	95
Bed Material	SiO ₂	Al ₂ O ₃ 36-54 grit	SiO ₂	SiO ₂	SiO ₂	SiO ₂	Final Bed Run 15	Final Bed FBC-16	Final Bed FBC-17	Final Bed Run 18

a. O₂ supplied to nozzle only does not include O₂ from fluidizing air and atomizing air.

Run 13

During this run the calciner was operated with the continuous inert bed (CIB) mode, using concentrated PW-7 type feed. A new and larger bank of sintered metal filters (26.7 ft^2) was installed. These significantly reduced pressure drop and allowed higher feed rates.

Run 14

A capacity test using the CIB operation showed feed rates up to 40 ℓ/hr during this run. A continued low-pressure drop across the new filter bank continued. A larger feed nozzle (60100-120 cap) was used. Some penetration of feed across the 6.75 in. square bed to the opposite wall was noted. Product samples at the 40 ℓ/hr feed rate and 525°C operating temperature showed some nitrate gas evolution.

Run 15

This run demonstrated the use of a tube type feed nozzle with the CIB operating mode. The nozzle, made from 1/2-in.-dia and 1/4-in.-dia tubes (Figure 15), was directed down into the bed toward the fuel nozzle. Significantly reduced blowback was required during this run. Short pulses each hour were effective in maintaining a 6 to 8-in. water ΔP .

Run 16

Use of a tube nozzle with the CIB operation was again verified in this run. The nozzle air ratio was varied over a range of 200 to 520. Some chunks of calcine were found in the bed after the run; however, no effects on operation were noted. During this run no blowback was used at any time to clean the sintered metal filters. The pressure drop rose from 5 to 15 in. of water, and the permeability decreased from 0.4 to 0.2 ft/min-in. of water but was leveling as the run ended. Little or very infrequent blowback may be required with this operation.

Run 17

A slightly different feed composition, PW-8a, was calcined. This material represents a proposed NFS type waste containing high sodium and iron (1.0M Na , 0.65M Fe).

Run 18

This was a short demonstration run to generate some CIB product for vitrification tests. Typical operating conditions were used. The only difference in operating equipment was the use of a large gas cap on the fuel nozzle. This cap allowed higher oxygen flows as well as resulting in lower nozzle pressure for both oxygen and kerosene.

Run 19

This run coupled the calciner with the ICM to produce 194 kg of glass in a 12-in.-dia finned can. The CIB operation was used, and a special frit void of SiO_2 was added to the melter. Cesium and 10% of the flowsheet ruthenium were used in the PW-7a-2 feed. The coupled system operated very well.

CHEMICAL ASPECTS

Feed Makeup

Simulated wastes with appropriate chemical substitutions as described in Table 15 are used as feed for the calcination experiments. The use of MoO_2 (for molybdenum and technetium substitutes) has created some problems in feed handling as the material does not dissolve. Agitated feed tanks are required, and pumps, valves, flowmeters, etc., must be able to handle the undissolved material. The use of manganese (as $\text{Mn}(\text{NO}_3)_2$) has sometimes been used as a technetium substitute and reduces the amount of undissolved solids.

A submicron-sized silica additive, when added in small quantities (~1 to 2 wt% of feed), has been effective in keeping the feed somewhat emulsified. Larger quantities (4 to 8%) can actually jell the feed. This material also is claimed to aid off-gas filtration. Only minor testing has been done with this material.

Calcination

Calcination of wastes using the continuous inert bed process is a combination of coating particles, coating and abrading by particle collision,

and spray drying. The majority of the calcine exits the vessel with the off-gas stream, leaving the bed predominantly inert SiO_2 .

Figure 24 shows photomicrographs of the inert material (SiO_2), the bed, and overhead plus bed. As can be seen, the SiO_2 material is round and regularly shaped before addition to the bed. Once in the bed, the particles crack either from thermal shock or phase change. Various degrees of coating occur, depending on operating conditions, type of feed, etc.

Sodium Behavior

Sodium was a concern because of its detrimental actions in conventional calcination processes. Sodium nitrate decomposes to a sticky material between about 300 and 800°C. Hence calcination in that range has been acceptable only with either low quantities of sodium (<0.25M) or by the use of diluents or additives. With the CIB operation, sodium levels of 0.6M are routinely handled, and quantities up to 1M have been calcined. No attempts to calcine feed containing more than 1M have been made. Hence an upper limit is not known.

Several factors contribute to the ability of this process to handle sodium. Due to the addition of inerts, the bed turnover is more rapid than with conventional calcination. Thus any agglomerated particles are swept out of the bed faster. There is also a reaction with the SiO_2 particles forming a silicate. This reaction is not reaching completion but is occurring to some degree. Increasing the temperature of the bed would accelerate this reaction and if high enough could lead to the formation of Na_2O . With the high nitrate and water atmosphere, however, formation of Na_2O is difficult. Other clues suggesting that silicate is being formed are that 1) nitrate material balances are insufficient to account for all the sodium in the sample, 2) the crystalline phase of SiO_2 identified at low operating temperatures cannot be identified when the same samples are heated to >800°C, 3) water-soluble silicates were found in the heated sample, and 4) water-leached samples of product were neutral (had NaNO_3 been significantly present they would have been basic).

SiO₂ Starting Bed 100X

FBC-12 Bed and Overhead 100X

FBC-15 Bed 100X

FBC-14 Bed 50X

FIGURE 24. Photomicrographs of Calcine and Bed Material

Some feed compositions, such as the NFS type PW-8a, contain iron in significant quantities. When this material was calcined (Run 17), the product was checked to see whether the sodium might also be reacting with the iron to form sodium ferrate ($\text{Na}_2\text{Fe}_2\text{O}_4$). Only trace amounts could be found, indicating this reaction is insignificant.

