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Spray Solidification of Nuclear Waste

by
**W. F. Bonner
H. T. Blair
L. S. Romero**

August 1976

**Prepared for the Energy Research
and Development Administration
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Battelle
Pacific Northwest Laboratories

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INTRODUCTION

It is advantageous to solidify liquid radioactive waste from the reprocessing of nuclear fuels to reduce the potential dispersibility of toxic radionuclides in the waste. Current Federal regulations require solidification of high-level liquid waste to a stable form within 5 years of reprocessing and shipment to a Federal Repository within 10 years. Similar regulations are expected soon for some other wastes from commercial fuel reprocessing. Due to the cost of high-level liquid waste storage tanks and the backlog of fuel to be reprocessed, it is preferable to solidify waste as it is generated. Commercial fuel reprocessing is not currently under way in the United States. But startup of one or more plants is expected near the end of the decade. Waste solidification facilities are therefore needed soon.

Solidification of radioactive wastes poses special problems and requires unusual considerations due to the radiological, chemical, and physical properties of the waste. Since the regulation does not specify the solidified waste form, the product from many solidification processes may be applicable. Throughout the world, most high-level waste solidification processes ultimately incorporate the toxic waste constituents into a highly nondispersible borosilicate glass. Processes being developed for this purpose include: in England, in-canister drying and melting of waste; France, rotary kiln calciner and continuous metallic or ceramic melter; Germany, spray and rotary dryers plus continuous metallic melters; United States, spray and fluidized bed calciners plus in-can and ceramic melters.

An extensive U.S. ERDA research and development program is currently under way at Battelle's Pacific Northwest Laboratory (PNL) to provide industry with solidification systems for converting high-level waste to nondispersible forms. This effort, termed the Waste Fixation Program (WFP), is concentrating on equipment and waste form development and demonstration. Large-scale development of selected near-term vitrification processes is currently being emphasized. After extensive evaluation of the available solidification processes, Battelle personnel held discussions with anticipated United States nuclear fuel reprocessors. The spray calciner and in-can melter

process was selected as the system most ready for accelerated development. This process is currently being designed for near-term vitrification of commercial fuel reprocessing waste. This report includes much of the data available on the heated-wall spray calcination part of this vitrification process.

CONCLUSIONS

The many positive features of the spray calcination process have led to its selection for continued development and full-scale design and demonstration.

The spray calciner is a relatively simple machine. Its components are few and uncomplicated; thus maintenance is minimal, and the equipment lends itself well to remote use. Operation is simple and is easily automated to minimize the need for operator attention. Startup and shutdown can be performed in less than an hour without producing additional waste.

Spray calcination is versatile in that a wide variety of waste compositions and concentrations can be calcined under easily maintainable conditions. Spray calcination of all known currently projected U.S. commercial nuclear fuel reprocessor high-level liquid wastes (HLLW) and mixed high- and intermediate-level liquid wastes (ILLW) has been demonstrated. Feedstock modification by additives is not required. Waste concentrations of from near infinite dilution to less than 225 liters (60 gal) per tonne of fuel are calcinable with equal ease without changes in operating conditions. Wastes have been calcined containing over 2M sodium. Thus waste generated during plant startup and shutdown can be blended with normal waste and calcined. At flowrates up to the calciner's capacity, feed concentration, composition, and/or flowrate can normally change rapidly by over a factor of two without requiring operator action.

Wastes containing mainly sodium cations can be spray calcined by addition of finely divided silica to the feedstock. The amount of silica added corresponds to that required for vitrification of the calcine; thus the vitrified product volume is not increased by the calciner feedstock modification.

A remotely replaceable atomizing nozzle has been developed for use in plant-scale equipment. The 6-mm (0.25-in.) orifice and ceramic tip offer freedom from plugging and erosion. The nozzle is expected to operate well for several months without replacement.

Calciner capacity of over 75 ℓ /hr (20 gal/hr) has been demonstrated in pilot-scale equipment. This is roughly the capacity required to calcine the high-level and intermediate-level liquid waste from a 5 tonne/day nuclear fuel reprocessing plant if the waste is concentrated to 378 liters (100 gal) per tonne of fuel prior to calcination. Scaleup calculations indicate that much higher flowrates are attainable with larger scale equipment.

Sintered stainless steel filters are effective in deentraining over 99.9% of the solids that result from calcining the feedstock. These filters have proved sufficiently rugged, easily cleaned, and otherwise reliable for long-term operation of the spray calciner.

Since such a small amount of radionuclides escapes the calciner, the volume of recycle required from the effluent treatment system is very small. The noncondensable off-gas volume is also low, less than 0.4 m^3/min (15 scfm) for a liquid feedrate of 75 ℓ /hr (20 gal/hr).

Vibrator action maintains the calcine holdup in the calciner at less than 1 kg; thus the liquid feedrate relates directly to calcine flowrate. Safety problems associated with holdup of calcine are avoided. The calcine produced is very fine and reactive, enhancing a post-treatment step such as vitrification.

Successful remote operation and maintenance of a heated-wall spray calciner have been demonstrated while processing actual high-level waste. During these operations radionuclide volatilization from the calciner was shown to be acceptably low.

A major barrier to industry adoption of the heated-wall spray calciner is the lack of long-term operating data with a large-scale unit. Such testing and demonstrations should be carried out.

Furthermore, operation and maintenance of a plant-scale spray calciner and related equipment by remote means should be demonstrated. Operation of plant-scale equipment in an actual plant operating configuration is needed to assist detailed design preparations and to avoid potential plant startup problems.

BACKGROUND

In conventional spray drying, a secondary stream of heated gas conveys the necessary heat to the droplets being dried. Since the large amount of secondary gas required necessitates additional decontamination of effluents, in the late 1940s Allen⁽¹⁾ proposed heating the dryer walls to supply the needed heat. This process was developed to convert uranyl nitrate to an oxide form at the Oak Ridge Diffusion Plant. Extensive development of a similar process was conducted by Gauvin⁽²⁾ in the mid 1950s. His work focused on pyrolysis of industrial wastes at the Pulp and Paper Research Institute of Canada.

These experiences led Allemann⁽³⁾ to apply the heated-wall spray calcination technique to calcining radioactive wastes at Hanford in 1959. In his nonradioactive laboratory-scale tests, numerous variables were studied. They included feed composition, feedrate, operating temperature, and use of feedstock additives such as phosphate, sugar and borate. The effects of these variables on powder product properties, denitration, and wall scaling were established. Allemann concluded that spray calcination is adaptable to a wide variety of compositions and is an easily controlled process.

The spray solidifier was tested extensively in a nonradioactive pilot plant and in design verification tests^(4,5) before the Waste Solidification Engineering Prototype (WSEP) runs were started using radioactive waste. In the cold pilot plant studies, over 6000 liters (1,600 gal) of simulated waste were calcined in about 440 run hours. The WSEP program was designed to yield information needed for technical, economic, and safety evaluations of the spray calciner. About 8,600 liters (2,300 gal) of high-level aqueous radioactive waste containing 25 million curies were successfully solidified in 13 demonstration runs over a 3-year period with a total run time of about 580 hr.⁽⁶⁾ In the WSEP program, remote operation and maintenance of the calciner, feed system, and effluent treatment system were demonstrated with use of an overhead crane and master-slave manipulators.

The current Waste Fixation Program (WFP) began at Battelle, Pacific Northwest Laboratory in 1972. As part of the program, the heated-wall spray calciner is currently being prepared for full-scale remote operation in connection with a full-scale in-can melter as a total waste solidification system. This is a final step in preparation for inclusion in a commercial fuel reprocessing plant. Recent development has resolved questions concerning atomizing nozzle wear and blockage, interior wall scale accumulation, and spray calcination capacity. To date over 800 hr have been logged processing simulated high- and intermediate-level wastes in the WFP. This amounts to a total of over 1,800 operating hours in both radioactive remote maintenance hot cells and nonradioactive contact maintenance area.

CALCINER CHARACTERISTICS

OPERATION

During spray calciner operation, liquid waste is metered and pumped to the spray calciner at a pressure of 1 to 2 atm. The waste is pneumatically atomized in an internal mix nozzle and sprayed into the top center of a cylindrical calcination chamber as shown in Figure 1. The atomized liquid waste in the form of 70- μm diam droplets is sequentially evaporated, dried, and calcined as it plummets through the calcination chamber.

FIGURE 1. Spray Calciner

The chamber walls are heated to about 700°C by an external multizone resistance furnace. Inside the chamber sufficient heat is transferred to the droplets by a combination of radiation and convection to produce calcine containing typically less than 0.5% moisture. Drying of the tiny droplets occurs in a fraction of a second, thus minimizing volatilization of radio-nuclides and other effects of waste composition. Depositions on heat transfer surfaces within the calciner are prevented by the periodic operation of side-mounted vibrators.

On passing through the chamber, water vapor and atomizing air entrain 15 to 50% of the calcine particles, and more than 99.9% of the particulates are deentrained by porous stainless steel filters. The powder collected on the filters is periodically removed by a pulse of blowback air. After this it falls into the lower calciner cone and is discharged along with the calcine that falls directly from the calcination chamber. The essential calciner features are detailed later in the report.

ADAPTABILITY TO WASTE VARIATIONS

As long as the waste is pumpable, waste concentration has little impact on calciner operation. No difference in calciner characteristics was noted when operating with waste concentrations of from 200 to over 650 liters (60 to 170 gal) of waste per tonne of fuel. There is no reason to believe that further concentration or dilution would cause calcination difficulties. Furthermore, experience has shown that waste concentration and/or composition may change drastically during operation without requiring operator attention.

The spray calciner is insensitive to waste composition. Over the 12 years of development it has calcined many simulated and radioactive compositions. Most work has been with Purex wastes, notably that from the first extraction column. However, many other wastes have been successfully calcined. Most recently emphasis has been on high- and intermediate-level liquid wastes from commercial fuel reprocessing. Wastes ranging from nearly pure fission product nitrates such as anticipated from General Electric's Midwest Fuel Reprocessing Plant to compositions containing over 2M sodium

have been successfully calcined without requiring feedstock modifications. High-level, intermediate-level, and combined high- and intermediate-level waste compositions anticipated from the Allied General Nuclear Services (AGNS), General Electric (GE), and Nuclear Fuel Services (NFS) fuel reprocessing plants have been calcined successfully.

By addition of finely divided silica to the feedstock, wastes containing virtually all sodium cations can be calcined. Many wastes contain a high sodium content. Most ILLW, HLLW produced during reprocessing plant startup and shutdown, and the existing ERDA defense waste are very similar to the composition tested and are anticipated to calcine similarly. The SiO_2 added is that required for conversion of the waste to a silicate glass. Thus if a vitrified form is to be eventually produced, no increase in solidified waste volume is realized. In fact, addition of all the glass-forming chemicals to the feedstock in this manner would simplify the vitrification process and assure more accurate glass compositions.

