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STATUS REPORT
WASTE INCINERATION AND FIXATION FOR
WASTE MANAGEMENT, PRODUCTION, AND
REPROCESSING DIVISION OF THE
DEPARTMENT OF ENERGY
(July-December 1976)

Donald L. Ziegler

Jim W. White

Andrew J. Johnson

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Chemistry Research and Development
PILOT PLANT DEVELOPMENT

Rockwell International

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U. S. DEPARTMENT OF ENERGY
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Incinerators
Waste Management
Residue Fixation

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STATUS REPORT WASTE INCINERATION AND FIXATION FOR
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Alton R. Teter, and Seng F. Chung

Abstract. Fluidized bed incineration and waste fixation processes are being used to process the types of wastes expected from nuclear fuel reprocessing and production plants. Test incineration runs have been made on two types of wastes: high efficiency particulate air (HEPA) filters and tributyl phosphate-solvent solutions. Laboratory-scale vitrification equipment was used to produce glass pellets from incinerator ash and blends of other expected waste streams. Computer modeling gave an expected product integrity life of over 2,000 years.

INTRODUCTION

The generation of electrical power by nuclear-fueled facilities gradually has increased over the past several years. Further increases are scheduled in the number of nuclear plants, which means a concurrent increase in the amount of nuclear fuel required. The reprocessing of spent nuclear fuel, instead of using virgin material for new fuel elements, would extend the available supply of nuclear material. One of the operations that reprocessing plants, in addition to fuel preparation and fabrication plants, require is safe and efficient waste handling facilities. A large volume of this waste is low specific activity (LSA) waste and alpha waste comprising general trash and filters that are combustible.

Incineration of this combustible material and processing of the residue into a form that is safe for transportation and storage would effect both a reduction in weight and in volume. Any methods for accomplishing this task should be directed by regulations now being prepared for waste acceptable

by the permanent repository. Although these regulations have not been fully codified, some of the proposed guidelines call for the waste to be non-combustible, free of probable outgassing material, and in a form resistant to leaching. Segregating the waste, according to levels of radioactivity, into categories such as transuranic (α), LSA plus intermediate level waste (ILW) (α , β , and γ), and high level (β , γ) is a possibility. The work discussed in this report is within the preceding boundaries.

The incineration method used for this work was made possible by a fluidized bed incinerator (FBI); an FBI pilot plant unit (9 kg/hr waste) had been built at the Rocky Flats Plant. General-plant processing wastes are burned in a primary fluidized bed of sodium carbonate. This burning provides in situ neutralization of the hydrochloric acid that results from the large amount of polyvinyl chloride plastic contained in the waste. The low temperature process (below 625 °C in the primary bed and the fluidized catalyst afterburner) permits a total metal system to be used. There is no need for high-temperature refractory linings. Neutralization of acid gases in the primary bed and the use of sintered metal filters in off-gas lines negate the need of a liquid scrubber.

Residues from the FBI are in the form of a fine powder (composed of neutralization products), fly ash, and catalyst fines generated by bed attrition. Experiments are underway on a fixation process to convert this material into a form acceptable at a permanent repository. By utilizing other waste streams present at a nuclear fuel reprocessing plant, and the use of a small amount of additives, a glass product can be produced.

The major components of a process system for the glass are now being developed. These are (1) melt reactor, (2) forming equipment, and (3) glass annealer.

Suitability of the glass product as a permanent storage form is conditional on its physical and chemical properties. Physical properties such as hardness and breakage resistance in drop tests will be measured on the finished product. The measurement of chemical properties, such as leach resistance, is now in progress. The long-term storage properties were modeled with the use of a computer program to calculate the effect of plutonium-generated helium on the integrity of the glass pellet.

SUMMARY

An incineration-residue fixation system is being developed for processing wastes generated at a nuclear fuel reprocessing facility. Incineration is accomplished in a previously developed and operational pilot-plant fluidized-bed incinerator. Current waste-fixation development is directed towards vitrification of the residues.

Incineration of general plant waste demonstrated the need for separation of contained tramp metal by a mechanical operation. The average tramp metal content was around 8.5% by weight; contained metal was of all sizes and types. An improved waste classifier has replaced the originally installed model. The new model, currently being evaluated with plant waste, eliminates much of the gearing and mechanical operations involved in the first classifier.

Incineration of plenum filters to reduce weight and volume plus the elimination of contained volatiles was tested. The filter media, representing an average of 40% by weight of a filter, is not materially altered by incineration; frames of pressed wood burn readily. Reduction in volume was about 4.4 to 1, while 2 to 1 weight reduction was obtained. The residues are a mixture of fine powder and strands of glass fiber that is an ideal feed material for vitrification.

A tributyl phosphate-solvent mixture was burned in a lab-scale fluidized-bed incinerator using a mixed bed of sodium carbonate and catalyst. The objective was to tie up the phosphate as thermally stable sodium phosphate and prevent the escape of volatile phosphorous pentoxide. No difficulty was experienced in the incineration of the material, as the burning characteristics were similar to other organic solvent incineration in the fluidized bed incinerator. Laboratory analysis of all residues for phosphate were obtained and averaged for two runs. An average phosphate recovery of 103.1% was calculated.

Vitrification studies were first made on proposed waste streams from a nuclear fuel reprocessing plant handling light water reactor fuel. Compositions of the ash from incineration of combustibles and that of the noncombustible streams were calculated. Based on individual waste stream components, a general blend that could be used as vitrification feed was obtained.

Laboratory scale equipment is being used to test various components under consideration for a complete vitrification process. Melt reactors, both Joule-heated and standard resistance types, have been designed and are being fabricated. Castings of waste composition glass were made to evaluate the product as to desired form and size. Cup molds, sliding molds, and wiped-film peak molds were used to form various sizes of glass pellets. The forming method that appears most promising is to use a glob cutter, or plug valve, at the melt reactor outlet and drop the molten glass onto a flat plate. The free-form glass shape now being evaluated is about 18 mm in diameter by 6 mm in height. Optimum annealing time for this product is being determined.

