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FLUIDIZED BED INCINERATION
OF TRANSURANIC CONTAMINATED WASTE

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ABSTRACT

A 9 Kg/hr pilot scale fluidized bed incinerator is now being used for burning various types of radioactive waste at Rocky Flats Plant. General solid combustible waste containing halogenated materials is burned in a fluidized bed of sodium carbonate for in situ neutralization of thermally generated acidic gases. A variety of other production related materials has been burned in the incinerator, including ion exchange resin, tributyl phosphate solutions, and air filters. Successful operation of the pilot plant incinerator has led to the design and construction of a production size unit to burn 82 Kg/hr of plant generated waste. Residues from incinerator operations will be processed into glass buttons utilizing a vitrification plant now under development.

This work was conducted as a part of a U.S. Department of Energy Contract EY-76-C-04-3533,

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1. Introduction

For the past 16 years, a conventional incinerator has been used at the Rocky Flats Plant to burn waste containing recoverable amounts of plutonium. During these years, the major problems have been equipment corrosion, short refractory life, nuclear safety limitation, poor off-gas quality and mechanical problems in the aqueous scrubber. Various types of incineration systems were investigated that might offer improvements over the older system, and it appeared that fluidized bed incineration had certain advantages for transuranic waste. The chief advantages are in situ neutralization of acid gases generated by thermal decomposition of waste, a uniform, relatively low temperature combustion that results in an easily recoverable plutonium oxide in the ash, a dry off-gas system, and the elimination of refractories.

Refractory linings are of greater concern in radioactive waste incinerators than in other applications of refractories. Removal of damaged refractory linings and the subsequent rebricking of the conventional incinerator has been a difficult task; recovery of plutonium compounds that have penetrated the used refractories and disposal of this refractory waste material has been even more difficult. Another recovery problem is the high-fired (more than 800°C) refractory plutonium oxide in the ash from conventional incinerators. Multiple acid leachings are required to recover the plutonium prior to disposal of the ash. The low-fired plutonium oxide in the FBI ash can be recovered effectively with a single acid leach.

2. Equipment

A pilot scale fluidized bed incinerator (FBI), shown in Figure 1, was designed to incinerate general plant combustible waste at a 9 Kg/hr rate [1]. The unit was installed in a canyon type enclosure for operation with radioactive waste. Waste is emptied from drum containers into a large sorting box, shredded by low speed cutters, tramp metal removed by air classification, and then screw conveyed into a hot bed of fluidized sodium carbonate (Na_2CO_3). Waste is burned or decomposed at a temperature of about 550°C, and acid gases react with the basic bed material to form corresponding sodium salts. The primary bed has a cross sectional area of about 0.1 m² and an overall height of 1.5 meters from the bottom of the conical distributor section up to the outlet. The ash, sodium salts (NaCl, etc.) and some sodium carbonate are elutriated from the bed with the flue gas stream. Flue gas exiting the primary reactor passes through a cyclone separator where the major ash quantity is removed. The gas then flows into a fluidized bed of catalyst where excess combustion air is added for complete combustion of unburned hydrocarbons in the flue gas. The afterburner is 0.6 m in diameter by about 1.4 m high. Afterburner flue gas is cleaned by a second cyclone separator and sintered metal filters, then passes through an air jet ejector which provides motive force for gas flow through the incinerator. This mix of ejector air-process gas is blended with room air to produce a gas temperature below 60°C before it passes through process high efficiency air filters. The filtered gas is further cleaned by four stages of high efficiency filters before release to the atmosphere. Normal operating conditions and material composition are presented in Table I.

3. Waste Feed Preparation

Waste is received in standard 210 liter drums after it has been assayed by an automated drum counter. The assayed waste drum is dumped into a large sorting box, bags cut open, and large pieces of tramp metal removed by hand. Since the waste is known to contain tramp metal, no metal detectors or x-ray type equipment is

used to survey the waste. As the waste is hand sorted, it is fed into a hydraulically driven, low speed shredder with counterrotating cutting blades. The low speed shredding produces very little dust; this eliminates the danger of a dust explosion in the system. Torque sensing devices stop the shredder and reverse the rotation if a tough piece of metal gets into the blades. Fire protection is provided by a Halon extinguishing system that will flood the waste preparation section with Halon if a fire should occur.