Many of the waste compositions tested are listed below. Additional details are shown in Appendix B. The reference wastes are based on LWR reactor fuel enriched with ^{235}U . Actinide and fission product concentration are based on the ORIGEN computer code for fuel with a 33,000 MWd/tonne burnup at a power level of 3000 MW. The WFP reference wastes are concentrated to 378 g/tonne. During the WFP all waste compositions tested were compatible with spray calciner operation.

"Clean" HLLW

The waste composition designated PW-4b is a GE type waste from a plant wherein no chemical salts are added during reprocessing. The waste is almost totally fission product salts with some corrosion products. Uranium and plutonium loss to the waste is 0.1%.

"Dirty" HLLW

The dirty waste, designated PW-6, was based on an early planned waste from Allied General Nuclear Services (AGNS), Barnwell Nuclear Fuel Reprocessing Plant. It represents a waste which is moderately high in salts, notably 2M sodium. This composition may be representative of the waste after addition of ILLW to other waste. Uranium and plutonium loss is 0.5%.

AGNS Wastes

The currently projected AGNS HLLW has been designated PW-7. It is a moderately clean waste containing 0.1M iron and phosphate. It also contains 0.15M gadolinium, added during processing as a soluble poison for criticality control. Loss to the waste of 1% of the uranium and plutonium present in the fuel is assumed.

The anticipated ILLW consists mainly of solvent wash wastes and decontamination wastes. However, waste from many other sources such as liquid samples, scrubber solutions and ion exchange regeneration solutions will be included. This waste is mainly sodium, phosphate, and uranium.

Due to currently proposed Federal regulations requiring similar treatment and storage of high- and intermediate-level waste, plans are formulated for combining the two streams before calcination. The AGNS combined waste, termed PW-7a, contains 0.6M sodium at the reference concentration.

NFS Future Wastes

The current flowsheet at Nuclear Fuel Services (NFS) West Valley, New York, Fuel Reprocessing Plant calls for use of sacrificial steel dissolver baskets. Iron from the baskets contributes most of the 1.3M iron in the NFS HLLW labeled PW-8. The waste is moderately high in salts, as shown in Appendix B.

Proposed minor modifications in the NFS process flow sheet can result in decreased iron in the waste. Plans are also being considered for addition of sodium-containing wastes which will raise the sodium concentration to about 1.2M and reduce the iron content to about 0.9M. This waste is called PW-8a.

Waste produced during plant startup and shutdown will be low in fission products and actinides but high in salts, notably sodium. During a prolonged startup period, storage tankage may not be sufficient, requiring that these wastes be solidified without blending. Such wastes could contain over 90% sodium cations.

Pre-WFP Wastes

A large variety of waste compositions processed in the spray calciner prior to the current WFP have not been retested using the improved equipment. Based on current experience, however, similar or improved calciner performance is assured with the newer equipment. Appendix C is a table summarizing these compositions. Most of the compositions were wastes from the Purex flowsheet, but wastes such as ferric nitrate solutions simulating Darex type wastes were tested as well as two compositions simulating the caustic neutralized high aluminum waste from the Redox process.

Purex wastes were studied in greater detail. A variety of acid killed, neutralized, and acidic wastes were tested with and without fission products. Neutralized waste containing up to 6M sodium was calcined, and feed additions of reducing agents such as sugar were found successful in decomposing low-melting sodium nitrate. A summary of experience with these wastes is given by Allemann⁽³⁾ and by Kaser.⁽⁷⁾

ATOMIZATION

The key to successful spray drying is proper atomization of the liquid waste as it is sprayed into the heated calcination chamber. The liquid is dispersed into droplets small enough to dry before striking the chamber wall or cone at the bottom of the chamber. If the particles did not dry, they would stick to the wall and produce a scale that reduces heat transfer into the chamber. Experience at PNL has shown that a droplet mass median diameter of about 70 μm is adequate for successful operation with the waste compositions, chamber configuration, and temperature range studied. Satisfactory nozzles have been developed for the pilot- and plant-scale calciners.

Background and Description

In the early design verification testing (DVT) phase of the WSEP program, an external-mix atomizing nozzle located at the top center of the heated chamber was used because it does not require a pressurized liquid feed supply. The siphon action of this type of nozzle eliminates the need for a feed pump and minimizes the consequences of a leak or a break in the

feed line. External-mix spray nozzles also are not subject to rapid wear because the atomizing gas and liquid mix after leaving the nozzle. However, the droplets produced by the nozzles used were not of uniform size. Coarse droplets generally formed in the center of the spray pattern which were not dry when they left the chamber. The partially dry waste thus produced collected in the cone and occasionally plugged the exit.⁽⁸⁾ Also the performance of these nozzles was sensitive to the pressure in the calciner chamber. An escalating pulsing of the liquid flowrate resulted from variations in the chamber pressure caused by filter blowback. This pulsing further deteriorated adequate atomization. However, subsequent experience with improved design external-mix nozzles at Karlsruhe, Germany,⁽⁹⁾ has shown that use of this type of nozzle is possible if desired.

Because of unsatisfactory performance of external-mix atomizing nozzles during DVT, Kaser conducted a study to evaluate several promising nozzles and identify the one most suitable for use in the heated-wall spray calciner.⁽¹⁰⁾ Spraying Systems Co.* Setup No. 42 was selected as the most satisfactory nozzle, and many of its performance characteristics were studied. This atomizing nozzle, shown in Figure 2, is an internal-mix nozzle which requires a pressurized liquid feed system. To assure that liquid waste is not pumped through the atomizing gas lines to areas outside the hot cell, pressure sensors are located in the gas and liquid lines. These sensors are connected to a switch that will deenergize the liquid pump if the gas pressure falls to less than 1/4 atm greater than the feed pressure at the nozzle. Also a radiation detector is located at the point where the gas line penetrates the cell wall. The detector activates an alarm if a source passes that point in the line.

The internal-mix atomizing nozzle selected is incorporated into an all-welded assembly shown in Figure 3. This assembly includes a bellows-sealed, pneumatically operated, cleanout needle for removing obstructions from the 2.5-mm (0.100 in.)-diam liquid orifice and 3-mm (0.125 in.)-diam air cap orifice. When the pneumatic, two-way piston is activated, it drives

*North Avenue at Schumale Road, Wheaton, IL 60187.

FIGURE 2. Spray Calciner Nozzle with Boron Carbide Insert

FIGURE 3. Atomizing Nozzle Assembly for Hot Cell Application

a stainless steel rod down through the two orifices. Deactivation retracts the rod. Packing gland seals around the rod were investigated but are less satisfactory than the bellows for remote operation. This nozzle and assembly design was used successfully throughout the WSEP program and is currently used in some of the low-throughput WFP demonstration work.

Nozzle Plugging

Steam, hot air, and ambient temperature air were evaluated as atomizing gases during the DVT and WSEP. The steam and preheated air caused nozzle plugging because they baked waste in the orifices. Therefore, the cleanout needle was designed into the nozzle assembly. At Karlsruhe, Germany, where superheated steam is used as the atomizing gas in their nuclear waste spray calciner, severe nozzle plugging problems were recently solved by cooling the liquid line and nozzle.⁽⁹⁾ Nozzle plugging has been eliminated at PNL by using ambient temperature air, by placing a sieve with 1-mm (0.04 in.) openings in the liquid waste line before the nozzle, and by flushing the feed line and nozzle with water before each startup and after each shutdown. The only treatment given the atomizing air is filtration to remove entrained oil introduced by the compressor. Even less plugging potential is anticipated with the Spraying Systems Co. Setup No. 72 nozzle because both orifices in this nozzle are 6 mm (1/4 in.) in diameter. This nozzle was tested at liquid feedrates of over 75 l/hr and will be used in the spray calciner designed to support a fuel reprocessing plant handling 5 tonnes of uranium fuel (MTU) per day.

Calcine tends to accumulate in the form of a hollow, cylindrical stalactite around the exit of the spray nozzle during operation of the calciner. But this crust does not seem to hinder atomization or calcination. Kaser studied the effects of these crusts and/or obstructions inside the mixing chamber of the nozzle and found that neither significantly affected droplet size.⁽¹⁰⁾

Nozzle Orifice Enlargement

Enlargement of the nozzle air cap orifice by abrasion has been reduced to below the detection limit of 15 μm after 1,000 hr of service by using caps fabricated from 96% alumina. Wear by abrasion and corrosion of the orifice in the 303 stainless steel air cap supplied with the nozzle was detected during the long duration runs made in the WFP, while enlargement of the nozzle liquid orifice was not observed. Enlargement of the air cap orifice was detected after an average of 30 hr of operation with each new air cap. The enlargement was readily discernible from a decrease in both liquid and air pressures accompanied by an increase in flowrates. As the orifice diameter increased, the droplet size increased and wall scaling would have eventually resulted.

The increased diameter of the air cap orifice is thought due to abrasion by particles in the slurry feedstock. These particles can reach near sonic velocity when exiting the nozzle. To resist abrasion, air caps were fabricated from 96% alumina and 304L stainless steel with B_4C inserts in the critical wear area as shown in Figures 2 and 4. (Tungsten carbide inserts were rejected because the nickel binder used in them is susceptible to corrosion by the nitric acid in the waste solution. Silicon carbide caps were rejected due to the cost of fabrication by hot pressing and diamond grinding.) These nozzles were evaluated for resistance to thermal shock, abrasion, and corrosion in actual service in the pilot-plant calciner and in a nozzle test station which simulated the flowrates but not the temperatures in the calciner. Both materials are significantly more resistant to wear than are the metal caps, but the alumina cap is superior to the B_4C cap and costs less to produce. One alumina cap which has logged over 900 hr in the nozzle test station and 45 hr in the calciner has experienced less than 15 μm (0.0005 in.) increase in the orifice diameter. Therefore, many thousands of hours of calciner operation can be expected before nozzle wear necessitates replacement of the air cap.

Although the orifice did not wear, the air caps fabricated from 96% alumina broke where the retaining ring, which holds the cap on the fluid nozzle, caused a bending moment which put the ceramic in tension. To

FIGURE 4. Atomizing Nozzle with Modified Alumina Air Cap

prevent this the air cap and retaining ring were redesigned as shown in Figure 4. With this design the alumina was placed in compression when the nozzle was assembled. This cap did not break, but stalactites formed more persistently on the nozzle. Therefore, the nozzle assembly design shown in Figure 5 is now being fabricated for use in the full-scale spray calciner. This design is based on Spraying Systems Co. Setup No. 72, which has 6-mm (1/4 in.)-diam orifices in both the air cap and fluid nozzle that will permit fluid flowrates of over 200 l/hr.

The alumina air caps are more susceptible to damage by thermal shock than are caps of stainless steel. But temperature measurements from a thermocouple imbedded in the ceramic tip show that even under the worst conditions the shock is not severe enough to crack the nozzle. The most severe thermal shocks occur when the calciner is heated to the operating temperature before the water flush is turned on or when the feed and air are turned off simultaneously while the calciner is hot. Consequently, whether liquid is flowing or not, rapid temperature changes in the nozzle can be avoided by maintaining the atomizing air flowrate at the processing level while the calciner is at the operating temperature. This is normally done as an added precaution.