Product integrity at a permanent repository will depend on physical and chemical characteristic of the environment and of the glass composition. One of the factors, helium generation within the glass from contained plutonium, was computer modeled. At the probable maximum plutonium level of 0.3 weight per cent (wt %) plutonium oxide, over 2,000 years will elapse before the undiffused helium exceeds its solubility at the glass yield strength.

DISCUSSION

Fluidized Bed Incineration

Solid Waste Handling

The pilot-plant fluidized-bed incinerator (FBI) used in this work was fully discussed in the 189C Fluidized Bed Incineration and Residue Fixation for Commercial Fuel Reprocessing Plants (a report describing the initial proposal). The only modification that has been made in the system is replacement of the prototype waste classifier with a newly designed model. Other modifications will be made, as necessary, to handle the various forms of new types of waste generated by nuclear fuel reprocessing plants.

The improved air-classifier installation for removing tramp metal is an excellent example of the value in actual experience handling process waste. In the incineration process, as originally conceived, a classifier would not be necessary because plant waste is sorted at the point of origin into separate drums for materials such as metal, glass, and combustible waste. The pilot plant was operated on simulated waste, at startup, to measure various parameters such as chloride retention and waste capacity. When this portion of the program was completed, incineration of actual plant waste began. The amount of tramp metal contained in the combustible waste was much larger than expected, and hand sorting was not effective. It became necessary to design, fabricate, and install an air classifier compatible with air handling restrictions imposed by radioactive contamination in the waste.

Tramp metal is a common problem with incinerators that are fed shredded waste by means of a screw feeder. A ram-type feeder requiring packaged waste does not obliterate this problem; waste must be sized to fit in the package. Large tangles of tape and plastic sheet that fill half of a 207-liter waste drum have been encountered in plant waste generated from maintenance operations. Metal in waste containing recoverable amounts of radionuclides must be removed, whether from the unburned waste or the resultant ash. The problems mentioned have become evident only with scaled-up efforts in radioactive waste incineration. There

probably would be additional problems if old waste, now buried in Idaho, is exhumed for incineration or further processing.

Solid combustibles usually consist of general process waste such as paper, plastic, rubber, and cloth. Most of this waste contains only small amounts of radioactive contaminants, or is from an area where radioactive materials are processed and is only suspect of being contaminated. As there is no simple method (one that would accomplish it in a realistic time span) for measuring low levels of rad contamination down to the 10 nCi/g limit, all of this waste is handled as though it is contaminated. Solid combustibles constitute the highest volume waste category generated at a nuclear fuel reprocessing facility. A 750-metric-tonne-per-year plant will have a total of about 1475 m³ (52,000 ft³)¹, with one-third of this being alpha combustible and the remaining two-thirds being low-specific-activity waste.

This is a large volume of waste to ship for storage at a DOE site, and it is a fire hazard in its original form. Incineration offers a means for reducing the volume and weight while producing a residue amenable to further processing. Further processing could mean recovery of contained radionuclides or conversion to a form acceptable at a permanent repository.

Incinerator Feed Preparation

In the original procedure, waste bags were dumped from the waste drums into a large sorting box where they were cut open and the tramp metal removed by hand sorting. Combustibles then went into a dual shredder system. The first system had thick blades (15 mm) and the second shredder had thinner blades (6 mm), thus providing a shredded waste easily handled by the screw feeder into the incinerator. When incineration of low activity waste from process areas started, however, the amount of tramp metal contained in the waste was much higher than expected. Over the course of several week-long incineration runs with process waste, a record was kept on the weight of tramp metal found. The average metal content was around 8.5% by weight; contained metal was of all

sizes and types. Unfortunately, all of this metal was not readily visible when wound up in the plastic and tape in the jumble of waste. Some metal was fed inadvertently into the shredders.

Tough metal objects such as 15-mm-diameter stainless steel bolts that are fed into the primary shredder will cause jamming and self-reversal of the shredder blades because of the built-in torque-sensing device. If the metal can not be chewed up by the blades, the shredder is manually stopped and the metal removed with tongs. The thick blades are not damaged by this action; however, some metal passed through the first shredder and damaged the thin-bladed secondary shredder. Major damage appeared to be caused by deflection of the thin blades to the extent that they engaged the side combs. Pieces and chunks of the side combs fell into the screw feeder and damaged the screw flights during the course of several runs.

To ensure safe and efficient operation of the shredder and screw, it was apparent that some type of mechanical metal-separation system was necessary. Metal detectors to find the hidden metal in the trash would only complicate the system and not solve the real problem of removing the metal. An air classifier similar to those tested at Stanford Research Institute² was designed and fabricated.

The shredder system was modified, with the air classifier installed under the primary shredder. The coarse-shredded waste dropped onto a conveyor belt that carried the waste to a rotary valve feeding it into an upward moving air stream. Heavy material fell through the air stream into a collection glove box, while the lighter fraction was air-conveyed to a cyclone separator positioned over the second shredder. Cyclone-separated waste was ground by this thin-bladed shredder and fell into the incinerator feed-screw hopper, while the air stream was recirculated back through the air classifier.

Over two metric tonnes of waste were incinerated using this system. Modifications of the classifier proceeded as continuous week-long operations revealed trouble points. The high dust loading of the shredded waste caused slippage of the conveyor belt on the idler roller; driving power was supplied

to both rollers to correct the slippage, and a vacuum system was installed to remove dust from under the belt. The rotary valve, used to introduce waste to the air stream, was fitted with air-jet agitators to prevent bridging. Very wet waste was also prone to holdup in the separation chute of the system. This could be alleviated only by slowing down the shredder feed rate.

