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HIGH-LEVEL WASTE SOLIDIFICATION: APPLICABILITY OF
FLUIDIZED-BED CALCINATION TO COMMERCIAL WASTES

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INTRODUCTION

The origin and disposition of high-level radioactive wastes generated during the processing of power reactor fuel are shown in Figure 1. Based on one tonne of fuel used in a nuclear reactor to generate electricity, 100 - 300 gallons of liquid high-level high-heat radioactive waste is generated. Economic and technical considerations will dictate the length of time the high-level wastes are stored as liquids; however, guidelines in the Federal Register propose that all high-level wastes be solidified within 5 years after reprocessing to reduce the potential for accidental release to the environment.

Current guidelines also call for solidification in a form suitable for on-site interim storage and subsequent transfer to a Federal Repository; the solids should be amenable to post-calcination treatment (eg, glassification, particle coating, encapsulation in a metal matrix, etc.). The primary purpose of this paper is to briefly review candidate solidification processes; emphasis will be on our experience in plant-scale fluidized-bed calcination of AEC high-level wastes and concepts for fluid-bed calcination of typical high-level wastes from commercial fuel reprocessing plants.

CANDIDATE SOLIDIFICATION PROCESSES

The basic processes of evaporation and decomposition are similar for all solidification systems, and all are capable of continuous operation. A schematic diagram of a solidification process is shown in Figure 2. Waste solution entering the calciner is evaporated and decomposed; water vapor and gases from waste decomposition are swept from the calciner while metallic and fission product oxides remain as calcined solids. Fission products and chemical pollutants

ABSTRACT

Candidate processes for commercial high-level waste solidification are radiant-heat spray calcination, rotary-kiln calcination, and fluidized-bed calcination. Radiant-heat spray and rotary-kiln calcination have been studied only on a pilot-plant scale; plant-scale fluidized-bed solidification of AEC high-level wastes has been operating for more than ten years. Cold pilot-plant studies using the radiant heat spray and fluidized-bed processes are currently underway on simulated commercial wastes.

Encouraging results to date show that the existing fluid-bed solidification process pioneered at the Idaho Chemical Processing Plant is applicable to commercial waste processing with modest process and equipment modifications. These modifications are mainly in areas connected with uncontrolled heating during postulated collapse of the fluidized bed, off-gas cleanup, and equipment design for compatibility with total remote maintenance.

FIGURE 1

SOURCE AND FLOWPATH OF HIGH-LEVEL WASTES
IN THE NUCLEAR FUEL CYCLE

FIGURE 2 **BASIC WASTE SOLIDIFICATION PROCESS**

are removed from the off-gas using either a condensing or a non-condensing system; the specific off-gas treatment system depends on the activity level of the waste calcined and the justification for an acid recovery system.

Fluidized-bed solidification is used on a routine basis at the Idaho Chemical Processing Plant (ICPP) in the processing of AEC high-level wastes⁽¹⁾; radiant-heat spray calcination has been demonstrated at Hanford by Battelle Northwest⁽²⁾; rotary-ball kiln calcination was developed primarily at Brookhaven National Laboratory⁽³⁾.

Product from any of these processes can be converted to glass-like materials to reduce the leachability by water and to increase the thermal conductivity. The major differences in the various processes are: (1) the operating conditions, (2) throughput rates, (3) initial product properties, and (4) state of development

FLUIDIZED-BED CALCINATION

A schematic diagram of a fluidized-bed calciner is shown in Figure 3. Waste solution sprayed into a heated fluidized bed of granular solids evaporates on the surfaces of particles. At steady-state operating conditions, particle growth by feed deposition, particle elutriation, attrition, and removal of bed particles result in a steady-state particle size distribution. Bed temperatures in the range 400 - 500°C are normally used; at ICPP, process heat is currently provided by in-bed combustion of kerosene atomized by oxygen through three wall-mounted spray nozzles. The process flowsheet for fluid-bed calcination in the Waste Calcining Facility (WCF) is shown in Figure 4. Details of the calciner vessel are shown in Figure 5.