Installation of an air classifier for tramp metal removal was not considered initially, since all waste collection is administratively controlled with separate receptacles for combustibles, metal, etc. However, when the incineration of production generated waste was started, the amount of metal in the combustible waste made it necessary to add the equipment. A zig-zag type unit was first used, but it was not workable in a canyon type operation. The present classifier is a much simplified unit that has proven quite reliable. Table II shows separation results achieved in four representative runs, each about 100 hours duration.

The first two runs were general production combustible waste, while the waste burned in the last two runs included large quantities of shoe covers and coveralls. Snaps and buttons that remain attached to fragments of cloth, along with small metal objects, are air conveyed to the feed hopper from where they are screw fed into the incinerator. The tramp metal collects at the bottom of the fluidized bed and can be easily drained out without disturbing operation of the incinerator.

4. Reaction of Chloride With Sodium Carbonate

A major objective of this process is to neutralize the HCl at the point of generation to eliminate acidic gas corrosion in the system and negate the need for aqueous scrubbers. The chloride-containing wastes are burned in a fluidized bed of sodium carbonate, where the nascent HCl reacts with the bed material to form sodium chloride. Results from thermal analysis show that HCl is generated by decomposition of polyvinyl chloride at about 250°C, well under the 550°C operating temperature of the incinerator. The HCl should therefore be freed for reaction as soon as the polyvinyl chloride enters the bed. Incinerator runs with prepared waste, containing known amounts of polyvinyl chloride, were made using various bed depths above the waste entrance to determine the effect on chloride retention; no differences were found in the bed depth range of 0.1 to 1.3 meters above the entrance.

The bed material used was 500-1000 micron size sodium carbonate granules. Analysis, by x-ray microscopy, of the used bed particles indicated there was a dense shell of high concentration NaCl surrounding a core of unreacted Na_2CO_3 . This finding led to the installation of jet grinders in the bed to abrade off the NaCl shell and expose the core Na_2CO_3 for continued reaction. Utilization of Na_2CO_3 , using jet grinders in the bed, has been demonstrated in the 70-80% range without the release of detectable amounts of HCl in the off-gas.

5. Flue Gas Afterburning

The use of a fluidized catalyst afterburner is an important feature of the process. The catalyst is effective at lower temperatures than are required for open flame afterburning; this eliminates the need for refractory lined equipment. As shown in Table III, the catalyst is effective in producing a high quality flue gas.

6. Incineration Operations

The pilot scale incinerator has now been in service for years. Over this time a large variety of waste have

been burned for testing purposes and for disposal of manufacturing wastes; Table IV contains a partial listing. Solid wastes that are usually submitted in small batches, such as partially decomposed or contaminated laboratory chemicals, are generally mixed with the general solid waste during incineration. Liquids that are miscible are also mixed; this provides an even K_j (BTU) feed for a prolonged period. The incineration of combustible liquids is important, since no shipment of radioactive liquids is allowed from a nuclear facility.

The major combustible waste streams generated at a nuclear facility can be roughly grouped into four major categories:

1. General production generated plastics, paper, cloth, etc.
2. Tributyl phosphate-solvent mixtures from Purex process.
3. Organic ion exchange resin
4. High efficiency particulate air (HEPA) filters.

All of the categories have been burned in the FBI, the last three during the past year. The first category was covered in the previous section; the others can be briefly summarized.

7. Tributyl Phosphate - Solvent

During the incineration of tributyl phosphate (TBP)-solvent mixtures, large amounts of phosphorous pentoxide are formed as shown in equation one (1):

In conventional incineration systems, the P₂O₅ sublimates and condenses in the cooler portion of the exhaust system. The anhydrous material is classified as a flammable solid that readily absorbs moisture, forming phosphoric acid which is very corrosive to ferrous metals and alloys. A method for safely trapping the P₂O₅ is necessary for a viable incineration system. Burning the TBP-solvent in a fluidized bed of sodium carbonate-catalyst results in a reaction as shown in equation (2):

The thermally stable sodium phosphate is removed with the ash.