While most of the day-to-day adjustments could be easily made over the course of a run, installation of this system in a canyon revealed the difficulties that might be encountered with even a relatively simple system installed for remote operation. As remote operation is one of the goals of this development program, a more trouble-free design was desirable. Experience gained with the pilot system pointed out possible alternate methods of waste classifications.

Air Classifier II

Major objectives in the design of an improved air classifier were (1) avoidance of sharp turns and transitions where waste could get caught and (2) elimination of the belt conveyor and rotary valve. A high-differential pressure blower was purchased to replace the surplus air mover that had been used on the first air classifier.

Several different designs were tested by building simple sheet-metal systems having configurations that could be changed easily. Experimentation with these systems resulted in a final model that performed well with test mixtures of shredded waste and tramp metal. A unit was designed with the proper air flow needed to handle waste feed for the pilot plant FBI. A sketch of the unit, fabricated and installed, is shown in Figure 1.

The coarse shredded waste from the primary shredder drops directly into the separator throat of the classifier. Turbulent air, produced by the side entry, goes up through the throat and carries the combustibles over to the cyclone separator, which is located above the second shredder. The cyclone drops the waste out of the air stream into the secondary shredder. There, the narrow blades complete the shredding of waste prior to incineration.

FIGURE 1. Air Classifier II for Separating Tramp Metal from Combustible Waste

Separator air is recirculated through the system, and there also is a small bleed stream vented into the sorting box. The throat area is adjustable by means of the movable side panel; positioning of this panel is controlled by a remotely operated actuator. A

viewing window in the throat area allows visual observation of the waste-air stream interaction. Optimum throat area depends on the density of waste being shredded. A narrower opening is used for wood than is used for paper or sheet plastic.

Incineration of High Efficiency Particulate Air Filters

Used high-efficiency particulate-air (HEPA) filters are in the waste stream of virtually all facilities operating with nuclear materials. A typical plant that reprocesses 750 metric tonnes of commercial fuel annually generates about 57 m³ (2,000 ft³) of these filters a year.¹ The great majority of these are very low in contained radioactivity; only a small percentage contain recoverable amounts of radioactive elements. All are treated as contaminated waste, however, and must be shipped to approved waste sites for storage.

The filters most used are the 0.6 X 0.6 X 0.3 m (2 X 2 X 1 ft) size having a volume of 0.1 m³ (4 ft³) with a weight averaging 19 kg (42 lbs) per filter. At the present time, the filters are compacted before being packaged. As currently practiced at some facilities, this involves pressing in the sides to a diamond configuration, binding with wire, bagging, and packaging for shipment. Actual shipping volume is not decreased to a large extent because of all the void space in the crate. Procedure with the more contaminated filters varies from the above. The filter media is cut from the wooden frame with a saber saw, the wood frame sectioned with a saw, and the components drummed for shipment.

Both methods effect a volume reduction of the filter, but involve considerable labor and time. The combustible wooden frames will not be acceptable for permanent storage. Filter media that has been exposed to volatiles and nitric acid fumes, or a mixture of the exposed media in a shipping container, could cause pressurization of storage drums. Although incineration of the HEPA's would not materially affect the asbestos filter material and fiberglass filter media, it would destroy the wooden frames and contained volatiles. Incineration of filters appears to be a viable method of processing.

Used filters were obtained that had been used in filter plenums for non-radioactive processes. Filters were crushed to a size that would fit through the glove-box entry and were brought into the sorting box. There they were torn apart and fed into the shredder-classifier system. The air-classifier throat adjustment functioned well; the shredded frame

wood was carried over to the second shredder while framing nails freed by the shredder dropped out of the air stream.

The material delivered to the feed screw was a well mixed blend of shredded wood and filter media. Trouble was experienced at this point. The tapered feed screw is constructed to have a 5:1 compression ratio so that a gas seal is formed by the waste at the entrance to the primary bed. This operates effectively with shredded general waste, but the shredded filter material was nearly incompressible. The feed screw could not take the strain of long-time operation; the run was terminated after a throughput of 89 kg of filters.

Near the conclusion of the run, a test was performed to find a compression ratio that would be usable with the filter material. Expanded styrene pellets were mixed with the filter material in the feed hopper, and the mixture was fed into the incinerator. A mixture of one part filters to two parts expanded pellets was handled easily by the feed screw. A feed screw with a compression ratio of 2.5:1 should take 100% shredded filters; the possibility of fabricating a screw that would fit the present screw barrel is being considered.

Table 1 gives the number and size of filters that are shredded and fed into the incinerator. Most of the waste filters generated in a nuclear fuel plant would be the 0.6- X 0.6- X 0.3-m size used as exhaust plenum filters; the smaller size filters are inlets and exhaust filters on glove boxes. The weight percent of frame and media was determined by sawing the media out and weighing the two portions from representative filters.

Binding of the feed screw prevented the attaining of a steady-state operation in the FBI. Preliminary data indicated, however, that the wooden filter frames had enough heat content to make it unnecessary to add supplemental fuel. With the media being non-combustible, large amounts of residue were collected. These residue were weighed and sampled for analysis. Reduction, by incineration, was approximately 4.4 to 1 in volume and 2 to 1 by weight. The residue was a low-density material with a loose-bulk density of 0.26 and a 0.49 tap density. Composition of the ash, given in

TABLE 1. High Efficiency Particulate Air (HEPA) Filters Burned

Size (m)	No.	Weight (kg)		Total
		Frame	Media	
0.6 x 0.6 x 0.3 (2 x 2 x 1 ft)	4	46.8	29.6	76.4
0.2 x 0.2 x 0.15 (8 x 8 x 6 in.)	8	12.8	4.0	16.8
				93.2
		Removed from Feed Box		4.5
		TOTAL BURNED		88.7

TABLE 2. Composition of High Efficiency Particulate Air (HEPA) Filter Ash

Component	Quantity (%)
Silica	37.2
Alumina	5.5
Catalyst	11.4
Carbon	6.5
Sodium Sulfate	1.2
Sodium Phosphate	4.6
Magnesia	30.8
Iron Oxide	1.6
Calcium	1.2

Table 2, is a good mixture for the vitrification process. The sodium phosphate present is from the fire-retardant added to the pressed wood frames.