Additional details of the inerts, calcine, and calcine with sodium, can be seen in the electron microscope photographs, as shown in Figures 25 to 32.

Cesium and Ruthenium

Cesium, normally substituted for by potassium, has sometimes been added to the feed to see if it volatilizes from the calciner. Condensate and off-gas samples showed less than 1 ppm when $\sim 0.05\text{M}$ Cs was in the feed. When runs were made directly coupled to the in-can melter, DFs across the total system were 10^4 to 10^5 .

Very little ruthenium-associated work has been done with the calciner due to the expense of the material and the questionable analytical capabilities with the low levels of addition. Once a 0.0055M ruthenium feed was calcined while connected to the in-can melter. Total DFs across the calciner melter system (feed to condensate) were 10^4 .

Off-Gas Scrubbing

Recirculated NaOH was used first to scrub the NO_x from the off-gas. If the solution was left recirculating too long, Na_2CO_3 would precipitate out, fouling the tank, pump, and lines. Either a water or nitric acid scrub or more frequent changing of the NaOH solution is required to prevent this occurrence. The CO_2 scrubbed is generated from the combustion of kerosene in the calciner.

Nitrate and Water in Calcine

The nitrate retained in the product is dependent on the nitrate content in the feed, calciner operating conditions, and calcination temperature. Since the product is vitrified immediately following calcination, normally NO_3^- and H_2O content is not determined because it is driven off in the melter.

FIGURE 25. Silica Sand Used as Inert Bed Material

~600X

FIGURE 26. Agglomerated Particles Caused by High Sodium (1M) High Magnification

~200X

FIGURE 27. Fines Material Reaching Filters

~200X

FIGURE 28. Filter Fines

~20,000X

FIGURE 29. Pure Calcine from Conventional Operation

~200X

FIGURE 30. Pure Calcine Surface

~20,000X

FIGURE 31. Particle of Inert Bed Coated with Calcine

~200X

FIGURE 32. Surface of Coated Inert Bed Particle

~20,000X

Should calcine storage be required, especially in a sealed container where pressure could build, the nitrate and water must be reduced. Use of the CIB process allows high-temperature operation of 700 to 800°C to be accomplished easily. With a refractory-lined vessel temperatures of about 1100°C would appear practical. Operating at these temperatures would significantly reduce residual nitrate and water. Figure 33 shows the thermogravimetric analysis of the product, fines, and bed for typical material from Run 16. As can be seen, a total weight loss of ~6.5% (2.5% H₂O, 4% NO_x) is typical. Figure 34 shows the nitrate analysis of product samples from specific runs.

FIGURE 33. Thermogravimetric Analysis Data (CIB Material)

FIGURE 34. Nitrate Analysis of Product Samples

CONCLUSIONS

1. Continuous inert-bed calcination provides a significantly improved operating technique when applied to commercial HLLW solidification.
2. Calcination followed by a directly coupled vitrification system (either a ceramic melter or in-can melter) is easily accomplished using developed operating techniques.
3. Sophisticated feed nozzle design is not required for calciner operation.
4. Sodium levels in HLLW to 0.6M were easily calcined, 1M Na appears practical also.
5. Sintered metal filters operated quite satisfactorily during all testing phases.
6. Scale-up to equipment needed for commercial plant operation will require no significant additional development.
7. In-bed combustion is a significant positive factor in improved calciner operation and flexibility.

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APPENDIX

Shown here are three figures:

- A.1, a flow diagram of process equipment and instrumentation,
- A.2, a photograph of the newly installed pilot-scale calciner and its control instrumentation,
- A.3, a photograph showing materials in the CIB and vitrification process and their proportional relationships.

A brief glossary follows.

FIGURE A.1. Flow Diagram of Process Equipment and Instrumentation

FIGURE A.2. Fluidized Bed Pilot Plant Facility at PNL

FIGURE A.3. Materials Used in the CIB and Waste Vittrification Process

GLOSSARY

Attrition Index	Percent of a 50-g sample of -35 +48 Tyler mesh particles remaining in this size fraction after a 60-min exposure in a 1-in.-I.D. glass tube to a high-velocity air stream from a 0.015-in. dia jet supplied with 100 psig air.
Incipient Fluidizing Velocity	The air velocity at which the bed is expanded and the particles begin to be suspended.
Jet Grinder	High-velocity air stream that causes the particles to fission upon impact with other particles or a rigid surface.
L/D	Ratio of bed height to diameter; the greater the ratio the more difficult to fluidize.
MMPD	Mass mean particle diameter. Fifty percent of the mass is associated with larger particles and fifty percent with smaller particles.
NAR	Nozzle Air Ratio, ratio of volume of atomizing air to volume of liquid to the feed nozzle per time unit. (Calculated at metered temperature and calciner pressure.)
O ₂ /Kerosene Fuel Ratio	Volumetric ratio of atomizing oxygen to fuel. The stoichiometric ratio is ~2100, assuming complete combustion.
Permeability	$\frac{\text{acfm of off-gas}}{\text{filter pressure drop} \times \text{filter area (ft}^2\text{)}}$
Porosity	Particle void space. Value was calculated as the difference between the reciprocal of the particle density and the reciprocal of the absolute density expressed as ml/g.

Replacement Time

Time required to replace a given percent of the fluidized bed (assumes perfectly mixed, stirred tank)

$$\% = 1 - e^{-Pt/W} \cdot 100$$

W = wieght of material in bed

P = solids addition rate

t = time

Superficial Fluidizing
Velocity

Velocity of air flowing through the vessel calculated at bed temperature and vapor space pressure, based on cross section of empty vessel.

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