8. Organic Ion Exchange Resin

The organic ion exchange resin used for nuclide separation is usually a styrene base compound that should readily burn. However, if burned in an incinerator with a grate, the resin melts and drops through, mixing with the residues and complicating trans-uranic recovery. Agitation of the resin to expose it to combustion air is the best way to burn it, and the suspension of the resin beads in a fluidized bed probably achieves maximum exposure of the bead to oxidation.

The resin is usually received under standing water and is drained just before feeding to the incinerator. No further drying is attempted; the resin burned contains 45-55% water. One effect of the high water content in the resin beads was noted when two different feeding methods were compared—conveying it into the bed beneath the surface and conveying it in at a higher level to allow it to fall on the surface of the fluidized bed. If added above bed, an effect similar to corncobbing is seen. The resin bead explodes due to interstitial steam generation, and the small fragments are carried out before complete combustion is achieved. However, when the resin beads are introduced beneath the surface of the bed, premature resin carryover is eliminated and combustion occurs in the bed media.

9. HEPA Filter Incineration

Nuclear facilities generate large quantities of HEPA filters, usually containing only low levels of radioactive contaminants. The large building ventilation filters consist of approximately 60 percent combustible wood and a remainder of non-combustible media and asbestos spacers. Burning the entire filter will result in only about a 50% weight reduction, but it eliminates possible trapped materials that could cause outgassing from media packaged for shipment and produces a volume reduction. Combustion of the HEPA filters in the fluidized bed process has been successfully demonstrated, both mixed with general waste and as a single feed.

10. Conclusions

During four years of operation, most of the types of wastes that are generated at nuclear facilities have been burned. These included actual production wastes that are often quite different from the simulated wastes burned during experimental operations. Based on this experience, the following conclusions can be formed.

1. Operating temperatures in the incinerator and after-burner are low enough to eliminate the use of refractories.
2. Shredding of waste, with air classifier tramp metal removal, and the feeding of the shredded material has been demonstrated to be satisfactory.
3. Efficient HCl neutralization has been accomplished up to a level of about 80% Na_2CO_3 utilization.
4. Most of the wastes generated at a nuclear facility can be burned in a fluidized bed incinerator.

11. Production Scale Incineration

Successful demonstration of the advantages of a fluidized bed incinerator led to the design and construction of a unit sized to handle the waste generated at Rocky Flats. The production sized unit has been designed to burn 82 Kg/hr of waste containing up to 0.001 g Pu/g of waste; installation is nearly complete. The flow diagram shown in Figure 2 illustrates the design changes required for a 9 to 1 scale up of the pilot unit. The front end of the system, or waste preparation and feeding equipment, is similar to the pilot plant only much larger. Waste is added to the center of the primary reactor to aid in lateral mixing in the combustion bed. Because of the large amount of heat generated, the afterburner is water-cooled to permit a smaller size vessel to be used. Flow through the reactor, operating at a pressure negative to the canyon enclosure, is provided by four blowers. A heat exchanger is used up-stream from the blowers to cool the exhaust gases and reduce the volume. At the 1830 m elevation level of Rocky Flats, this is an important consideration.

An extensive series of tests using metal coupons in the pilot plant FBI were conducted to determine candidate materials for use on the large size unit. The low operating temperature and absence of acid gases in the system resulted in very little corrosion of any of the metals tested. While Inconel 600 was the least affected, it was found that 316 stainless steel was more than adequate. Major vessels on the large unit were therefore constructed from 316 stainless steel, with piping constructed of 304 stainless steel.

12. Process Area and Operation

A major consideration for any process installed in a nuclear facility is the space requirements. Buildings constructed for the

containment of radioactive materials must conform to rigid safety standards with respect to earthquake, tornados, fires and related hazards. Any reduction in space requirements for a process gives significant savings. The dry off-gas system of the FBI results in eliminating the space required for conventional scrubbers and associated equipment, with an estimated 50% reduction in required space.

A computer has been installed to collect operational data at pertinent points while the incinerator run is in progress. All materials entering the process and all residues exiting are weighed and the weights logged into the computer. At the end of each run the computer then calculates and prints a summary showing total weight of materials burned, total time, and average wt/hr burning rate. Results from laboratory analysis of the ash and in-line instrument analysis of the flue gas are fed into the computer and a material balance is obtained showing the various products generated.