FIGURE 3 FLUIDIZED - BED CALCINER

Figure 4 Schematic of the WCF System

FIGURE 5 Calciner Vessel Details

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An air fluidizing velocity of 1-1.3 ft/sec is maintained near the bottom of the 4-ft diameter bed; a fluidized-bed height sufficient to cover the feed nozzles with the bed particles is necessary to minimize spray drying. Spheroidal granular particles ranging from 0.1 - 1 mm in diameter are removed from the calciner and pneumatically transported to solids storage. Transport gas is returned to the top of the calciner and combined with the calciner off-gas for cleanup.

The off-gas cleanup system consists of a cyclone for removal of larger particles (eg, $> 20 \mu$), a high-energy wet scrubbing system for removing solid particulate in the range 3 - 20 μ , silica gel adsorbers for removal of volatile ruthenium, and High Efficiency Particulate Air (HEPA) filters for final cleanup before atmospheric release through a stack.

Scrubbing solution from the wet off-gas cleanup system is recycled to the feed on a batch basis. The rate of scrubbing solution recycle is governed by the solids carryover rate of the particular waste being calcined and the maximum permissible dissolved solids concentration in the scrubbing solution.

The capacity of a given size fluidized-bed calciner primarily depends on the maximum rate of heat input (power density) without sintering of bed particles and maximum rate of feed input above which particle agglomeration from excessive moisture occurs. Throughput rates in the plant-scale facility are as high as 10 gal/hr-ft² of cross-sectional area of the bed; rates in a pilot plant as high as 28 gal/hr-ft² have been achieved.

RADIANT-HEAT SPRAY CALCINER

A simplified sketch of a radiant-heat spray calciner is shown in Figure 6. Waste solution atomized at the top of the calciner is spray dried and swept out of the cylindrical vessel. The vessel is usually electrically heated; the maximum operating temperature (typically 700°C) is limited by the potential for sintering and sticking of calcine to the vessel walls.

Effective operation of the spray calciner depends upon good atomization. The atomizing nozzle must break up the feed solution into small enough droplets (on the order of 50 to 100 microns diameter) to permit drying and calcining of the feed during its short residence time (about 10 seconds) in the calciner.

Spray calcination requires that the sintering point of the calcined solids be higher than the temperature of the calciner walls. Otherwise, the calcine will stick on the calciner walls and reduce heat transfer rates. In practice, the sintering temperature, or "stick point", of the calcine should be greater than 700°C to permit reasonable operating rates.

The suspension of feed droplets passes through zones of evaporation, drying, and calcination, and results in a finely divided powder ranging in size from .001 - 0.1 millimeters. Water vapor and volatile decomposition products, together with the gas used to atomize feed, are usually separated from the product by blow-back filters outside the calcination vessel, although the use of cyclones could be considered. Product, because of its high porosity, small size, and low bulk density is collected in pots below the calciner for subsequent melting if suitable additives have been used in the feed. Pots in a plant facility would be transferred remotely to a final repository.

FIGURE 6 RADIANT-HEAT SPRAY CALCINER

The capacity of the radiant-heat spray calciner is difficult to predict; the maximum capacity is reached when incompletely dried particles deposit excessively on the calciner wall. The general factors affecting processing rates for a spray calciner have been only qualitatively investigated. In general, the limiting factors affecting the processing rate are the transmission of heat into the calciner to produce a dry free-flowing calcine and the transmission of heat into the melter or pot to produce a fluid melt. These, in turn, are influenced by the feed composition, feed atomization, and furnace temperatures. The processing rate for a 36-inch diameter spray drive^{on} is probably limited to a maximum of 25 gph.

ROTARY-BALL KILN CALCINER

A schematic diagram of the rotary-ball kiln calciner is shown in Figure 7. In rotary-ball kiln calcination, waste solution is fed onto a bed of metal balls in a slowly rotating cylinder. The calciner is electrically heated to a temperature between 600 and 800°C. Product formed from deposition of metallic oxides on the moving balls is pulverized during kiln rotation into particles varying in size from .13 to .16 millimeters. Product overflows from the calciner co-current with the off-gases and enters a cyclone or metallic filters for solids-gas separation. In development studies, product usually has been collected in pots below the calciner.