FIGURE 5. High-Capacity Atomizing Nozzle

Using Spraying Systems Co. Setup No. 42, Kaser⁽¹⁰⁾ determined that the major process parameter governing atomization is the volumetric ratio of the atomizing air and the liquid waste flowrates, which corresponds to the ratio of the pressures of the two fluids. Kaser's study concluded that the mass median droplet diameter is a linear function of the ratio of liquid to air flow. An air-to-liquid flowrate ratio of 600 was determined to give a suitable droplet size when using a simulated Purex waste solution. To produce

this size droplet when using the larger Setup No. 72, a flowrate ratio of about 300 is used, which requires a liquid pressure of about 1 atm. Successful calciner operation has been demonstrated using either nozzle.

CALCINATION CHAMBER

The calcination chamber is a large externally heated, vertical tube into which atomized liquid waste is sprayed at the top center. Waste enters the spray calciner as tiny droplets in a stream traveling at near sonic velocity. As they enter the static calciner gas, the air droplets induce a high degree of turbulence in the calciner. The turbulence intensity was determined by Allemann and Johnson⁽³⁾ using eddy diffusivity measurements. At a point 11 column diameters below the nozzle the Reynolds Number was 80,000 to 90,000. The combination of radiant heat transfer to the droplets and particles, coupled with violent convective heat transfer within the entire calcination chamber, allows evaporation and calcination at a high rate.

Waste droplets exit the atomizing nozzle in a full cone configuration. Although high turbulence is encountered near the nozzle, the conical spray configuration is maintained due to droplet momentum. The spray cone becomes less well defined, however, as liquid is evaporated and the remaining constituents become more susceptible to the turbulence. Under normal operating conditions, particles are sufficiently small that drying has progressed to the point that on striking the wall they do not adhere.

Equipment Description

Early calciner development was performed with a 33.6-cm (13-1/4 in.) ID by 2-m (6-1/2 ft) tall calciner. Since the spray chamber was designed to be removable, the calciner was later enlarged to 53.5 cm (21-in.) ID by adding a short conical shaped reducing section to the larger chamber as shown in Figure 6 and bolting it in place. Important calciner parameters are listed in Table 1.

The small-diameter, ceramic fiber insulated furnace used for radioactive demonstration contained three independently controlled zones. The furnace

FIGURE 6. Developmental Spray Calciner

used for nonradioactive work was brick insulated and rather large. It contained two zones with a layer of high-temperature brick between zones through which holes were bored for insertion of the side-mounted vibrators.

Calcine produced in the spray chamber falls into a conical section where it and calcine discharged from the filters combine and flow by gravity to the melter below. Experience both at PNL and at Karlsruhe, Germany,⁽⁹⁾ with other geometries for combining the two calcine streams has shown that the filters should be as close to the calcination chamber as possible. All surfaces are sloped at least 60° from horizontal to avoid calcine accumulation.

TABLE 1. Spray Calciner Design Features

Calcination Chambers

Inside diam, in.	13-1/4	21
Height, in.	78	78
Total heat transfer area, ft ²	22.5	35.7
Material	Hastelloy X [®]	310 Stainless Steel
Wall thickness, in.	3/8	3/8

Furnace

Type	Electrical resistance, 2 zones, 3 phase, 240 volts
Control	Silicon controlled rectifier
Power	80 kW (40 kW each zone)
Heating Elements	Nichrome
Maximum Temperature	1100°C

Atomizing Nozzles

Type	Pneumatic, internal mix
Atomizing Gas	Air
Manufacturer	Spraying Systems Company
Air Cap Material	Type 303 SS with or without 96% alumina insert
Setup Number	42 72
Liquid Orifice Diameter	0.100 in. 0.250 in.
Air Cap Orifice Diameter	0.125 in. 0.250 in.

Filters

Total Number	15
Size	2 in. diam by 2 ft long
Total Surface Area	15 ft ²
Mean Pore Size:	65 µm
Material of Construction	316 SS, internally reinforced

Vibrators

Type	Pneumatic, dry lubricant
Location	Top Side
Size	1200 VMS 1300 AC
Motive Air Pressure	70 psi 40 psi
Manufacturer	Cleveland Vibrator Company

[®]Registered trademark of Cabot Corp., 1020 W. Park Ave., Kokomo, IN, 46901.

Although it is not likely to be needed during normal operation, an emergency pressure relief system is designed into the system to bypass the filters and other potentially blocked equipment, if needed. Pressure relief piping connects into the top calciner flange and to a seal pot designed to allow flow when a preset calciner vacuum is not maintained.

Calciner Capacity

When the calciner capacity is exceeded, insufficient heat is transferred to the atomized droplets, and moist particles strike and adhere to the wall, producing a rapid scale buildup. The increased scale reduces the rate of heat transfer into the calciner, and the calcine moisture content rapidly increases. This reduction of heat transfer to the waste is discernible from a reduction in both power input and furnace temperatures when the calciner temperature is controlled by internal thermocouples.

When calcination conditions become such that the calcine moisture content exceeds about 4%, the calcine is not free flowing and filter differential pressure increases; thus the flowrate at which this occurs has been selected as the definition of calciner capacity. With low-sodium waste this point is sharply defined, and calcine produced at 5 to 10 l/hr less than the defined capacity contains less than 1% moisture.

Capacity determination runs were conducted to observe the effect of calcine feed type, wall temperature, and calciner diameter. Both clean GE type waste (PW-4b) and high-sodium waste (PW-6) were tested at wall temperatures of 500 and 700°C in both the 33.6-cm (13-1/4-in.) and the 53.5-cm (21-in.) calciners. The small feed nozzle and the top-mounted vibrator were used during most tests.

The capacity runs were conducted by beginning feed at a flowrate believed to be below the maximum capacity. As the feedrate was increased about hourly by about 2 to 3 l/hr, conditions were monitored to determine the onset of rapid wall scaling. A calcine sample was taken just before increasing the feedrate, and a visual observation was made of calcine dryness. (At about the 4% moisture level, very little dust results when the sample jar is shaken.)

From the beginning of the capacity tests it was obvious that the spray calciner had greater capacity than previously supposed. Unfortunately, the pilot-scale unit available was sized for 15 to 20 l/hr, and several components such as filter area were not capable of the capacity desired. Filter capacity was resolved by operation of a parallel venturi scrubber or at times by bypassing the filters altogether. Due to equipment limitations, use of the atomizing nozzle with a 3-mm (1/8-in.)-diam orifice in the early tests resulted in median droplet sizes as large as 120 μ m at higher flowrates. Although not greatly larger in diameter than the usual 70 μ m droplet, the volume is five times larger and drying times are correspondingly longer. This problem was overcome in the last test by using the nozzle with a 6-mm (1/4-in.)-diam orifice. Since the calciner furnace was designed for lower flowrates, the power required for high flowrates was not available. During the last capacity test with clean waste and 700°C wall, the furnace was not capable of producing the required heat; thus the calcination chamber temperature decreased considerably at over 70 l/hr, and the capacity is known only as "over 76 l/hr." This flowrate is very near the waste calcination capacity required for a 5 tonne/day fuel reprocessing plant.

Figures 7 and 8 show the results of the heated-wall spray calciner capacity tests. Because of the relatively poor performance of the top-mounted vibrator, some decrease in capacity was noted when calcining wastes containing large amounts of sodium. At a sodium concentration of 2M the capacity decrease was about 15% at a wall temperature of 700°C and about 35% at 550°C. This decrease was due to the thin, typically 1 mm, calcine layer that deposits on the wall and reaches equilibrium in the first 2 hr of operation with high-sodium waste. The layer was not removed by the action of the top-mounted vibrator in use at the time but appears to pose no problem aside from slightly reduced capacity. Since these tests, however, side-mounted vibrators have successfully prevented wall scale with high-sodium feeds. Thus it is expected that in the future high- and low-sodium wastes can be calcined at equal rates.

FIGURE 7. Calciner Capacity when Processing Low-Sodium Wastes

FIGURE 8. Calciner Capacity when Processing High-Sodium Wastes

As predicted, higher capacity is obtained at higher wall temperatures. A decrease to 550°C from 700°C decreases the capacity about 20%. Thus for maximum capacity the chamber should be run at the highest temperature consistent with the calcine melting point and equipment life.

As calciner diameter increases, the surface area available for heat transfer increases as well as the droplet residence time in the heated area; thus a capacity increase with diameter is expected. To avoid moist particles striking the calciner wall, sufficient heat transfer must occur in flight. In the absence of turbulence the point of impingement on the calciner wall is determined by the spray angle and the calciner diameter. With turbulence the point is closer to the nozzle. If heat transfer through the calciner wall were the limiting transfer mechanism, one would expect capacity to be proportional to the calciner surface area above the impingement point. Since this area increases radially as well as longitudinally for a given spray angle, the capacity would increase with the square of the calciner diameter. Such was observed when calcining GE type waste at a wall temperature of 550°C; the 53.5-cm (21 in.) calciner capacity was about 2.5 times the capacity of the 33.5-cm (13-1/4 in.) unit. The calciner wall heat transfer area above the impingement point is also very near 2.5 times greater, indicating that for the calciner sizes investigated, the rate limiting mechanism is heat transfer at the wall. Based on the above simplified analysis, the extrapolations in Figure 7 are made. These show that a 75-cm (30 in.) calciner is expected to easily process over 150 ℓ /hr. It is expected, however, that with increasing calciner diameter a point will be reached where the controlling heat transfer mechanism is no longer the rate of transfer through the wall but the rate of transfer to the droplet. Since the droplet time in flight increases linearly with increasing calciner diameter, at this point capacity may become proportional to the first power of diameter.

Scale Prevention

Deposit formation on the interior calciner wall can slowly form an insulating layer which reduces calciner capacity and is thus to be avoided. Experience has shown that scaling is accentuated when wastes containing large

amounts of sodium are processed or under conditions where moist particles can impinge on the wall. A very thin scale forms, however, in the absence of either. It appears that particle adhesion to the wall is activated by any of several mechanisms: 1) partial melting of the particle on contact, 2) sufficient particle moisture or acid content to cause stickiness but insufficient to cause descaling as vaporization occurs at the hot wall, 3) sintering.

Under proper conditions wall scale is minimal and extended operation is possible. But to extend the flexibility and operability of the unit, vibrators have been introduced to keep wall scale to an inconsequential amount. Experience with a top-mounted vibrator showed that successful operation was possible with a wall scale up to 2 mm thick. However, side-mounted vibrators can prevent wall scaling problems even with sodium-containing wastes.

During the WSEP program, vibrators were found to be necessary, but because of the need to work with a calciner already installed in the hot cell, vibrator application was not optimized. During the runs a free-piston, air-operated vibrator mounted on the calciner cover performed satisfactorily for removing wall scale, but initial difficulty was encountered in constructing a sufficiently rugged mounting bracket. A technique was improvised: a vibrator was bolted to a heavy metal cylinder which fit over a dowel pin on the calciner cover flange. The cylinder's weight prevented the assembly from bouncing off the pin when the vibrator was operating. This technique proved satisfactory, but vibrators had to be replaced frequently because of lubrication problems caused by the high temperature environment. Also because of the location, the vibrator action loosened the nozzle assembly fittings. The vibrator was normally actuated for 2 sec of every minute with an air supply pressure ranging from 2.7 to 4 atm.