The basic function of the computer system remains one of process monitoring and analysis of information. However, the computer concept will be expanded in the future to include process control. Changes in feed rates, air-nitrogen ratios, temperature and fluid gas flow rates will be sensed and proper controls automatically adjusted. At all times there will be manual over-ride to allow for operator intervention.

Test runs on the incinerator, scheduled to begin near the first of the year, will be made using non-radioactive material. After initial check out of components and computer operation, the incineration of low level transuranic combustible waste will begin. It is also planned to install a liquid feed system to burn a present backlog of organic wastes. Operation of the incinerator is expected to significantly reduce waste shipments from the Rocky Flats Plant.

13. Waste Immobilization

13.1 Immobilization Technique

Residues from both the pilot plant and production scale FBI's will be in the form of fine powders, normally measuring less than 20 microns in diameter. For residues containing recoverable amounts of plutonium, this is an ideal form for the acid dissolution process used. Residues resulting from incineration of low level transuranic waste do not contain recoverable amounts of plutonium and the residues are shipped without further processing.

The planned establishment of a permanent repository for radioactive waste will bring changes in waste forms that are shipped. Proposed criteria for waste acceptable at the repository will not permit the transporting and storage of fine powders; therefore, it appears certain that an immobilization process will be required for incinerator residues. There has been a considerable amount of work done on the immobilization of waste, with many different techniques used at various installations. In earlier work at Rocky Flats, a number of these techniques were used in the immobilization of sludges from the waste processing plants. A comparison of leach rates and volume effects is shown in Table V.

The increased emphasis on waste management practices and the planned establishment of a permanent waste repository led to further studies on waste fixation techniques, with more of an emphasis on incinerator ash. The proposed criteria for the repository discourages the storing of gas generators and combustibles or thermally unstable materials. This would tend to eliminate use of the plastic incorporation or coating. A low water content cementing process could possibly be used, but vitrification offers savings in weight and volume for a product meeting proposed repository criteria. Another factor was that incinerator ash contains a sizeable percentage of the compounds used in commercial glass manufacture.

A number of different processes have been investigated for converting high level radioactive waste to stable solids of low

solubility. There are obvious differences between the handling techniques required for high level and low level transuranic waste; there are also major differences in the composition of the waste stream that must be considered. These composition differences are important to the development of a viable fixation process for non-high level radioactive waste. In low level waste, there is negligible heat generation relative to that produced in high level waste; this eliminates the need for admixed heat conductors or special containers. Economy of operations also dictates against the use of expensive, melt resistant containers that are discarded along with the contained glass. Product glass should require only standard low level waste packaging.

13.2 Pilot Plant Operation

From the results of data collected during laboratory work, a vitrification pilot plant was designed and fabricated. Figure 3 shows the pilot plant now in operation. Feed material is mixed in an air blender and added to the feed hopper. A screw conveyor meters the mix into a resistance heated vitrification reactor constructed of Inconel 690, the metal found most resistant to corrosion in crucible tests. Molten glass drips onto a rotating plate, forming 5 mm glass buttons. This is similar to the button former used on the PAMELA process at Julick [2]. Buttons are raked off the forming plate into a vertical tube annealer; annealing time and temperature can be adjusted. Cooling of the annealed buttons is accomplished on a vibratory cooler that also conveys the finished product to the shipping container.

Glass buttons have been produced by the pilot plant from the ash resulting from incineration of a number of different waste streams. The amount of additives used as fluxing aids has been kept as low as possible, with only enough used to provide a glass melting in the 1050°C range and totally vitrified buttons. Glass at present is being produced from the components shown in Table VI. Silicon content of the glass is low, the only silicon present being that contained in the incinerator ash. However, there is alumina and chromia present that combine with the boron oxide to form the main structure of the glass.

Part of the vitrification project has been the inclusion of other production waste streams in the vitrification process. Good glass has been formed from a mixture of 55% incinerator ash, 33% filter aid, and 12% mineral resin replacing the straight 70% incinerator ash. This replacement mixture provides considerably more silicon in the glass with a consequent lowering of the melting point.