Liquid Waste

The major combustible-liquid-waste stream from a commercial fuel-reprocessing facility is projected to be a tributyl phosphate (TBP)-solvent mixture. This material is the extractant used in the PUREX process. The high radioactivity of some processed material causes partial decomposition of the TBP and changes its extractant properties. A facility with a capacity of 750 metric tonne per year of reprocessed fuel will generate approximately

5.7 m³ (200 ft³) of waste TBP-solvent mixture. The solvent used is a high-purity aliphatic hydrocarbon having a molecular range similar to kerosene; it has an extremely low aromatic and olefin content.

Incineration by conventional methods would perhaps be adequate for the solvent, but would produce large amounts of phosphorous pentoxide (P₂O₅) from the TBP thermally decomposing. The P₂O₅ sublimates and condenses out in the cooler portions of the exhaust system. The anhydrous material is a flammable solid that readily absorbs moisture and forms phosphoric acid, which is corrosive to ferrous metals and alloys. A method for safely trapping the P₂O₅ is necessary for a workable incineration system. Burning the TBP-solvent in a fluidized bed of sodium carbonate appeared to offer a way of reacting the phosphate portion to form thermally stable sodium phosphate.

Laboratory Scale Fluidized Bed Incinerator Tests

A quartz laboratory-scale fluidized-bed incinerator has been reassembled in a recently acquired development area. It is now available for test burning new materials before large scale runs are made on the pilot plant equipment. This allows small batches of test materials to be burned under easily controlled conditions, and the quartz equipment affords visual observance of the incineration process. A sketch of the 115-mm-diameter unit is shown in Figure 2. Configuration of the unit can be changed to allow various test conditions to be obtained.

A solution of approximately 10% TBP in solvent was prepared and injected into the bed with a diaphragm metering pump fed from a calibrated reservoir. The primary bed was either a chromic oxide-alumina catalyst or a mixed bed of sodium carbonate (Na₂CO₃) and the catalyst. A second fluidized bed of oxidation catalyst served as the afterburner for final gas cleanup. The proposed reaction with Na₂CO₃, shown below, would form the thermally stable sodium phosphate (Na₃PO₄).

FIGURE 2. Laboratory Scale (115-mm Diameter) Fluidized Bed Incineration System

The in situ reaction ties up the phosphorous and prevents the formation of P_2O_5 with its consequential problems.

Tributyl Phosphate-Solvent Incineration In Catalyst Bed

The first two runs were made using a primary bed of catalyst only; no sodium carbonate was added. The objectives were to (1) determine the phosphorous deposition as would occur in a conventional type of incinerator, (2) establish a comparison base for later runs with a mixed sodium carbonate-catalyst bed, and (3) determine if TBP-solvent incineration would present any new type of problem.

Solutions of 10% TBP in solvent were pumped into the base of the primary bed at a rate of about

0.3 l/hr. The solution, as would be expected, had enough heat content that no additional fuel was needed. A countercurrent packed-bed scrubber with recirculated water served as final cleanup before incinerator off-gas was discharged. At the conclusions of each run, samples of the primary bed, cyclone residue, and scrubber solution were submitted for analysis. Table 3 gives the calculated amount of phosphate added in the TBP-solvent mixture that was fed into the primary. Table 3 also shows the amounts of phosphorous, as phosphate, recovered from specified locations. Recovered phosphate is calculated from analytical results.

The first objective of the run was determined. Conventional incineration gives a random depositing of phosphorous compounds in different parts of the incineration system, and a water scrubber

TABLE 3. Phosphate Recovery From Catalyst Bed Incineration

	Run 1 (g)	Run 2 (g)	Average (g)	Average (%)
Added PO ₄ from TBP	84	119	101.5	
Recovered P as PO ₄				
Primary	0.42	2.42	1.42	1.40
Cyclone	0.02	0.32	0.17	0.17
Scrubber	0.89	0.38	0.64	0.63
				2.20

TABLE 4. Phosphate Recovery From Sodium Carbonate-Catalyst Bed Incineration

	Run 1 (g)	Run 2 (g)	Average (g)	Average (%)
Added PO ₄ from TBP	195.4	166.8	181.1	
Recovered P as PO ₄				
Primary	176.6	181.6	179.1	98.9
Cyclone	12.4	2.0	7.2	4.0
Scrubber	0.5	0.2	0.4	0.2
				103.1

is ineffective as a trapping method. The second objective, establishment of a base, was accomplished. Incineration behavior of a TBP-solvent mixture in an FBI was similar to incineration of the solvent alone. A large amount of black smoke and soot, similar to that from butyl rubber, has been reported to be produced during conventional incineration. This was not noted in the FBI runs, probably because of the intimate contact of catalyst, air, and solution producing total combustion. All three objectives of the runs were considered to have been met.

Tributyl Phosphate-Solvent Incineration In Sodium Carbonate Bed

Two more runs were made in a bed of 1:1 mixture of sodium carbonate and catalyst. The same conditions were used as in the previous two runs. In these runs, the major objective was to determine

the efficiency of phosphorous retention by reaction with the sodium carbonate bed material. Table 4 gives the results as calculated from analytical samples on the two runs.

The results indicate that phosphate is retained in the bed by reaction with the sodium carbonate bed material. Samples were submitted for scanning electron microscope and X-ray analyses in an attempt to positively identify the exact sodium-phosphate compound formed, but results have been inconclusive. More work is planned in this area as samples are collected.