The capacity of rotary-ball kiln calciners is limited by the effective rate of heat input into the kiln. During early pilot-plant studies with an eight-inch diameter, seven-foot (heated) length calciner at Brookhaven National Laboratory, the feed rate varied between three and five gallons per hour.

FIGURE 7 ROTARY BALL-KILN CALCINER

SOLID PRODUCT CHARACTERISTICS AND HANDLING

Values of product characteristics, which have been observed for various wastes processed during experimental work with each of the calciners, are shown in Table I. Unfortunately, identical wastes have not been processed in each of the calciners and direct comparisons are not meaningful. This primarily presents a problem in calculating comparative volume reduction factors. For comparisons made in this paper, experimentally obtained values of bulk density were used to calculate porosity and volume reduction factors wherever possible. Where experimental data were not available, a best estimate of bulk density or porosity was used, based on a range of experimentally obtained values from wastes that were calcined. Volume reduction factors, which depend on the concentration of the waste solution fed to the calciner, may differ from those in other publications due to a difference in definition. The values shown in Table I are on a comparable basis.

TABLE I

PROPERTIES OF CALCINED SOLIDS

	Fluidized Bed	Radiant-Heat Spray	Rotary-Ball Kiln
Average size, mm	0.1-1	0.002-0.13	0.13-0.16
Type	Granular	Granular	Granular
Bulk Density, g/cc	0.05-3.0	0.18-1.1	0.65-0.95
Gross Porosity, %	44-76	67-94	69-79
Typical Volume Reduction Factors	7-20	2-4	7-10
Thermal Conductivity	0.08 @ 40°C	0.05 @ 40°C	0.098
Btu/(hr)-(ft)-(*F)	0.22 @ 800°C	0.13 @ 200°C	(temperature not reported)
Nitrate Content, wt%	1-12 @ 300-500°C	Not reported	Not reported

FLUID-BED CALCINATION OF AEC WASTES

Development of the fluidized-bed calcination process for solidifying high-level liquid radioactive wastes generated at ICPP began in 1955. Initial studies were done at Argonne National Laboratory; specific development and process verification studies completed at ICPP formed the bases for the design and construction of the plant-scale Demonstration Waste Calcining Facility. This facility went onstream in December 1963 as the plant-scale Waste Calcining Facility (WCF) for solidification of aluminum-nitrate radioactive wastes⁽⁴⁾.

Though designed for processing only aluminum-nitrate wastes, during the last 10 years the WCF has processed a variety of wastes including aluminum nitrate, ammonium nitrate, zirconium fluoride, stainless steel-sulfate, and stainless steel-nitrate.

Decomposition of aluminum nitrate during calcination takes place according to the reaction,

forming both alpha and amorphous alumina; alpha alumina does not dissolve appreciably in the nitric acid scrubbing solution. Based on experimental studies, boric acid was found to suppress the formation of alpha alumina to tolerable levels in the scrubbing solution.

The major problem in the calcination of zirconium-fluoride waste is the release of copious quantities of fluoride by the reaction, $\text{ZrF}_4 + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 4\text{HF}$. Laboratory and pilot-plant studies confirmed theoretical predictions that fluoride could be retained in the calcined solids as CaF_2 by the addition of calcium to the feed. Operation of the WCF using a Ca/F mole ratio of 0.55 in the feed has resulted in satisfactory retention of fluoride in the bed and tolerable corrosion rates.

The major problem in calcining NH_4NO_3 waste was high pressure drops across the HEPA filters caused by a change of crystalline form of undecomposed NH_4NO_3 reaching the filters⁽⁵⁾. Lowering of the off-gas temperature entering the filters from 84°C to 80°C and blending the waste with aluminum nitrate eliminated the problem.

A minor amount of stainless-steel sulfate wastes blended with zirconium wastes has been calcined without difficulty. High fines carryover from the fluid bed to the off-gas system is currently being experienced during the calcination of a blend of aluminum nitrate and stainless-steel nitrate wastes. Properties of calcined solids generated during processing of aluminum nitrate and zirconium fluoride wastes are shown in Table II.