During the WFP, additional analysis of the problem led to acceptance of a vibrator manufacturing company recommendation. This was that two specially modified vibrators a size larger than used previously be mounted outside the calciner furnace to act on the sides rather than the top of the chamber. The vibrator and mounting are shown in Figure 9. The vibrator has an extended piston that passes through holes in the furnace and acts on impact pads

FIGURE 9. Side-Mounted Calciner Vibrator

attached to the sides of the spray chamber near the center of its length. The vibrators are located opposite one another on the furnace. This arrangement not only better limits wall scaling. It also locates the vibrators where they are less subject to overheating and less likely to cause damage.

To help determine the effect of vibration on the spray calciner a 100-hr test was conducted. In this the vibrators were activated frequently to simulate up to 4000 hr of operation. The diameter of the spray chamber across the impact pads and at 90° to the pads was measured before and after 4000 vibrator cycles acting on 700°C calciner walls. No measurable difference in calciner shape was found when measuring to 25 μm (0.001 in.).

To evaluate the spray calciner's ability to recover from off-standard operating conditions, a test was conducted with a thick layer of wall scale intentionally induced. Wall scale was caused by reducing the nozzle air atomizing pressure to less than half the normal value while deactivating the vibration cycle. After about 6 hr operation, wall scale up to 6 mm (1/4 in.) thick had accumulated in some areas of the calciner. A 3-sec pulse from the side-mounted vibrator effectively cleaned the wall. During normal operation, vibrators can be deactivated for over 24 hr without loss of calcine dryness. However, normally the wall is vibrated several times per hour to assure scale-free operation.

A thermal shock descaling technique for use during calciner shutdown has proved rapid and effective with even the most stubborn scale. It was demonstrated that a little water sprayed onto the hot (500°C) calciner wall creates sufficient thermal shock to dislodge the scale. Descaling can be done with less than 40 liters (10 gal) of water, and nearly all water sprayed from a properly designed nozzle can be vaporized by the hot wall. Should it ever be needed, this process requires 5 to 10 min and can be done with remotely operated equipment.

Thickness measurements were made on the calciner chamber wall at the time the 310 stainless steel, 53.5-cm (21 in.)-diam spray chamber was put into service and after 552 hr of simulated waste calcining at 700°C, including six heat up and cool down cycles. There was no detectable decrease in the wall thickness when measured with an instrument having a precision of 5 μm (0.0002 in.). Thus a calciner corrosion/erosion rate of less than 75 μm (0.003 in.) per year is expected.

Previously, spray calcination of wastes containing large quantities of sodium was limited by the formation of sodium nitrate which melts and adheres to the calciner wall at temperatures slightly over 300°C. It was observed that considerable sodium could be calcined if the weight of sodium ions did not greatly exceed the combined weight of the other cations in the waste. Such is the case with the early AGNS waste, PW-6, and current AGNS ILLW.

The success in calcining these wastes was attributed to the nonsodium cations producing stable compounds during calcination. These species reduce the stickiness of the calcine such that it can be dislodged from the wall by vibrator action.

Since silica and other glass-forming compounds must be added to calcine to produce a vitrified waste form, addition of silica to the calciner feed-stock was investigated as a means to calcine wastes containing virtually all sodium cations. A series of laboratory tests indicated that a reaction could proceed in the calciner to reduce the amount of free sodium nitrate and form a water glass. The reaction is: $2\text{NaNO}_3 + x\text{SiO}_2 \rightarrow \text{Na}_2\text{O} \cdot (\text{SiO}_2)_x + \text{gas}$. The reaction proceeds rapidly at temperatures over 550°C.

Tests conducted with the 53.5-cm-diam spray calciner have confirmed the usefulness of this reaction. Powdered SiO_2 with an average particle diameter of 20 μm (common diatomaceous earth used for filter precoating) was added to simulated reprocessing plant startup waste. This waste contained 2M nitric acid, 14 g/l sodium, 0.4 g/l fission products, 0.3 g/l corrosion products and 2.5 g/l phosphate. About 27 g/l silica was added to the waste prior to calcination. This amount of silica is required for the formulation of a good quality borosilicate glass. An early test with calciner walls at 750°C was not totally successful due to the formation of a glaze on the calciner interior. Later operation at lower temperatures yielded clean calciner walls. The calcine adhering to the hot calciner walls was observed to contain less than 0.5% nitrate while the bulk of calcine contained about 19% nitrate.

OFF-GAS FILTRATION

Description and Background

Due to the small particle size of the spray dried calcine, 15 to 50% of the solids are entrained in the calciner vapors. Early experiments with various types of dust removal equipment led to the adoption of sintered stainless steel filters. The filters adopted are shown in Figure 10.

FIGURE 10. Spray Calcliner Filter Assembly

During operation, solids filtered from the calcliner vapors are temporarily retained on the filter surface. With time the thickness of the deposited calcine increases and produces a corresponding increase in filter differential pressure. To remove the calcine layer a pulse of high-pressure air is directed into the filter from above. This reverse air flow dislodges the calcine and allows it to fall to the receiver below. The calcine removed from the filters is a very friable agglomerate.

The sintered metal filters in use were fabricated from appropriately sized metal powder that had been formed into a sheet of suitable thickness, then sintered. The plate thus formed is rolled into a tube and welded.

Another technique involves extruding the metal powder as a tube before sintering to form a seamless filter. One company grinds the external surface of the sintered filter to provide a smoother surface and make release of the cake easier. Varying the metal particle size can alter the filter pore size. Small pores provide the best filtration efficiency but also exhibit the largest resistance to vapor flow. This effect is largely offset, however, by the buildup of a calcine layer on the filter surface. This layer acts as a filtering media and produces a larger differential pressure. The sintered metal tube is reinforced and welded to a venturi as shown in Figure 10. Each venturi is welded into a plate as shown to form a filter bank.

Tests have been conducted with a combination of cyclone and filters and with various types of filters. As reported by Kaser,⁽⁷⁾ when a cyclone was used upstream of the filters, the filter cake was not easily removed by the pulsed blowback. With the cyclone, only the finest particles reached the filter, and these particles apparently formed an especially adherent filter cake.

Various filter media have been tested including porous alumina, fine woven wire, fine wound wire, sintered fiber metal, and sintered metal powder. Sintered powder filters appear to exhibit the best compromise between filter efficiency and ease of cleaning by pulsed blowback air. Alumina filters had 10-mm (3/8 in.) thick walls and pore sizes ranging from 10 to 100 μm (0.0004 to 0.004 in.). They were fragile and not effectively cleaned by pulsed blowback. Wire wound and woven wire filters were not as effective as sintered filters, and sintered fiber metal filters were expensive and required high differential pressure.

It is desirable to minimize calciner pressure surges caused by the pulses of blowback air. Variables which affect the magnitude of these surges are blowback pulse duration, blowback pressure, off-gas line flow resistance, and the fraction of filters pulsed simultaneously. Experience has shown that a short 1/4-sec pulse of 300°C air is as effective as longer pulses. With this short pulse, blowback pressures of up to 7 atm (100 psig) can be used to clean one-fifth of the filters without pressurizing the calciner.

Filter Effectiveness

Sintered stainless steel filters have found broad use in the nuclear industry in applications requiring high-efficiency filtration of thermally hot and/or highly radioactive vapors. Experience in spray calcination development during the last 15 years has demonstrated high reliability and high efficiency over a myriad of operating conditions. During operation, routinely less than 0.1% of the calcine particulates penetrates the filter.

Due to the large filter pore size relative to the calcine particle size, some calcine could pass through the filter. It was thus not surprising when filtration efficiency was observed to improve after a calcine coating had collected on the filters. During the first five WFP spray calcination runs the filters were undisturbed, and the effect of calcine buildup was observed. During the first run the average filter particulate decontamination factor (DF)* was about 700. During each successive run the DF steadily improved until during run 5 the DF had improved to 13,000. (Filter DF during individual runs is shown in Table A-1 of Appendix A.) Following this run, tests with filter washing were initiated which reduced the DF to near the clean filter efficiency. Since filters will normally not be washed, it is anticipated that in an operating plant the calciner filter DF for particulates will be well above 10^3 .

Filter Permeability Retention

Excessive filter differential caused by buildup of calcine on the filter exterior is prevented by use of a pulse of air to dislodge the calcine cake. The blowback system shown in Figure 10 is analogous to a jet ejector. The use of a venturi is intended to increase the entrainment of filtered gas by the blowback gas jet, thus decreasing the amount of external air required to clean the filters. Little information has been reported on venturi design; however, some work was done on understanding the effects of venturi shape on blowback performance.⁽⁷⁾ Figure 10 shows a venturi design which has been

*DF is calculated as the ratio of the weight of species entering the calciner to the weight of species observed in the combined condensate, scrub solution and scrubber effluent.

very effective in cleaning the sintered metal filters used in the WSEP and WFP spray calciners. With this blowback system a 4 to 5.5-atm (60 to 80 psig), 1/4-sec pulse of heated air delivered at intervals of 2 to 100 min effectively cleans the filters.

A rapid filter pressurization is believed desirable for uniformly removing calcine cake from the filter. Consequently, during the WSEP program, blowback air valves were located adjacent to the filters. Some problems were encountered, however, due to radiation-induced failure of the solenoid valves used. Valves which will withstand the radiation levels expected during processing of high-level waste are expensive and a nuisance to maintain in-cell. Therefore, a test is under way to determine whether out of cell placement of blowback valves is acceptable. At present, results show no detrimental effect on blowback efficiency when the valves are removed 16 ft from the filters.

Sintered stainless steel filters may not last indefinitely in continuous service due to gradual blockage of the filter pores. Since some calcine is smaller than the pore size of the filter, some particles penetrate the filter media and become lodged therein.⁽¹¹⁾ Calcine penetration is greatest at the surface but is rapidly reduced by larger particles which bridge over the pores, thus decreasing the effective pore opening and acting as a filter precoat. During filter blowback the precoat is partially removed and some particles are again free to enter the filter media. Unfortunately, not all particles inside the media are removed during blowback, and a slow accumulation occurs. The rate of accumulation is dependent on operating conditions and is observed eventually as an increase in differential pressure. Based on industrial experience,⁽¹²⁾ the spray calciner operating conditions are such that well over a year's operation is expected before pore blockage becomes a problem. At this time the filters could be washed or, more likely, replaced.