Successful results from the laboratory scale incineration indicated that a pilot plant run could be made on a larger scale. The pilot run will be made with the solvent type presently in use at SRP, Texaco P-4. A mixture of 15% TBP (by weight) in Texaco P-4 has been prepared and will be used in a continuous run.

Residue Fixation

Feed and Product Composition

A residue fixation process is being developed for conversion of various types of radioactive waste, generated at a commercial nuclear-fuel reprocessing plant, into a form suitable for transportation and storage. A typical 750-metric-tonne-per-year plant, such as Nuclear Fuel Service, Inc., generates low and intermediate level (ILW) radioactive combustible waste in five general categories:

1. Low-specific-activity processing waste.
2. Alpha-contaminated processing waste.
3. Degraded tributyl phosphate (TBP)-solvent mixture.
4. HEPA filters.
5. Organic ion-exchange resin.

These combustibles can be burned in a fluidized bed incinerator, and the residues can be combined with other ILW material plus additives for processing into an immobile glass product. Other ILW amenable to vitrification are diatomite filter aid

and mineral resins, which provide the bulk of the silica (SiO_2). Boric acid (H_3BO_4) and sodium carbonate (Na_2CO_3) are the additives that serve as glass fluxes.

Feed material used in the residue-fixation process development program will simulate waste materials generated in commercial nuclear fuel plants. The simulated feed will be prepared from chemical compounds and DOE transuranic (TRU) wastes generated at the Rocky Flats Plant. General processing wastes (LSA) and non-radioactive contaminated HEPA filters from exhaust plenums will be burned in the pilot plant FBI. The other FBI ash residues are obtained by incineration of non-radioactive TBP-solvent mixtures and organic ion exchange resins. Non-contaminated diatomite filter aid, mineral resin, sodium carbonate, and boric acid will be used to complete the mixture of materials for process feed.

The chemical composition of simulated waste streams to be used in the residue fixation program is tabulated in Table 5. The feed blend and overall composition entering the melt reactor are shown in Table 6. Organic resin ash presently is not included in the feed. When test burns are completed in the FBI, this residue will be included. It is expected that no gross amounts of additional chemical compounds will be present in resin ash; therefore, no significant change in the overall feed composition is expected.

Initial assessment of the feed streams and material balance calculations indicates that the feed streams are converted to 74.5 wt % glass and 25.5 wt % off-gas. The final glass product contains 67.1 wt % contaminated waste material and 32.9 wt % additives, which are in the form of boron oxide (B_2O_3) and sodium oxide (Na_2O). The calculated chemical compositions of the glass and off-gas products are shown in Table 6.

Glass has been produced in the Rocky Flats laboratory according to the feed blend shown in Table 6. The molten glass is tested to have a pour viscosity of approximately 30 to 300 poises at the melting temperature of 1000 °C. The expected benefits of operating the melt reactor at the relatively low temperature of 1000 °C are (1)

greater selection of material for construction of the reactor and (2) an increase of the reactor's operating life.

Melting Reactions

The literature indicates that an optical type glass containing up to 5% NaCl can be produced at a 1000 °C operating temperature.³ To contain NaCl in the glass melt, the reaction involving water vapor and NaCl at the melting temperature must be considered. This reaction

is used to produce salt-glazed sewer pipes and building tiles in the heavy clay product industry.⁴ To glaze the clay products, NaCl is fed into the natural-gas burner port at the end of the firing cycle where it is volatilized as Na^+ and Cl^- ions. In the presence of water vapor (from combustion air) and SiO_2 (contained in the feed), sodium oxide (Na_2O) is formed to produce a glassy glaze on the surface of the clay product, and gaseous hydrogen chloride (HCl) is discharged from the kiln stack. To prevent this reaction from occurring, no water should be present during the melting operation. Melting sodium sulfate (Na_2SO_4) produces sulfur in the form of sodium sulfide (Na_2S). It is desirable to contain this sulfur in the waste glass composition rather than to provide a scrubbing system for sulfur dioxide (SO_2) or sulfur trioxide (SO_3). When excess carbon is present in the glass batch, Na_2SO_4 is reduced to Na_2S , which is contained in the glass.⁵ This reaction is used to produce amber colored bottle and window glass, which requires melting temperatures as high as 1300 °C. Calculations indicate that sufficient carbon is present in the FBI ash composition to reduce Na_2SO_4 to Na_2S .

Fixation Equipment

The fixation process will require the following major equipment items: (1) melt reactor feeder, (2) melt reactor, (3) glass former, (4) glass annealer, and (5) off-gas scrubber. Additionally, a dryer for the feed or possibly a calciner that would also

TABLE 5. Chemical Composition of Simulated Waste Streams

Chemical Compound	Weight (%)				
	Alpha Waste Ash	TBP Ash	HEPA Filter Ash	Diatomite Filter Aid	Mineral Ion Exchange Resin
NaCl	5.0				
Na ₂ CO ₃	30.0				
Cr ₂ O ₃	10.0	3.0	2.5		
Al ₂ O ₃	35.0	10.4	14.4	2.4	24.9
SiO ₂	10.0		37.2	87.2	58.5
Na ₂ SO ₄	5.0		1.2		
C	5.0	0.5	6.5		
Na ₃ PO ₄		86.1	4.6		
MgO			30.8		
Fe ₂ O ₃			1.6	1.4	
CaO			1.2	0.5	13.7
Na ₂ O				3.6	
H ₂ O				4.9	2.9
	100.0	100.0	100.0	100.0	100.0