PLANT-SCALE OPERATING EXPERIENCE AT ICPP

PROCESS AND EQUIPMENT RELIABILITY

Generally, process reliability of fluid-bed calcination has exceeded expectations. On-stream factors greater than 86 percent were realized in the first four campaigns. However, calcination of fluoride waste during the past six years has begun to significantly corrode much of the equipment. A summary of WCF performance is shown in Table III. The major problems have been corrosion of valves, pumps, and some vessels and lines. Plugging of the off-gas cyclone, solids transport lines, and feed valves and nozzles are also major contributors to the downtime^(6,7,8,9,10).

PROCESS HEATING

Process heating during the first three campaigns was provided by an in-bed heat exchanger in which hot NaK was circulated. Design heat transfer rates were obtained; however, safety factors and the need to increase throughput capacity

TABLE II

TYPICAL PROPERTIES OF CALCINED SOLIDS

	<u>Fluoride-Bearing Waste</u>	<u>Acid Aluminum Waste</u>
Bulk Density, lbs/ft ³	100	70
Heat Generation Rate, Btu/hr-lb	0.1 - 0.2	0.4
CHEMICAL PROPERTIES		
Metallic Oxides (wt%)	43.3	89.2
Nitrogen as NO ₃ (wt%)	1.0	4.0
Water as H ₂ O (wt%)	1.0	2.0
Calcium as CaF ₂ (wt%)	54.2	0
Fission Product and Other Oxides or Fluorides (wt%)	0.5	4.8
RADIOCHEMICAL PROPERTIES		
Cs-137, Ci/lb	1.3	8
Sr-90, Ci/lb	1.6	6
Pu, Ci/lb	0.004	0.007

TABLE III

SUMMARY OF WCF PERFORMANCE

<u>Campaign</u>	<u>Duration (Days)</u>	<u>On-Stream Factor (1)</u>	<u>Average Net Feed Rate, Gal/hr</u>	<u>Major Problems</u>
1. 12/63 - 10/64 (NaK)	312	0.99	69	Plugging of feed nozzles and control valves. Valve bellows failure.
2. 4/66 - 3/68 (NaK)	724	0.86	66	NaK leak. Valve bellows Failure Transport line erosion.
3. 8/68 - 6/69 (NaK)	299	0.89	53	Pump failure. Plugging feed lines.
4. 8/70 - 1/71 (IBC)	156	1.00	67	Fuel nozzles severely eroded.
5. 9/71 - 5/72 (IBC)	232	0.71	75	Plugged off-gas cyclone.
6. 5/73 - 3/74 (IBC)	278	0.66	72	Valve bellows failure. Plugged solids transport line.

(1) Based on time radioactive feed introduced to calciner until the calciner is shut down to end campaign. Maintenance and decontamination between campaigns not included.

as simply as possible resulted in the development and installation of an in-bed combustion process.

In-bed combustion of kerosene is an inherently simple and thermally efficient method of process heating. Kerosene is atomized with oxygen through wall-mounted nozzles to maximize combustion efficiency. Combustion efficiencies greater than 88% are obtained at a calcination temperature of 500°C. In-bed combustion has proven to be a very reliable process heating system during the last three waste processing campaigns.

OFF-GAS CLEANUP

The most critical area of any waste solidification process is the removal of volatile and particulate radioactivity from the calciner off-gas prior to release to the atmosphere. Particulate decontamination factors across the off-gas system for the WCF have ranged from 10^5 to 10^8 . The only volatile radio-nuclide of any concern is Ru-106; a decontamination factor of 10^3 to 10^5 for Ru-106 was realized using silica gel adsorbers, scrubbers, and filters.

The off-gas cyclone, venturi scrubber, and the HEPA filters are the major devices for achieving the desired particulate removal. If significant quantities of volatile ruthenium compounds must be removed, silica gel adsorbers or the equivalent are required.

Calcination temperature and gas composition have the major influence on the formation of volatile and non-volatile ruthenium. Lower temperatures and an oxidizing atmosphere tend to promote volatile ruthenium formation; thus, mostly volatile ruthenium was formed using indirect heating. In-bed combustion at 500°C and the gaseous atmosphere has resulted in formation of essentially all

particulate ruthenium. A summary of our experience with ruthenium during waste calcination is shown in Figure 8.