In the WSEP calciner, sintered stainless steel filters were periodically washed to provide added filter permeability. Due to the low vacuum available for hot cell operations, the allowable filter differential pressure was limited to about 10 in. of water, which was below the design value. To prevent being forced to operate at reduced capacity, the filters were

periodically washed with water or nitric acid. This was done by trickling water into the filter from above the venturi while activating the blowback cycle. Good filter cake removal is obtained by this technique, and solids are flushed from many of the filter pores. Improved filter cleaning is obtained by use of nitric acid instead of flush water to combine physical removal forces with the chemical attack of the acid. Dissolution tests show that at room temperature about 3% of the GE type, PW-4b waste can be dissolved in water, while 6M HNO_3 dissolves about 65% of the calcine. It is not likely that filter cleaning by this method will be required in a waste calcination facility. But should it be required, the capability and procedure are available.

After being placed in WFP service, the spray calciner filter permeability* declined as shown in Figure 11. This occurred as the solids layer thickened and aged and as some pores plugged. After about 120 to 150 operating hours, the permeability became somewhat stable. During a 500-hr reliability test, filter permeability was observed to actually increase. But subsequent short runs where conditions varied widely produced slightly poorer permeability. It is anticipated that during longer term operation, filter permeability would remain at 0.2 to 0.3 ft/min/in. water differential pressure.

Once filter permeability stabilized it was noted that filter permeability was not reduced at higher filter face velocities even though the differential pressure was much greater. When the filter face velocity was later reduced, the differential pressure also returned to the previous value. However, as shown in Figure 12, during run 15 increased filter solids loading did produce a temporary decrease in permeability.

A calcine cake which is visually indistinguishable from the 150-hr equilibrium coating builds up on the filters after about 4 operating hours.

*Filter permeability is expressed in terms of actual filter face velocity in ft/min per unit pressure differential in inches of water. Since flow through the filter pores is basically laminar flow, filter DP is proportional to the throughput velocity. Thus, at a given temperature and solids loading rate, permeability remains constant over a large range of face velocities and accurately indicates filter blinding.

FIGURE 11. Filter Permeability During the WFP Spray Calcination Campaign

FIGURE 12. Filter Permeability During Run 15

The equilibrium coating varies randomly from about 1/2 to 1-1/2 mm (1/32 to 1/16 in.) thick along the filter. A picture of the equilibrium coating taken at the end of run DSS-15, after over 700 operating hours, is shown in Figure 13.

FIGURE 13. Spray Calciner Filters After
700 Hours Operation

During run 13, a capacity test, filter permeability was observed to decrease rapidly when the temperature of the vapor reaching the filters dropped below the dew point. The filter permeability decrease was indicated by filter differential pressure readings, and the calciner wall temperature was increased to heat the off-gas. The hotter vapors effectively dried the filters, allowing the permeability to return to normal without decreasing or discontinuing the calciner feed.

About 142 hr into run 15 under normal operating conditions, the filter differential pressure began to increase inexplicably and did not respond to blowback changes. The flow to the filters was accordingly reduced, and in less than half an hour the filter differential returned to normal, and regular flow through the filters was resumed. No explanation of this one-time occurrence has been found.

It was observed that whenever the solids loading to the filters was briefly reduced, the filters renewed themselves, and on resumption of normal filter loading the differential pressure improved. It appears that during long-term filter operation momentarily reducing the filter loading can reverse a temporary decrease in permeability.

Coupling of a melter to the calciner has not been noted to affect the operation of the spray calciner filters. The volume of gas exiting the melter is normally negligible when compared to the volume of vapors from the calciner. Thus it has no noticeable effect on filter differential. Volatile components from the melter that are trapped in the filter cake are only a small part of the solids collected there. Hence they are removed during filter blowback also without noticeable effect on the filters. The concentration of some volatile waste constituents is observed to be slightly higher in calcine removed from the filters. This indicates that these constituents are scrubbed from the vapors during passage through the filter calcine coating.

Filter Physical Ruggedness

Since the sintered stainless steel tubes used in filter construction can be somewhat brittle, reinforcing and bracing are designed into the filter assembly to prevent accidental breakage. Unsupported filters have been known to fail. During radioactive spray solidification demonstrations⁽¹³⁾ a crane boom fell and struck the filter housing, cracking two of the filters. Although not confirmed, unsupported sintered metal fiber filters in the waste calciner at the Morris Fuel Reprocessing Plant⁽¹⁴⁾ were suspected to have failed during installation or initial testing of the unit.

To avoid filter breakage, internal reinforcement with perforated support plates⁽¹³⁾ as shown in Figure 10 is used in all filter elements. Weld penetrations are such that both the perforated core and filter media are joined solidly to the end pieces. In addition individual elements are interconnected to form a single strong unit. If desired, commercially available vibration isolation techniques can provide further resistance to vibration-induced filter failure for each filter element or for the filter unit as a whole.

The low filter differential pressure likely to be encountered in the spray calciner is about 1% of the maximum allowable differential for unreinforced filters. It is therefore unlikely that failure due to overpressure will occur.

Because the calciner filters normally operate at about 300°C, use of ambient temperature blowback air could result in thermal shock to the filter. Vendors of sintered stainless steel filters, however, disagree on the need for heated blowback air. Some say that since the venturi is designed to draw back previously filtered hot vapors into the filter during blowback, thermal shock from using unheated blowback air is reduced. However, Kaser⁽⁷⁾ has shown that at spray calciner operating conditions the entrained air volume is actually somewhat less than the motive air volume. Thus a slight thermal shock may occur, and localized condensation can conceivably occur as a result of the cool blast. Heated blowback air has been used to avoid the possibility of either, but there is good evidence to indicate that it is not required. Tests are ongoing to determine the effects of unheated air.

AUXILIARY SYSTEMS

CALCINER FEED SYSTEM

Transfer of concentrated high-level radioactive slurries is a challenging problem. Experience at Hanford and other sites has led to the calciner feed system shown in Figure 14. This system was used during the WFP and, except for the feed strainer and duplicate pumps, was used during the WSEP program. With some modifications described below, this system is proposed for use in full-scale production plants. The important features of this system are detailed in this section of the report.

FIGURE 14. Process Flow Diagram for Developmental Spray Calciner

Feed Tank

During plant operation, waste will likely be jetted in batch transfers from a holding tank to the calciner feed tank. If a canister of waste solid such as glass is to be produced in a batch or a low-holdup melter, the liquid waste volume can be sized to produce one canister of solidified product.

This technique adds assurance of canister contents because liquid sampling is normally more accurate and easier than solids sampling. A single feed tank can be used by simply adding the next waste batch as the liquid level reaches a lower limit. This technique was routinely used in the WSEP and WFP.

Storage of waste slurries is complicated by the need to prevent settling of nondissolved species. Although spray calciner performance is not harmed by varying solids content in the feed, accurate melt formulation may be dependent on a known amount of solids entering the calciner and, subsequently, the melter. Deposition of solids in waste tanks may result in plugging, eventual hot spots, and accelerated corrosion.

An electric motor-driven propeller can agitate the feed tank, successfully maintaining homogeneity in the waste slurry. The agitator can be designed to provide the degree of mixing desired. In the WSEP, electric motor-driven agitators proved effective for suspension of HLLW solids and also were capable of sustained operation in high radiation service. Resistance to radiation can be increased by shielding the motor or other potential failure areas.

Agitation from one or more liquid jets is also being investigated for use in the feed tank. With a cantilever pump used to transfer the waste, over 200 l/min of pressurized feedstock is available for agitation. In a feed tank of around 1000-liter capacity this size jet could provide the necessary agitation.

Studies with simulated high-level waste slurries containing large amounts of suspended material have shown that agitation by air sparging does not maintain homogeneity throughout the tank. Accurate liquid sampling is thus virtually impossible. Without proper agitation, suspended solids predominating in the lower part of the tank are drawn into the calciner first, complicating accurate melt formation. Furthermore, pluggage of air holes in the sparge ring has been a continuing problem.

A pulse type agitation technique developed at Windscale, England, and employed at other installations⁽¹⁵⁾ has effectively prevented accumulation of solids in the bottom of large storage tanks. Applying this technique to

feed tanks, however, can result in less than optimum performance due to the predominance of solids near the tank bottom, the frequent pulsation required, and the continually changing liquid level.

Liquid level monitoring dip tubes are accurate and effective for determining tank volumes. In the WSEP program, plugging of the dip tubes in solutions with a high solids content was negated by periodically discontinuing the air purge to the dip tube. This allows liquid to enter the dip tube and dissolve deposits formed at the air/liquid interface. Plugging of waste tank dip tubes has not been encountered in WFP simulated nonradioactive wastes. Liquid level monitoring helps confirm the feedrate measured by electromagnetic flowmeters on the calciner feed piping.

Cooling coils are included in the feed tank to remove radioactive decay heat and heat from pumping and recycling the waste. It has been established that keeping the waste temperature at 40°C or less is advantageous in reducing the potential for drying and feed blockage at the spray calciner atomizing nozzle.

Transfer of Slurries

Many types of devices have been evaluated for transferring radioactive slurries. Air lift techniques have been developed and are routinely used for metering and transferring dilute suspensions. But handling of concentrated slurries at low flowrates by this technique has normally been unsuccessful. A pressure head is useful in preventing pipe and nozzle blockage and is required for certain atomizing nozzles. The continuous control valve cycling normally required with air lift systems in this service limits the life of the valve. In the WSEP, radioactive slurries were pumped with disposable in-line centrifugal pumps. Unfortunately, their short service life limits their usefulness.

On the other hand, experience of Savannah River Laboratory⁽¹⁶⁾ and other sites in pumping radioactive slurries with vertical cantilevered shaft pumps has shown that concentrated radioactive slurries can be routinely pumped. With this type of pump all seals and bearings are above and out of the liquid,

eliminating the need for seal-water or other complications. Experience at Savannah River with 35 cantilever pumps in a radioactive environment has shown that in high-level waste service this type of pump can be expected to operate 5 to 10 years without maintenance. These pumps typically are capable of high flowrates and are potentially capable of supplying feed tank mixing from a jet of recycled liquid waste.

Prevention of Line Blockage

The spray calciner feed system shown in Figure 14 consists of a pressurized feed recirculation loop from which a small portion of the total flow is metered into the calciner. High turbulence (Reynolds Number greater than 10^4) in the loop prevents solids settling. A short length of small-diameter tubing interconnects the recirculation loop, metering valve, flowmeter, and atomizing nozzle. The drawoff point is properly designed to extract a representative amount of the suspended solids, and all parts of the nonrecirculated feed line are sloped downward toward the calciner.

Although waste solids are finely divided as formed, experience with storage of concentrated liquid indicates that caking on vessel walls can and often does occur at the air-liquid interface. Dislodged caked solids in tanks and lines pose potential line blockage problems. This will likely be intensified in denitration vessels if the sugar denitration process is used.