TABLE 6. Waste Blend, Feed and Product Composition of the Vitrification Process

Waste Blend Composition (wt %)		Feed Composition (wt %) (Including Additives)		Product Composition (wt %)	
FBI ASH		NaCl	1.5	Glass	74.5
Alpha Ash	51.8	Cr ₂ O ₃	3.2	NaCl	2.0
TBP Ash	1.8	Al ₂ O ₃	13.7	Cr ₂ O ₃	4.2
HEPA Ash	10.9	SiO ₂	20.6	Al ₂ O ₃	18.4
Organic Resin Ash (future)		Fe ₂ O ₃	0.3	SiO ₂	27.6
		CaO	1.3	Fe ₂ O ₃	0.4
ILW		Na ₂ O	0.4	CaO	1.7
Diatomite	20.8	MgO	1.9	Na ₂ O	19.4
Mineral Resin	14.7	H ₃ BO ₃	28.9	MgO	2.6
	100.0	Na ₂ CO ₃	22.8	B ₂ O ₃	21.9
		Na ₂ SO ₄	1.5	Na ₂ S	1.1
		Na ₃ PO ₄	1.2	P ₂ O ₅	0.7
		H ₂ O	0.8		100.0
		C	1.9		
			100.0	Off-Gas	25.5
				H ₂ O	45.0
				CO ₂	55.0
					100.0 100.0

remove water of hydration might be necessary. This will be established by the laboratory process evaluation now in progress.

Melt Reactor Feeder

A combination dryer and feeder was investigated for removing water from feed materials and transferring the feed to the melt reactor. Two dryer and feeder methods that use waste heat from the melter were evaluated. The simplest feeder was a stack-type feeder in which hot gases from the melter flowed countercurrently through a relatively static column of feed. The stack feeder also acted as a particulate filter and a volatile products condenser. In the other feeding device, feed materials were distributed uniformly to blanket the top of the molten glass. Heat from the melt dried the feed. Power or heat input controlled the feed (melt) rate for both feeding devices.

Two designs of stack feeding device were evaluated. The first design was a vertical 38-mm-diameter tube with one end immersed approximately 13 mm below the melt line of the glass. When filled with the feed blend, the hot off-gases flowed up through the tube and intimately contacted the feed material. This drying technique resulted in severe bridging of the material across the tube as a result of sintering. Material could be fed only by continuous probing with a ceramic rod.

The second stack-feeding device tested was a 38-mm-diameter metal tube that was vertical, filled with feed blend, and had the reactor feed end positioned 25 mm above the glass melt surface. A 45° conical shroud, attached 50 mm above the tube end, surrounded the melt and feed addition area directly below the feed tube. The lower end of the shroud, extending below the melt line, contained the hot off-gases until they entered the feed tube through 1.6-mm holes along the sides. The gases then passed up through the blended feed. This feeding apparatus also resulted in some bridging and required limited probing to produce a continuous feed flow. The test, however, indicated that if the tube is located in a controlled temperature region, the drying method probably would be feasible.

To determine what chemical and physical changes occurred in the feed stack at various temperatures, heating tests were conducted in a muffle furnace. Feed samples were held in the furnace for one-half hour at various temperatures between 300 and 900 °C. In the temperature range from 300 to 450 °C, the feed blend did not change in volume but did increase in hardness. This hardness probably is caused by the cementing action resulting from salt crystal growth. Sintering and volume reduction took place in samples heated in the 500 to 600 °C temperature region. Material at 600 °C formed a hard-packed sinter with approximately a 50% volume reduction. Samples removed from the furnace in the 650 to 700 °C temperature region formed a foam glass, which was caused by entrapped gases, and expanded to the original volume. In the 700 to 900 °C temperature zone, the gas escaped and a dense glass was formed. These tests indicate that the stack devices will operate at a maximum temperature of 500 °C for drying and feeding.

Introducing feed materials above the melt, like a blanket, is expected to result in sufficient drying to limit HCl losses. This feeding and drying method will be evaluated on melt reactors presently being fabricated.

Melt Reactor

Design for a Joule-heated refractory melt reactor has been completed, and fabrication is in progress. The reactor will be operated to develop design criteria for the melting, forming, and annealing portions of the pilot plant. It will be heated by two sets of Inconel 690* electrodes. One set of electrodes having a 20 kW-SCR system operates the reactor melting section. The other set, which has a 7 kW-SCR system, powers the fining section of the furnace. Power supplies to each set of electrodes are controlled individually; therefore, it is possible to control the temperatures in both the melting and fining sections of the furnace. The furnace, containing refractories, compression frame, and heat shield, will be 71 cm long, 52 cm wide, and 33 cm high.

*Registered trademark of International Nickel Company.

Joule melter start-up will be accomplished by the use of sacrificial coils of Kanthal* resistance elements, which will be connected in parallel with the melting electrodes.⁶ After the batch feed is melted into a glass, the electric current is conducted through the glass between the electrodes. The start-up wire coils eventually will be consumed within the melt. The melter is designed for continuous operation and can be adjusted to idling (no feeding or melting) while the forming equipment is not being operated.

An alternate-type melt reactor uses a resistance type furnace. The melt chamber also is being designed for low-temperature (1000 °C) melting operation. Resistance type furnaces consume less power because they can be more completely insulated and have shown a history of long operating times when the elements are properly protected from products of the melting reaction. Use of the resistance type furnace would provide a system in which a metal melt chamber could be easily changed out in a remote type operation without creating an additional amount of contaminated waste. In addition, because a complex insulation system can be used on the resistance melt reactor, it is expected that no cooling water will be required for the reactor operation.

The possibility of using a Pyroceram** lining for resistance melter is also being investigated. This type of glass-ceramic material is used to fabricate missile nose cones and oven cooking ware, which have excellent heat shock resistance. Through the use of proper heat treatment, the ceramic material can be conditioned to operate continuously at temperatures as high as 1050 °C.⁷ Tests will be conducted with heat-treated oven ware to determine the rate of chemical attack from the simulated waste glass.

Glass Former

Marble forming machines exist that will form solid spheres from a continuous stream of molten glass,⁸

glass rods, or globs of molten glass. The machine of most interest for use with nuclear waste is one that produces marbles from a stream of molten glass since this eliminates the necessity of using a glob cutting device. Marble-forming machines used by the glass industry would be mechanically complex to operate in a remote cell; therefore, other forming methods are being investigated.