NEW WASTE CALCINING FACILITY

Unacceptable corrosion rates, too low a throughput capacity, and the high radiation exposures required by essentially total direct maintenance are the bases for building a New Waste Calcining Facility (NWCF) at the ICPP. Major improvements in the new calciner are summarized in Table IV. A simplified layout and elevation of the NWCF are shown in Figures 9 and 10, respectively.

Specific process and equipment improvements are as follows: (1) simplified and more reliable systems for controlling and metering the feed rate to each nozzle, (2) minimize the number of valves and pumps and remotely maintain those installed, (3) maintain acceptable corrosion rates by careful selection of materials of construction for handling existing and future wastes, (4) reduce to as low as practicable the atmospheric release of radioactive and chemical pollutants, (5) increase solids removal efficiency from calciner off-gas prior to entering HEPA filters, and (6) leaching of activity from final filters to minimize curies of activity placed in the burial ground.

PILOT-PLANT STUDIES

Development of process flowsheets and verification of the operability of proposed process and equipment improvements are major current areas of activity. Emphasis at present is on pilot-scale demonstration of a flowsheet for calcination of an intermediate-level waste containing 2 M sodium and on verification of a flowsheet for a stainless steel nitrate waste.

High-sodium wastes are difficult to calcine in any process because of the tendency of NaNO_3 to cause the solids to become "tacky". In the fluid-bed

INDIRECT HEATING

IN-BED COMBUSTION HEATING

FIGURE 8 FLOW PATH OF RUTHENIUM IN FLUIDIZED-BED CALCINATION

TABLE IV

SIGNIFICANT IMPROVEMENTS IN NWCF

- 1 - Based on latest process technology.**
- 2 - Improved feed rate control, metering, and blending.**
- 3 - Remote maintenance on valves, pumps, and flowmeters.**
- 4 - Improved equipment reliability and materials of construction.**
- 5 - Increased efficiency of off-gas cleanup system.**
- 6 - HEPA filter leaching and compaction**
- 7 - Increased capacity (3000 gpd net)**

FIGURE 9 NEW WASTE CALCINER FACILITY

FIGURE 10 NEW WASTE CALCINER FACILITY

calcination of sodium wastes, the bed particles can become "sticky" and agglomerate, making the process inoperable. The intermediate-level waste at ICPP has been combined with zirconium-fluoride waste to form a stable Na compound (NaAlF_6). However, long-term pilot-scale operation is yet to be demonstrated because of two major problems, formation of noded particles and uncontrolled particle growth during pilot-plant operation.

Stainless steel nitrate wastes have a very low attrition resistance; thus, a high proportion of solids are entrained and elutriated in the calciner off-gas resulting in an unacceptable load on the off-gas cleanup equipment or the inability to maintain a stable bed level in the fluidized bed. Flowsheets based on various blends with other waste are being tested to resolve the problem.

Process improvements currently under study are in the area of feed metering and control, off-gas cleanup, and calciner vessel design. Ultrasonic flowmeters are being tested for more accurate feed metering; an air-lift system is being tested for controlling the feed rate to each feed nozzle. Emphasis in off-gas cleanup is on increasing the efficiency of solids removal by the dry cyclone, increasing wet scrubbing efficiency by more efficient particle removal by the venturi scrubber, and leaching of radioactivity from the final off-gas filters (HEPA's). Calciner vessel configuration is being studied to increase fluidization quality and to minimize particle carryover by entrainment.

FLUID-BED CALCINATION OF COMMERCIAL WASTES

Based on the high degree of success at ICPP in calcining a variety of high-level wastes, the applicability of fluidized-bed calcination to commercial

wastes is apparent. The only process and equipment modifications necessary are those required as a result of the increased radioactivity of the commercial waste.

CONCEPTUAL PROCESS DESCRIPTION

A conceptual process for fluid-bed solidification of commercial high-level wastes is shown in Figure 11. The process is based on air fluidization using in-bed combustion heating. Calcined solids are removed from the fluid bed and from the bottom of a cyclone fines collector; the bulk of the fines can be separated from the product and redissolved if necessary to meet product specifications. Particulate solids are removed from the calciner off-gas by a high-efficiency venturi scrubber and a series of HEPA filters; a volatile ruthenium adsorber is included to decrease ruthenium releases to as low as practicable.