Restrictions in the feed lines (4.8-mm [3/16 in.]-diam electromagnetic flowmeter, and 6 mm [1/4 in.] atomizing nozzle in a plant size calciner) are potential plugging points that could require shutdown if appropriate provisions are not made. To prevent blockage at these points, a commercial type pipe strainer was installed in the WFP calciner feed system. The 1.3-mm (0.05 in.) strainer openings removed particles that could have blocked the 0.1-in.-diam electromagnetic flowmeter used in the early parts of the WFP. Approximately monthly flushes of the strainer produced pieces of undissolved feed make-up chemicals and general trash, such as metal shavings and glass pieces of unknown origin. The nozzle plugging problem has likewise been solved at the Idaho National Engineering Laboratory (INEL) Waste Calcination Facility (WCF).⁽¹⁷⁾ These internals in the feed tank act as a feed strainer.

Solids are allowed to slowly accumulate during operation and are later dissolved during a process shutdown. In forthcoming investigations a strainer will be tested on the inlet to the cantilever pump. Since the amount of solids material larger than 5 mm (3/16 in.) will likely be very small, cleaning of the strainer is not expected to be necessary. If desired, a basket type filter containing the accumulated oversize solids could also be used. In a vitrification facility the baskets could be remotely placed periodically or emptied into a canister to be filled with glass.

Flow Control

Of the many flowmeters available, the electromagnetic seems to offer the greatest utility for metering radioactive acid slurries. Although this metering system has many advantages, a major drawback is the small-diameter tube through which small flowrates of radioactive slurry must pass. Thus, in nuclear waste applications, meters are often oversized to allow passage of particles, and operation is in the extreme low flow velocity range. Such was the case in the WSEP program and the WCF. Operation with simulated wastes has indicated that high reliability can be obtained from this flow meter. But during actual radioactive operation in these programs problems with zero drift and other calibration problems were encountered. These may at least in part be attributed to oversizing of the radioactive units. The meters did provide at least semi-quantitative data for flowrate control which when coupled with periodic tank depletion data provided accurate flow rate information.

In the WFP the waste feedrate is automatically controlled by a diaphragm-operated valve containing a special spline for passing particles. The valve is controlled by a signal from the electromagnetic flowmeter. Up to an atmosphere pressure drop can be allowed across the valve. Thus solids lodging in the valve orifice are forced through. This makes little, if any, spline movement necessary and greatly improves valve life. Flow to the calciner is readily controlled within 2 %/hr of the setpoint value.

This feed system has been shown to effectively and reliably meter highly concentrated waste slurries to the calciner. Due to the turbulence in all parts of the system, solids are maintained in suspension and fed uniformly to the calciner.

CALCINER OFF-GAS

Description of Treatment Equipment

During the radioactive demonstrations of the WSEP program, vapors from the filters were routed through an extensive effluent treatment equipment train. As described by McElroy et al.,⁽⁸⁾ vapors passed sequentially through a tube and shell condenser, the deentrainment section of an evaporator, another tube and shell condenser, the fractionation tower of an acid fractionator, a third condenser, an air heater, HEPA filters, a caustic scrubber and final filtration prior to discharge.

In the WFP system shown in Figure 14, filtered nonradioactive calciner vapors pass through a condenser then a caustic scrubber prior to discharge into the building off-gas header where they are filtered then discharged to the building stack. The off-gas condenser is a tube and shell, single-pass unit containing 13.6 m^2 (146 ft^2) of heat transfer area. The caustic scrubber is 35 cm (14 in.) in diameter and packed with 0.26 m^3 (9.1 ft^3) of 2.5-cm (1 in.) stainless steel raschig rings. It is surmounted by a wire mesh mist eliminator. Isokinetic gas sampling taps are installed in both the condenser and scrubber vapor outlet lines, and a low-pressure drop rotameter is located downstream of the scrubber. The isokinetic sampling assembly is shown schematically in Figure 15.

Characteristics of Off-Gas

Particulates

Particulate material small enough to penetrate the coated sintered stainless steel filters is typically less than $1 \mu\text{m}$ in diameter and thus behaves much like vapor species. Analysis shows that the condensate contains elements in roughly the same ratio as in the calciner feed except for some volatile constituents.

FIGURE 15. Off-Gas Sampling System

During the nonradioactive demonstration, the calciner filter's efficiency was measured by analysis of mainly nickel and chromium in both the condenser and scrubber. Particulates were found in both the condensate and caustic scrub solution; about twice as much is retained by the packed bed scrubber as by the tube and shell condenser. Isokinetic sampling and analysis of the scrubber off-gas showed that comparatively little particulate material passed through the scrubber.

Volatile Constituents

During spray calciner development, volatilization of radionuclides has been observed to be small. Minor amounts of the potentially volatile elements, cesium, tellurium, and selenium, have been observed at times in calciner off-gas systems. In the WFP, however, analyses for these elements in the calciner effluents have been negative, indicating that much less than 1% of these elements are volatilized into the off-gas.

Tests using nonradioactive ruthenium spikes in the calciner feed have shown that ruthenium volatilization from the calciner and melter can vary from 0.1% to 6% of the feedstock ruthenium. These tests have been conducted since 1960 under numerous calciner conditions and feed compositions. Due to the complexity of ruthenium-nitrate reactions, the exact species of ruthenium present in high-level waste is unknown. Therefore highest confidence is placed in the WSEP tests in which actual high-level waste was solidified.⁽⁶⁾ During these tests ruthenium volatilized from the calciner and melter ranged from 0.7% to 2%. Volatilization data with current waste compositions and calciner/melter operating conditions show ruthenium loss at less than 2.5%. Calciner operation independent of a melter shows ruthenium losses of less than 1%. Recent data obtained while operating with a calciner wall temperature of 800°C indicates that less than 0.1% of the ruthenium is lost under these conditions. Operating with feedstock acid concentrations up to 7M has shown no statistically valid correlation of ruthenium volatilization as a function of feed acid content although the trend is for higher volatilization at higher acid levels.

Excessive efforts to reduce calciner ruthenium volatilization to zero are not justified, however, due to the evolution of ruthenium from other sources within the plant. Ruthenium removal and decontamination equipment must be installed in the plant effluent system irrespective of ruthenium loss from the calciner. For example, ruthenium is routinely observed in concentrator overheads. Under all operating conditions during the WSEP program from 0.4 to 2% of the feedstock ruthenium was volatilized from the concentrator.

Spectrographic analysis of the off-gas after passing through the condenser and caustic scrubber showed a typical concentration of 0.1% NO and 0.1% N₂O.

Volume

A favorable feature of the spray calciner is the small noncondensable off-gas volume. Table 2 shows that although air is used for atomizing and other essential functions, the actual consumption is low compared to the condensable components. Air leakage is another likely noncondensable source not shown on the table which could be large or small, depending on the design of components such as the calciner/melter connection.

TABLE 2. Calciner Off-Gas Volume Contributions

Source	Spray Calciner Effluent Volume, at Specified Calciner Feedrate			
	75 l/hr		150 l/hr	
	m ³ /min	scfm	m ³ /min	scfm
<u>Noncondensable</u>				
Atomizing air	0.4	15	0.7	25
Pressure sensor purge air	<0.01	<1	<0.01	<1
Filter blowback air	<0.01	<1	<0.01	<1
Other*	<0.01	<1	<0.01	<1
Total Noncondensable	~0.4	~15	~0.7	~25
<u>Condensable</u>				
Steam	1.6	55	3.1	110
NO _x **	0.08	3	0.17	6
Other*	<0.01	<1	<0.01	<1
Total Condensable	~1.7	~58	~3.3	~116
Total Calciner Effluent	~2.1	~73	4.0	~140

* Other species from the feed and reaction products

** 3M total nitrate

Temperature

Vapors from the calciner are uniform in temperature under a given set of calciner operating conditions. Variables such as calciner wall temperature and waste feedrate largely determine the off-gas temperature. Depending on calciner conditions, the off-gas temperature measured inside the calciner, in the lower part of the filter housing, may be 250 to 450°C while the temperature measured across the filters, in the calciner off-gas line, is 150 to 250°C.

Effluent Treatment

Concentration and Recycle

The calciner filters provide the primary effluent decontamination, greatly reducing the quantity of radionuclides to be removed by wet scrubbing techniques. Hence, the quantity of liquids recycled to the calciner can be minor. During the third WCF campaign⁽¹⁸⁾ the particulate concentration in the recycle stream was about 2 g/l. At this concentration the spray calciner recycle stream would be about 8 l/hr for a 5 MTU/day reprocessing plant.

Primary condensate from the calciner contains roughly the same volume and molarity of nitric acid as existed in the feed slurry. Having passed through the calciner, most species in the condensate are present as finely divided, undissolved, particulates; however, those soluble components such as cesium are ionic. The low concentration of radionuclides in the waste allows volume reduction by a factor of at least 50 before recycle to the calciner. The condensate is observed to boil to dryness without foaming.

WSEP Effluents

During the WSEP, vapors from the spray calciner and in-can melter were decontaminated by a factor of 10^{12} before discharge at less than 0.1% of 10 CFR 20 limits. Liquid effluents from the acid fractionator were about 10^2 above 10 CFR 20 limits and would require further treatment by ion exchange or evaporation before discharge.

Quench Scrubbing

During the WSEP spray calciner/metallic melter radioactive operations,^(6,13) volatilized ruthenium was observed to pass through the condenser and evaporator deentrainment tower without reaching equilibrium with the liquid phase and being scrubbed from the vapor. To improve ruthenium removal, slightly crushed pall rings were dropped into the tubes of the tube and shell calciner vapor condenser. Condensation and water sprayed into the condenser wet the packing and markedly improved the removal of vapor phase ruthenium. Since calciner vapors contain very little particulate matter, a packed bed vapor scrubber was designed for use at this point in the off-gas train. The scrubber

was built with an enlarged lower section for high liquid flowrates to condense and cool the incoming vapors while the upper packed section provides intimate vapor-liquid contact for maximum ruthenium removal.

During run 6 this technique was tested. Hot off-gas from the calciner filters was routed directly to the scrubber, where it was contacted counter current with cooled 6M NaOH. Thermocouples placed at 30-cm (12 in.) intervals along the packed column indicated that, with normal liquid flow, heat transfer is completed in the lower foot of packing. Problems with solids deposition at the hot gas inlet were not observed, and, within analytical accuracy, removal of the feedstock nitrates and particulates from the off-gas was equally efficient using either the series condenser and scrubber or the quench scrubber mode.

Although a packed scrubber is efficient for use with the relatively clean calciner off-gas, further evaluation is required to determine whether it is the optimum equipment type. In the unlikely event of a filter rupture, sufficient unfiltered calcine could escape the calciner to potentially plug the packed bed. Less efficient but also more blockage resistant equipment like venturi scrubbers should be evaluated for quenching and scrubbing the calciner off-gas.

DIRECT CALCINER/MELTER COUPLING

A favorable characteristic of a spray calciner coupled to an in-can melter (SC/ICM) system is its ability to function reliably as a unit, without requiring intermediate storage of calcine. Systems which operate with large radionuclide inventories in the dry form and systems that cannot be started or shut down rapidly require provisions to store significant quantities of calcine. In the event of off-standard operations the inventory must be dumped or the product must be stored during the shutdown operation. The spray calciner operates with negligible calcine inventory and can be shut down instantaneously if desired. It is passively safe. Redundancy can be introduced by the use of two full-size in-can melters, and since the atomizing air flowrate is a function of the waste feedrate, design of the spray calciner to process well above the required normal operating flowrate does not require

routine treatment of a larger volume of noncondensable off-gas. Thus the incentive for adding intermediate calcine storage to possibly increase onstream time is minimal.