13.3 Future Work

The wire coil resistance heaters on the Inconel vitrification reactor are to be replaced by glowbar heaters to provide a higher operational range in temperature and an extended operational time. This should permit compensation for unexpected large changes in feed composition by the addition of more heat if necessary.

A small ceramic vitrification reactor using in-melt electrodes has also been assembled. At the conclusion of comparative tests on both reactors, a choice can be made of which to use in the scaled up model. Whether or not annealing is necessary will also be determined before the system is installed in a canyon for the vitrification of radioactive waste.

TABLE I
FLUIDIZED BED INCINERATION
SYSTEM FOR DOE TRU WASTE
OPERATING CONDITIONS

	<u>Primary</u>	<u>Afterburner</u>
Combustion %	27	73
Temperature °C	550	550
Gas Velocity M/Sec	0.7	0.5
Bed Depth M	0.5	0.5
Bed Material	Na ₂ CO ₃ - Catalyst	Catalyst
Bed Material Size Microns	500-1200	500-1200
Control Variable	Oxygen	Fuel

TABLE II

Tramp Metal Removal From Combustible Waste

<u>Run No.</u>	<u>% Metal in Feed</u>	<u>Removal Efficiency % Hand Sorting</u>	<u>Air Classifier</u>	<u>% into Incinerator</u>
1	6.8	58.9	35.3	5.8
2	11.1	64.3	28.3	7.4
3	9.6	47.0	38.0	15.0
4	<u>6.8</u>	<u>67.9</u>	<u>20.4</u>	<u>11.7</u>
Average	8.6	59.5	30.5	10.0

TABLE III

Flue Gas Composition Exiting Afterburner

	<u>Amount Present</u>
Oxygen (%)	7.5
Carbon Dioxide (%)	5.0
Carbon Monoxide (PPM)	77
Total Hydrocarbons (PPM)	54

TABLE IV

Materials Burned in Fluidized Bed Incinerators

<u>Solids</u>		<u>Liquids</u>
1. PVC plastics	8. Rubber	1. Naptha
2. Paper	9. Wood	2. Methylene Chloride
3. Latex cocoon	10. HEPA filters	3. Tri-chlor
4. Shoe covers	11. Leather	4. Hydrazine
5. Ion exchange resin	12. RO Membranes	5. Oil
6. Polyethylene	13. Fulflo filters	6. Waste Chemicals
7. Waste chemicals		7. Methyl Cellulose
		8. Tributyl Phosphate

TABLE V

Product Evaluation Tests at RFP

<u>Type</u>	<u>Relative Product Wt. Ratio</u>	<u>Relative Leach Rate</u>
RFP Production Sludge	1.0	1,000
Sludge in Asphalt	0.99	220
Sludge in Gilsonite	0.97	197
Calcine in Gilsonite	0.93	132
Calcine	0.49	108
Calcine in Asphalt	0.93	90
Cemented Sludge	1.5	12
Cemented Calcine	1.23	1
Vitrified Sludge	0.23	1

TABLE VI

Glass Button Composition

<u>Component</u>	<u>Percent</u>
Incinerator Ash	70
B_2O_3	20
Na_2O	10

[1] Ziegler, D. L., Johnson, A. J., Meile, L. J.: "Fluid Bed Incineration", Proc. GVC/AIChE-Joint Meeting and Jahrestreffen 1974 der Verfahrens-Ingenieure, Vol. III, Paper E3-4, Munchen 1974. *(Renamed as RFP-2016)*

[2] VanGeel, J., Eschrich, H., Heimerl, W., Grziwa, P: "Solidification of High-level Liquid Wastes to Phosphate Glass-Metal Matrix Blocks", Proc. Symp. Management of Radioactive Wastes from Nuclear Fuel Cycle, Vol. 1, pp 341-359, OECD Vienna 1976.

Figure 1

FLUIDIZED BED INCINERATION SYSTEM

Figure 2

VITRIFICATION PILOT PLANT CONSISTS OF (1) FEED HOPPER, (2) SCREW CONVEYOR, (3) VITRIFICATION REACTOR, (4) ROTATING PLATE, (5) VERTICAL TUBE ANNEALER, (6) VIBRATORY COOLER AND (7) OFFGAS FILTER.