An off-gas condenser is included after the wet scrubbing system to assure a sufficient decontamination factor for ruthenium and for nitric acid recovery. The condensate would normally be processed and broken into two fractions; a bottoms fraction would be recycled back to the calciner feed and a "clean" concentrated HNO_3 stream would be recycled for headend dissolution.

MAJOR CONSIDERATIONS

PROCESS RELIABILITY

Experience in the fluidized-bed calcination of AEC high-level wastes has shown the process to be basically reliable. Instrumentation of the process is straightforward, and no unique instrumentation is required. Equipment items projected to have the highest frequency of maintenance are replacement of fuel and feed nozzles, valves in the calciner feed and wet off-gas scrubbing systems,

FIGURE 11 COMMERCIAL WASTE CALCINATION FLOWSHEET USING AIR FLUIDIZATION AND IN-BED COMBUSTION

and scrubbing solution pumps. Since the plant will most likely be total remote maintenance, careful design and use of spare equipment is mandatory.

PROCESS HEATING

In-bed combustion was selected as the method of heating because of the high thermal efficiency, inherent simplicity, and the negligible amount of volatile ruthenium apparently formed during calcination. Combustion efficiency needs to be improved over the present 88-90 percent to decrease the impact of unburned hydrocarbons entering the volatile ruthenium adsorbers. Also, use of a shrouded fuel nozzle shows promise in decreasing particle attrition from the combustion nozzles.

OFF-GAS CLEANUP

Removal of particulate matter and volatile radionuclides by the off-gas system must be assured. The bulk of the removal of solid particulates occurs in the wet scrubbing system (high-energy venturi scrubber or equivalent) and the HEPA filters; volatile ruthenium, if formed in significant quantities, must be removed by an off-gas condenser and/or a volatile ruthenium adsorber.

A distinct advantage of in-bed combustion over indirect heating is the apparent formation of particulate ruthenium instead of volatile ruthenium. While using indirect heating in the WCF, most of the ruthenium passing the wet scrubbing system was volatile. Analyses of the off-gas leaving the wet scrubbing system while using in-bed combustion have revealed negligible volatile ruthenium.

The keys to obtaining the desired particulate decontamination factors (feed to stack release) are solids particulate removal using a high-efficiency venturi scrubber and HEPA filters that are kept dry and bonded to the filter frame with

a stable adhesive. If as low as practicable ruthenium releases are to be realized, the quantity of volatile ruthenium formed must be minimized and off-gas condensation and solid ruthenium adsorbents will probably be necessary.

Other options which should be given consideration in off-gas cleanup are off-gas recycle and steam fluidization⁽¹¹⁾. In commercial waste calcination, reduction of atmospheric NO_x releases, the process economics of recycling HNO_3 , and ruthenium removal from the off-gas by condensation fit well into a scheme using off-gas recycle. A portion of the off-gas from the condenser would be recycled to the calciner as a fluidizing gas and possibly for other uses (eg, solids transport, purges, etc.). This concept would result in a minimum volume of off-gas requiring final cleanup prior to atmospheric release. Steam fluidization would also theoretically reduce the quantity of off-gases released to the atmosphere. Though in-bed combustion results in additional off-gas generation, its favorable impact on ruthenium behavior is worth the cost of the increased volume of gas released.

CONDENSATE CLEANUP

Condensate from the off-gas condenser will require processing with the goal of forming an intermediate-level waste for recycle to the calciner feed and a concentrated HNO_3 stream for use in headend dissolution. Because of the increasing environmental restraints on release of low-level waste to ground, the system should probably be designed to eliminate such releases.

PRODUCT PROPERTIES AND HANDLING

The product from a fluid-bed calciner will be a granular material; the particle sizes will range from a few microns to near 1 mm diameter. Based on ICPP experience, the water content will likely be less than one weight percent; nitrate content of the final product is estimated in the range of 4-12 weight

percent and is strongly dependent on NaNO_3 content. As estimate of the properties of a typical commercial waste calcine is shown in Table V.