The added complexity required with intermediate calcine storage would, in fact, likely decrease the onstream time of the process. Due to the thermal properties of high-level waste calcine, small air or water cooled storage bins must be used. Such bins would require considerable head room and would likely require addition of a calcine transport system to reelevate the calcine prior to discharge to the next treatment process. The complexity of such a system and the potential for problems in emptying the storage bins will reduce the onstream time.

Storage of heat-generating calcine is complicated by the poor thermal conductivity of powders and granular materials. When heated sufficiently, the calcine will sinter and release significant quantities of NO_x and H_2O .^(19,20) Depending on calcine sodium content, agglomeration occurs over a range of 300 to 900°C.⁽¹⁹⁾ Because sintered calcine may be difficult to remove from a bin, it is anticipated that the maximum allowable routine storage temperature would be well below 800°C. Based on this centerline temperature and on recent thermal conductivity measurements of simulated commercial HLW calcine,⁽¹⁹⁾ bin thicknesses were calculated for calcine generating 90 watts of heat per kilogram, which corresponds to waste about two years out of reactor. The number of bins required to store calcine from two weeks operation was also assessed. The results are in Table 3.

TABLE 3. Storage Bin Requirements for Calcined HLW

<u>Bin Configuration</u>	<u>Maximum Thickness, cm</u>	<u>Number of Bins Required for 14 Days Storage</u>
Slab shaped bin, externally water cooled (2.5 m high x 1.2 m wide)	10	10
Slab shaped bin, free air convection cooled	7	15
Cylindrical bin, externally water cooled (2.5 m high)	14	70
Cylindrical bin, free air convection cooled	9	170

Operation of the heated-wall spray calciner while directly coupled to either a continuous metallic melter or a batch in-can melter has been demonstrated at PNL both in the nonradioactive pilot plant and under actual radioactive hot cell conditions.^(4,6,7,13) The couplings between calciner cone and melter were as close as 14 cm (5-5/8 in.) or as distant as 1.2 m (3 ft, 10 in.). In all instances the melter off-gas was vented through the coupling section into the cone below the calciner and out through the sintered metal filters. No adverse effect on the performance of the calciner or the filters has been observed as a result of the coupling to the melters.

The spray calciner is well suited to feeding a melter because it produces the calcine at a constant rate. Therefore, it is possible by unsophisticated control to meter the frit into the melter at a rate proportional to the calcine generation rate. However, due to holdup on the filters, the calcine discharge rate from the cone is not completely constant. It tends to increase momentarily when the filter blowback or calciner vibrators are activated. The calcine produced by the spray calciner is good feed for a melter: its small particle size with large surface area results in rapid reaction with the glass formers and in homogeneous blends. The calcine is also low in volatiles content.

CHARACTERISTICS OF SPRAY CALCINE

The product of calcining simulated high-level liquid waste in the heated-wall spray calciner is a very fine, dry powder consisting mainly of metal oxides with some alkali metal nitrates and waters of hydration present.

Calcine particle size distributions were obtained by U.S. Standard sieve analysis, Fisher Subsieve analysis, Zeiss particle size analyzer, and Quantimet 720 projection size distributions. The results are presented as histograms in Figure 16. This presents the size distribution both in terms of percent of total particles and percent of total mass. While 65% of the total number of particles are in the "diameter" range of 1 to 5 μm , these particles account for only 15% of the mass. Only 17% of the total particles are of "diameter" 6 to 20 μm , but they account for 75% of the mass. The large particles, over 1 mm, were analyzed and found to be of the same composition as the rest of the calcine except for higher water content and associated nitrate.

FIGURE 16. Spray Calcine Size Distribution

Recent tests by a cyclone manufacturer show that spray calcine can be removed from the vapor stream with a cyclone separator. Tests with an 8-in.-diam cyclone at a pressure differential of 4 in. of water showed removal efficiencies of over 95%.

Calcine physical characteristics presented in Table 4 are a function of waste composition and calciner operating conditions. During normal operation calcine bulk density varies from 0.5 to 1.3 g/cc, with the lower density corresponding to the higher sodium content. Particle densities as measured by helium displacement are 3.8 to 5.1 g/cc, which are in agreement with those predicted by calculating the weighted average of the theoretical densities of the metal oxides expected in the calcine. The exact oxidation state of the species present in the calcines is not known because x-ray diffraction analysis shows an amorphous structure.

TABLE 4. Properties of HLW Spray Calcines

Characteristic	PW-4b	PW-6	PW-7a	PW-7
Aerated Bulk Density, g/cc	0.85	0.41	0.69 - 0.92	
Working Bulk Density, g/cc	0.97	0.48	0.87 - 1.04	
Packed Bulk Density, g/cc	1.24	0.61	1.15 - 1.33	
Compressibility, %	32	33	40 - 31	
Angle of Repose, degrees	42	39	43 - 42	
Particle Density, g/cc	4.4	3.8	5.1	
Surface Area, m ² /g	20	11	14	
Nitrate Content, wt%	<1	19 - 42	2 - 22	<1 - 2
Moisture Content, wt%	<1	<1	<1 - 4	<1
pH of Equilibrium Aqueous Slurry	4.5	5.0		

Micrographs obtained with a scanning electron microscope and presented in Figure 17 show the morphology of calcine particles. The particles do appear to be noncrystalline. The active surface area of the calcine powder is 10 to 20 m²/g, which accounts in part for the high calcine reactivity.

"Clean" Waste PW-4b at 2000X

AGNS HLLW and ILLW at 1000X

High-Sodium, PW-6 Waste at 1000X

FIGURE 17. Spray Calcine Photomicrographs

The calcine moisture content is normally less than 1% but can be as high as 4% without significantly decreasing the flowability of the calcine. Calcine nitrate content is a strong function of waste sodium content. Under proper calcination conditions, nonalkali metal nitrates present in the feedstock are converted to oxides. However, calcine from wastes containing alkali metal nitrates contains nitrate in less than stoichiometric quantities. Tests show that from 10 to 75% of the feedstock alkali metal (mainly sodium) nitrate can be decomposed during calcination.

The nitrate content of the calcine significantly affects the thermal stability of the calcine. Ross⁽¹⁹⁾ has studied the maximum storage temperature of calcined PW-4b (low sodium) and PW-6 (high sodium) type high-level wastes. He found that the calcined PW-4b could be heated to 900°C and still be free flowing when cooled. However, calcined PW-6 agglomerated at 310°C or higher because it contained NaNO_3 , which melts at 307°C. He also studied the gas release from calcines as they are heated and found the volume of gas released to be proportional to the nitrate content.

Experience with the calcine shows that it is floodable, it dusts, it is hygroscopic, it is difficult to feed at a constant rate with volumetric feeders, and it has a high surface activity. Bin storing, conveying, or transporting of the calcines is not recommended. However, the calcines make good feed for a pressing and sintering⁽²⁰⁾ or melting process because they are very active. They have also been successfully agglomerated in a disc pelletizer at PNL.⁽²¹⁾

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DESIGN OF A SPRAY CALCINATION FACILITY

Commercial nuclear fuel reprocessors are not currently operating in the United States. Projected startup dates for the first plants on line range from the late 1970s to the early 1980s. Current Federal regulations allow storage of high-level waste as liquid for a maximum of 5 years. However, due to the high cost of high-level liquid waste storage tanks, early solidification is preferred. Thus solidification facilities are needed near the end of the decade.

Since disposal requirements for intermediate-level waste may be similar to those for high-level waste, plans are being formed for mixing high and intermediate-level waste prior to solidification. Such a plant, operating at a nominal 5 tonnes of fuel per day will produce 118 ℓ /hr of combined high- and intermediate-level waste if the waste is concentrated to 567 ℓ /tonne (150 gal/tonne). The capacity required in a solidification facility is dependent largely on the degree of water evaporation performed prior to calcination. If desired, the calciner feed could likely be concentrated to 378 ℓ /tonne (100 gal/tonne) or less. Calciner throughput is also dependent on the volume of the recycle stream from the effluent treatment system. However, due to the small amount of solids penetrating the calciner filters, this stream is small. If 0.1% of the calcine penetrates the calciner filters and the recycle stream particulate content is 2 g/ ℓ , the recycle volume will be less than 8 ℓ /hr. Recycling 2% of the feedstock ruthenium would increase this solids content to 3 g/ ℓ . The total calciner feedrate is thus about 126 ℓ /hr, as shown in the spray calcination flowsheet, Figure 18.

Work in the WSEP program and the WFP has been directed to technology development and demonstration of the total solidification system. The various equipment pieces in the process from liquid waste storage through canister decontamination and off-gas treatment have been developed, and design is currently under way for a full-scale remotely operated and maintained vitrification facility to begin operation in the early 1980s. The spray calciner is an important part of the facility.

	Incoming ^(a) Waste	Effluent ^(b) System Recycle	Calciner Feed	Atomizing Air	Calcined Solids	Filter Blowback Air	Calciner ^(b) Off-Gas
<u>Liquid or Solid</u>							
Flowrate, ℓ /hr	118	8	126		14		
Solids Content, ^(c) g/ ℓ	75	2	70		1,100		
Solids Content, ^(c) g/hr	15,600	16	15,600		15,600		
<u>Vapor</u>							
Flowrate, m^3 /min				0.85		<0.001	3.5
Flowrate, scfm				30		<0.1	122
Solids Content g/ m^3 /min				0		0	0.004
Solids Content g/hr				0		0	16

- a. Combined HLLW and ILLW concentrated to 567 ℓ (150 gal) per tonne of fuel from a 5 tonne/day nuclear fuel reprocessing plant.
- b. Solids content based on 0.1% of total particulates penetrating the filters.
- c. Reported as calcined solids.

FIGURE 18. Spray Calcination Flowsheet for a 5 tonne/day Fuel Reprocessing Facility

PHILOSOPHY OF OPERATION AND MAINTENANCE

The spray calciner and related equipment are inherently simple and will be designed for ease of operation and maintenance.⁽²²⁾ Use of equipment containing moving parts or other low-reliability items is minimized. Those few items requiring moving parts will be designed for maximum reliability and will either be designed for rapid changeout, or, if warranted, an installed spare will be provided. Major pieces of equipment are constructed from material exhibiting a high degree of resistance to corrosion and other operating conditions.

The spray calcination process is easily automated and should require operator attention only for inspection or in the event of off-standard operations. The calcination process is inherently continuous but can easily be adapted to batch operation if conditions warrant. To assure product quality and accountability it may be desirable that the contents of one waste tank be deposited in one solidified waste container. Transfer of waste to the calciner feed tank and tank sampling will likely be batch operations.