Two types of cavity molds are being studied for forming pellets (solid right circular cylinders) from a continuous stream of melted glass. The first type is the wiping-type cavity mold that would slide into a stream of molten glass under the melt reactor orifice. The cooled, formed pellets in the mold are discharged downward by gravity. Tests indicate that this type of mold would have to be at 850 to 1000 °C so that the glass would have the proper viscosity to maintain a liquid seal between the sliding mold and the stationary reactor orifice. In addition, tests indicate that the formed pellets would have to be discharged from the mold at a temperature of less than 550 °C to avoid deforming them. Graphite molds used in the forming tests oxidized badly at temperatures in excess of 500 °C in an air atmosphere. Graphite molds could be used at the required temperature range, however, in an inert or reducing atmosphere. Black iron molds commonly used in the glass industry operate at maximum peak temperatures of 700 °C.⁹ Operating temperatures in excess of 700 °C cause an inter-face reaction between the metal and molten glass, which results in the forming of a porcelain enamel type bond. To prevent sticking, it may be possible to spray the mold cavity with a mixture of graphite and silicone oil-based lubricant prior to each filling.

A peak cavity mold, similar to an egg carton, also has been investigated. Using the peak mold, the peak portion of the mold should split the continuous stream of glass to fill the next cavity. This type of mold would again operate continuously; however, it would not be necessary to maintain a seal between the flow orifice and the mold. Tests indicate that molds must operate in a 850- to 1000 °C temperature range to prevent premature solidification of the glass on the inclined surface.

*Registered trademark of Kanthal Corporation, Amelia Place, Stamford, Connecticut.

**Registered trademark of Corning Glass Works, Corning, New York.

Free-form buttons can be produced by intermittently interrupting a stream of molten glass flowing onto a moving plate. The interruption can be caused by a glob cutter or a plug valve at the reactor discharge. This forming method currently is favored over other methods because it is mechanically simple to operate, does not require a high temperature mold, does not require a special atmosphere for the molds, and does not require the use of mold lubricants. The pellets can be removed from the moving plate by a stationary plow.

Glass Annealer

Annealing is necessary to remove stresses from glass that were developed during the forming operation. If not removed, the glass products will shatter upon cooling as a result of these internal stresses. Conventional annealing equipment is not desirable for remote operation because of the high maintenance requirements of mechanical conveyors operating in a high-temperature environment. Tests are underway to develop a simplified method with low-maintenance-type equipment for annealing operations.

The literature indicates that the length of annealing time required for glass objects is dependent upon the thickness and size of the article.¹⁰ At the proper annealing temperature, the glass must be soft enough so that the internal stresses are removed, yet rigid enough so that the glass does not deform during the annealing period.

The glass produced from simulated waste materials is expected to exhibit a viscosity of approximately 10^{14} poise at 530 °C during the annealing operation. Tests conducted by re-treating previously formed waste glass pellets showed the pellets are rigid at 550 °C, can be dented by pressure at 575 °C, and deform under their own weight at 600 °C.

Pellets from 12.7 to 50.8 mm in diameter have been cast to determine the approximate required annealing times. The 12.7-mm-diameter pellets produced by pouring glass melt into a preheated graphite mold and held at 530 °C for approximately 15 minutes could be removed intact and relatively strain free. Pellets 50.8 mm in diameter by 50.8 mm

high must be annealed between 8 and 16 hours before they can be removed intact.

The conventional annealing operation requires the formed glass pellets to be belt-conveyed through a temperature-controlled oven; this is not desirable for remote operation and maintenance. The first annealing concept tested here involves a 19-mm-diameter tube, shaped in a helical coil, that accepts and discharges the pellets one at a time. The second method tested used a 75-mm-diameter vertical tube that intermittently releases several pellets at one time. While both of the above concepts appear feasible, work will be directed toward development of a system to provide annealing on the plate used for free-forming the glass buttons.

Helium Diffusion Studies

Glass pellets produced from nuclear waste will contain low amounts of non-recoverable plutonium; helium will be generated during alpha decay of this contained plutonium. Helium gas will be diffused out to the atmosphere because of the driving force of the helium concentration gradient between the solid and gas phases and the helium concentration gradients along the radii of the pellet. By a material balance of an infinitesimal volume increment of a sphere, a partial differential equation for helium generation and diffusion in the solid phase can be written as

$$\frac{\delta C_s}{\delta t} = \frac{1}{r^2} \frac{\delta}{\delta r} \left(r^2 D \frac{\delta C_s}{\delta r} \right) + H_0 e^{-\lambda t} \quad (1)$$

Similarly, for the gas film phase—

$$-D \frac{\delta C_f}{\delta r} = k_c (C_f - C_0) \quad (2)$$

The initial and boundary conditions for these equations are

$$\begin{aligned} C_s &= 0 & \text{when } t &= 0 \\ C_f &= 0 & \text{when } t &= 0 \\ C_f &= C_s & \text{at } r &= a \\ \frac{\delta C_s}{\delta r} &= 0 & \text{at } r &= 0 \end{aligned}$$

where H_0 = helium generation rate at
 $t = \text{time} = 0$, mole/cm³ · yr⁻¹

C_s = concentration of helium in solid,
 mole/cm³

C_f = concentration of helium in gas film,
 mole/cm³

C_0 = concentration of helium in air,
 mole/cm³

k_c = mass transfer coefficient of helium
 in gas film, cm/yr

λ = plutonium decay constant
 $= 2.841 \times 10^{-5} \text{ yr}^{-1}$

D = diffusivity, cm²/yr

a = radius of the sphere, cm

r = variable radius, cm

Certain assumptions are made for the above equations in solving helium gas generation and diffusion. These assumptions are as follows:

1. The initial plutonium concentration is distributed uniformly in the glass sphere, and helium generation is uniform in the glass (independent of radius position).
2. At initial time, helium concentrations in glass and in gas film are zero.
3. The helium concentration in air is assumed to be zero at any time.
4. The change of helium concentration with respect to radius at center and at any time is zero.
5. At solid-gas film interphase (glass surface), the helium concentration in solid equals the helium concentrations in gas film.