Calcine can be withdrawn from the fluidized bed by gravity flow into a receiver or transported pneumatically to a separate packaging call. The product can be stored as collected from the bed and off-gas cyclone, or the elutriable fines can be separated by air classification, redissolved, and recycled. Product is suitable for interim storage or can be converted to other forms to decrease leachability and increase thermal conductivity.

TABLE V

ESTIMATED PRODUCT PROPERTIES OF FLUID-BED CALCINE
PREPARED FROM COMMERCIAL WASTES

Bulk Density, lbs/ft^3	140
Heat Generation Rate, Btu/hr-lb	~ 150
Metallic Oxides, wt%	30 - 40
Nitrogen as NO_3 , wt%	4 - 12
Water as H_2O , wt%	< 1
Fission Product Oxides, wt%	60 - 70
Mass Mean Particle Diameter, mm	0.3 - 0.6
Thermal Conductivity, $\text{Btu/hr/ft/}^\circ\text{F}$	0.18-.22
Porosity, %	0.4 - 0.5
Heat Capacity, $\text{Btu/lb-}^\circ\text{F}$	~ 0.2

SAFETY CONSIDERATIONS

The major safety concern in fluid-bed calcination is the potential for rapid heatup and sintering of a collapsed bed and the attendant damage to the calciner vessel. Cooling of the bed by fluidizing air cannot be relied on to dissipate the decay heat. Primary and secondary fluidizing air systems may fail; a more probable circumstance is the inability to operate the off-gas cleanup system, thereby negating the use of fluidized air.

Based on the above, a reliable method for emergency dumping the bed into a container(s) from which the decay heat can be dissipated is required. The specific design for emergency dumping can be obtained by applying sound engineering design principles. During the ten years of experience with fluidized beds at ICPP, any condition (process or equipment) which would require dumping the bed would be detected over a period of several hours. Thus, emergency dumping within a few minutes is a highly unlikely occurrence.

CONCLUSIONS

Plant-scale operations during the last ten years and pilot-plant studies have revealed no major problems with fluid-bed solidification. The basic process currently used at ICPP is applicable to commercial waste solidification. Process and equipment modifications necessary for commercial waste calcination are: (1) calciner vessel design for emergency bed dumping, (2) design compatible with total remote maintenance, (3) off-gas condensate for potential volatile ruthenium and NO_x removal, and (4) off-gas condensate cleanup. Calcined product is suitable for interim storage or for post-calcination treatment.

REFERENCES

1. J. A. Buckham and J. A. McBride, "The Fluidized Bed Waste Calcination Process," a paper presented at the IAEA Symposium on "Solidification and Fixation of Liquids by Calcination" in Vienna, October 1962.
2. J. L. McElroy, et al, "Waste Solidification Program Summary Report, Volume II, Evaluation of WSEP High-Level Waste Solidification Processes," BNWL-1667, July 1972.
3. B. R. Wheeler, et al, "A Comparison of Various Calcination Processes for Processing High-Level Radioactive Wastes," IDO-14622, April 1964.
4. L. T. Lakey and J. R. Bower, Editors, "ICPP Waste Calcining Facility Safety Analysis Report," IDO-14620, December 1963.
5. D. W. Rhodes, "Chemical Development Work in Support of Fluidized-Bed Calcination of Radioactive Wastes at the Idaho Chemical Processing Plant," ICP-1025, August 1973.
6. R. E. Commander, et al, "Operation of the Waste Calcining Facility with Highly Radioactive Aqueous Waste," IDO-14662, June 1966.
7. G. E. Lohse and M. P. Hales, "Second Processing Campaign in the Waste Calcining Facility," IN-1344, March 1970.
8. C. L. Bendisxen, et al, "The Third Processing Campaign in the Waste Calcining Facility," IN-1474, May 1971.
9. J. A. Wielang, et al, "The Fourth Processing Campaign in the Waste Calcining Facility," FY-1971, ICP-1004, March 1972.
10. J. A. Wielang, W. A. Freeby, "The Fifth Processing Campaign in the Waste Calcining Facility," FY-1972, ICP-1021, June 1973.
11. W. A. Freeby, et al, "Summary Evaluation of Candidate Fluid-Bed Solidification Processes for Use in the NWCF," ICP-1046, March 1974.