Once the concentration profile was obtained by solving the above equations, the total moles of helium diffused at time t years was calculated as

$$Q_t = \int_0^t DA_s \left(\frac{\delta C_s}{\delta r} \right)_{r=a} dt$$

where Q_t = total helium diffused at time t years,
 moles

A_s = surface area of the sphere, cm²

The net helium gas remaining in glass spheres is the difference between the helium generated and the helium diffused out through the sphere. Comparing Q_t with the solubility of helium gas in glass at the pressure of the yielding strength, the time when the glass pellets will fracture can be found.

A computer program was developed to solve Equations 1 and 2 by numerical methods. Input data were plutonium concentration (Ci/g glass), diffusivity (cm²/yr), radius (cm), and final storage time (years).

Helium diffusion in glass pellets was calculated for initial concentrations of 0.3 to 3% plutonium oxide (PuO₂), and pellet radii of 0.5 and 1.27 cm. Calculations were based on the diffusivity of 2.5×10^{-14} cm²/s for helium diffusion in borosilicate glass¹¹ and the helium solubility $-s = 1.5 \times 10^{-16}$ atoms per cubic centimetre at 400 °C and 730 mm Hg.¹¹ This value is equivalent to $s = 3.7 \times 10^{-2}$ cm³/cm³ glass at 25 °C and a glass-yielding strength of 16.5 MPa (2400 psi). Figure 3 shows the helium gas remaining in glass versus storage time for an initial concentration of 3 wt % PuO₂ and pellets radii of 0.5 and 1.27 cm. The helium gas concentration in glass pellets will exceed the solubility value of 3.7×10^{-2} cm³/cm³ in about 235 years. Figure 4 shows the helium gas remaining in glass versus storage time for an initial concentration of 0.6 wt % PuO₂ and pellet radii of 0.5 and 1.27 cm. The helium gas in those pellets will exceed the solubility in about 1220 years and 1230 years for pellet radii of 1.27 and 0.5 cm respectively. Results show that the initial plutonium concentration affects significantly the length of storage before the pellets could fracture. Figure 5 indicates that the helium gas in pellets of 0.3 wt % PuO₂ pellets will exceed the solubility at about 2420 years and 2460 years for pellet radii of 1.27 and 0.5 cm respectively.

The waste generated at a commercial fuel reprocessing plant as ash and ILW is expected to be converted to a glass containing only 0.3 wt % PuO₂ as an average value. Helium gas concentration in glass is the net difference of helium generation and helium diffusion. Helium generation is independent of radius, and helium diffusion is dependent on radius. The calculated helium concentration in the glass

FIGURE 3. Helium Gas in Glass Pellets Versus Storage Time for Initial Plutonium Concentration of Three Weight Percent Plutonium Oxide

indicates that the helium generated is much greater than the helium diffused; thus, the pellet diameter does not affect significantly the glass breakage time.

The value of the diffusivity of helium gas in glass may vary with the composition and the structure of the glass. At present, there is no measured value for the specific glass pellets. This diffusivity, from literature, may vary from the order of 10^{-14} cm²/s to the order of 10^{-8} cm²/s for borosilicate glasses. For conservative purposes, the lowest value was selected. In other words, if the actual

diffusivity is higher than that used in the calculation, the storage periods before fracturing will be longer than the calculated values.

It is assumed that fracturing occurs when helium gas remaining in glass exceeds the solubility at its yielding strength. This is based on the model in which there are no voids in the glass. If there are small bubbles in the glass pellets, these bubbles will hold more helium gas and could result in a longer period without fracturing.

FIGURE 4. Helium Gas in Glass Pellets Versus Storage Time for Initial Plutonium Concentration of 0.6 Weight Percent Plutonium Oxide

FIGURE 5. Helium Gas in Glass Pellets Versus Storage Time for Initial Plutonium Concentration of 0.3 Weight Percent Plutonium Oxide

To minimize the possibility of fracturing during long-term storage, improvements on increasing helium diffusion and tensile strength of the glass will be considered. For instance, a change in the amount of Na_2O and silicate in glass will affect the magnitude of diffusivity, and a temperature-controlled tempering will increase the tensile strength. Other improvements will be investigated.

CONCLUSIONS

The fluidized bed incinerator can effectively burn combustible waste of the types expected from a nuclear fuel reprocessing facility. Ash from incineration, plus other waste streams, is convertible to a good quality glass. From work thus far, the following conclusions can be drawn:

- A separation system is necessary for removal of the relatively large amount (8.5 wt %) of tramp metal found in general production combustible waste.
- The second generation air classifier now installed operates effectively for all waste types tested.
- Incineration of HEPA filters, at least the wooden frame portion, appears to be a viable method of weight and volume reduction. A volume reduction of 4.4 to 1 and a weight reduction of 2 to 1 was attained.
- HEPA filter (frame plus media) ash is an ideal feed for a vitrification process both as to composition and form.
- Incineration of the TBP-solvent mixture, the major combustible liquid waste stream generated at a nuclear fuel reprocessing plant, was effective in tying up the phosphate in a sodium carbonate fluidized bed.
- A survey of waste streams expected from a reprocessing plant was completed; a glass product was prepared in the laboratory that contained 67% simulated reprocessing plant wastes and 33% additives.
- Both Joule-heated and resistance-heated types of melt reactor should be tested.
- The most promising glass-forming method is a glob cutter, or plug valve, at the melt reactor outlet that drops molten glass onto a flat plate.
- At the probable average plutonium content of 0.3 wt %, computer modeling calculated a product integrity of over 2,000 years.

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