Current projections of the in-cell radiation levels while solidifying waste from commercial power reactor fuel indicate that fields up to 10^7 R/hr are to be expected in the solidification cell. Thus sustained use of equipment containing organic materials is to be avoided. Consequently, the process is designed for totally remote operation and maintenance. Insofar as feasible, maintenance will be performed with the overhead crane. All equipment will be fitted with lifting devices and will be arranged in the cell to allow unrestricted crane access. Use of Purex type and other totally remote connectors will be maximized. Where use of a master slave manipulator is required for infrequent maintenance, provision will be provided for its temporary installation and use.

Maintenance activities will be viewed through shielding windows located at strategic locations in the cell wall. The need to use in-cell television for viewing of maintenance activities will be minimized.

Contact maintenance in the solidification cell would require extensive decontamination and is considered unjustifiable from the viewpoints of both economics and personnel radiation exposure.

Instrumentation will be provided to assure safe and economical process control. Local readout of in-cell information will be available in locations as needed, but all control and recording instrumentation plus most of the indicating meters will be located in the control room. Pressure sensing lines connected to the process will terminate at the transmitter, which will be located so that potentially contaminated lines are within controlled areas. All signals transmitted to the control room are electronic.

Extensive experience in operating and maintaining solidification equipment under hot cell conditions was gained during the previous WSEP program. Those operations demonstrated that the spray calciner can be operated and maintained under remote conditions. Much of the equipment used during these tests is described by Schneider⁽²³⁾ and Bond.⁽¹³⁾ The in-cell unit was capable of solidifying about 15 l/hr of radioactive waste, but much of the equipment such as the calciner and filters can simply be enlarged to provide the greater capacity needed for a 5 tonne/day reprocessing plant. Extension of the semi-remote, manipulator-operated features of this equipment to fully remote, crane-operated features is readily achieved in most cases.

EQUIPMENT FEATURES

The components of the spray calciner and feed system were described previously. The equipment described is adaptable to remote operation and maintenance of a full size facility.⁽²²⁾ Further details specifically applicable to a full size solidification plant are included in this section.

The basic functions of the feed system are: 1) deliver pressurized waste to the feed nozzle, 2) monitor the waste feedrate, 3) control the waste feedrate. The basic feed tank functions are: 1) store and continuously monitor the liquid waste volume, 2) maintain liquid homogeneity insofar as possible, 3) remove heat generated by radioactive decay and mechanical

work, 4) allow insertion and operation of the cantilever waste pump and other required equipment, and 5) permit acquisition of a representative waste sample.

The basic functions of the spray calciner are: 1) atomize then dry and partially calcine liquid waste, 2) provide primary effluent decontamination, and 3) deliver calcined solids at a near constant rate for post-treatment such as vitrification. The spray chamber of a calciner capable of sufficient processing capacity is about 75-cm (2-1/2 ft) diam by 2.5-m (8 ft) tall. Including the top-mounted atomizing nozzle and the lower cone, the overall height of the unit is about 4.5 m (15 ft). The sintered metal filters are mounted to one side of the 1.5-m (5 ft)-diam calciner furnace, bringing the overall width to 2 m (7 ft). The cell envelope required is thus 1.5 m x 2 m x 4.5 m (5 x 7 x 15 ft).

Normal maintenance can be completely remote. Potential failure items such as the atomizing nozzle have been designed for replacement using only the cell crane. The atomizing nozzle has been designed into a fully remote Purex connector as have many other equipment components. The capability of multiple pipe connection in this unit permits connection to the calciner as well as coupling to both the atomizing air and liquid waste. Although nozzles are designed to last many months, nozzle replacement can be performed during about 1 hr of down time.

Two side-mounted vibrators are mounted on opposite sides of the calciner to provide redundancy. Wherever practical, backup equipment is installed. Again the vibrators are replaceable with only the in-cell crane and without requiring calciner shutdown. Many of these designed remote features of the full-scale spray calciner are described by Siemens and Bonner.⁽²²⁾

The WSEP radioactive demonstration calciner was so constructed that the entire calciner chamber could be removed by disengaging four bolts. The assembly was placed on the floor, where the furnace could be lifted off for repair or replacement. In the planned calciner, the furnace is designed to lift off the calcination chamber in four sections. Thus additional cell height is not required for furnace replacement should it ever be needed. An alternative concept incorporates the use of a clam shell furnace.

The filters required for a full size calciner can fit into a rectangular box about 50 x 100 x 90 cm tall (1-1/2 x 3-1/2 x 3 ft). As a rule of thumb, about 0.1 m² (1 ft²) of filter surface area is used per liter/hr of waste calcined. Thus a calciner designed for 150 l/hr incorporates about 100, 5-cm diam by 1 m long (2 in. x 3 ft) filters. Experience has shown that at the design blowback conditions (1/4 sec pulse every 10 min) and filter face velocity (about 60 cm/min [2 ft/min]) the agglomerated calcine discharges readily as a cake from the filter and very little is captured by an adjacent operating filter. Also, if at least 1 cm (3/8 in.) clearance is allowed between adjacent filters or the filter housing and the filter, cake bridging between filter elements is not observed.

Calcine is removed from the calciner and transmitted to the melter or other receiver by gravity. All calciner surfaces are sloped a minimum of 60° from horizontal to prevent calcine holdup. Further assurance of calcine transport is provided by the mild vibration of the lower calciner caused by the spray chamber vibrator. It is highly desirable to eliminate calcine holdup. This will help prevent uneven calcine discharge to the next processing step and calcine sintering into large agglomerates due to self-heating.

Calciner off-gas will contain less than 0.1% of the nonvolatile feed constituents but possibly up to 2% of the feed ruthenium. After removal of the condensable portion of the calciner off-gas, the volume requiring further treatment will be only about 1 m³/min (40 scfm) even if 0.3 m³/min (10 scfm) air inleakage is assumed. Parallel decontamination of vapor and liquid effluent streams by wet scrubbing coupled with liquid concentration was effective during the WSEP program and could be used if desired. On the other hand, it is likely that this relatively small amount of noncondensable off-gas can be treated by another effluent system within the plant.

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APPENDIX A: WASTE FIXATION PROGRAM RUN SUMMARIES

At the time of this writing 32 formal test runs have been completed with the WFP spray calciner for a total of well over 800 operating hours. This section contains some details of the individual runs. Much of the information herein is also presented and interpreted in the body of the report.

The spray calciner used in the WFP was originally built for nonradioactive testing during the WSEP program. It was retrieved from storage and reactivated with only a few items such as the filters and atomizing nozzle replaced. Much of this original equipment has since been modified as developments have occurred.

Since the goal of the WFP is to develop complete solidification systems, early runs including 2-8, 10, and 15 were performed coupled to the Inconel 690 continuous metallic melter, and calcine produced was fluxed and melted at 1150°C to form borosilicate glass. The frequent calciner runs at similar conditions during this period were designed largely to gain information about the melter. However, invaluable information on the calciner was gained during this time. Many of the recent runs have been conducted with the spray calciner coupled to the in-can melter.

DSS-1 (Developmental Spray Solidification, Run 1)

This was a short preliminary run, the purpose of which was to shake down the equipment, train the operators, and gain preliminary data on solidifier operation. The equipment for this and several subsequent runs consisted of the 33.6-cm (13-1/4 in.)-ID spray chamber, a Spraying Systems Setup Number 42 atomizing nozzle with a type 303 stainless steel tip, the top-mounted vibrator, and 15 sintered stainless steel off-gas filters. The feed to the calciner consisted of deionized water, and the calciner furnace temperature was set at 700°C. Following half an hour operation at 10 ℓ /hr, the feedrate was increased to 18 ℓ /hr for 1-1/2 hr, after which the calciner was shut down. During the run, a large temperature change in the calciner wall was noted when the feedrate was changed. To minimize this, furnace control was changed from thermocouples near the heating elements to thermocouples welded to the calciner interior. All equipment operated well, and less than 0.03 m³/min (1 scfm) air inleakage was observed.

DSS-2

This was the first spray calcination test in the WFP with simulated waste. The clean, GE type high-level waste designated PW-4b was calcined at the nominal composition, 378 ℓ /tonne of fuel. It presented no operating problems in the spray calciner or the attached continuous metallic melter. The run lasted 5.5 hr at a feedrate of 6.5 ℓ /hr. During the run a misaligned seal in the in-line feed pump began leaking and required replacement. The calciner furnaces, which are controlled by calciner wall temperature, were observed to operate about 50°C hotter than the wall. Prior to service, the spray calciner wall was sand blasted preparatory to determinations of wall thickness. After the run, the same texture was observed, indicating essentially no scale buildup on the wall. Filter permeability was observed to markedly decrease as a steady-state, 2-mm (1/16 in.) calcine layer built up. During the run the permeability decreased from 13 to 3.5 ft/min-in. of water.

DSS-3

During this run, PW-4b waste composition was calcined at 16.5 ℓ /hr for 5.5 hr. Again the melter was connected to the calciner. The calciner feedrate was uniform throughout the run. The electromagnetic flowmeter coupled to the automatic valve controlled the feedrate to within 1 ℓ /hr of the set point. Several times during the run, feedrate spikes were observed; these were apparently due to solids momentarily lodging in the control valve, resulting in controller action. No plugging problems were observed in the 3-mm (1/8 in.) atomizing nozzle orifice, the 2.5-mm (1/10 in.) flowmeter or the 20-mesh strainer in the feedline. However, many pieces of scale and foreign material large enough to plug the flowmeter and/or spray nozzle were removed from the strainer. Opaque depositions on the tube of a rotameter placed in series with the electromagnetic flowmeter rendered the rotameter unreliable. After the run it was removed from the line.

During the run a leak occurred in the atomizing nozzle cleanout needle packing, and the calciner was shut down while the packing was tightened. Otherwise operation was very smooth. After the run a skirt of calcine about

3 mm (1/8 in.) long by 1 cm (3/8 in.) OD by 1 mm (1/32 in.) thick was observed around the spray nozzle tip. It is probable that a spot of calcine observed on the calciner wall following the run resulted from irregular flow patterns caused by the uneven deposition in the nozzle. The spot of scale was about 30 cm (1 ft) in diameter and about 1 mm (1/32 in.) thick. The lower 20 cm (8 in.) of the calcination chamber where it is not heated was observed to be covered with a uniform 2-mm (1/16 in.) scale. Filter inspection showed calcine coatings similar to that following run 2 on all but three filters. Each of these had a coating about 3 mm (1/8 in.) thick over the entire element. Investigation showed that the blowback airline to these three elements was partially blocked. After repair one pulse restored the three filters to normal appearance.

DSS-4

This run was conducted with PW-4b waste at a feedrate of 15 l/hr. During the 9.2 hr of constant operation, attempts to obtain an internal temperature profile were not successful. It was observed that with the instrumentation in use, the flowrate can vary by about 0.5 l/hr over a period of 15 min. Internal temperatures are very sensitive to liquid feedrate, and thermocouples available did not respond rapidly enough to obtain a reliable temperature scan. It was learned, however, that 25 cm (10 in.) directly below the spray nozzle the probe temperature was greater than 350°C, indicating that drying was nearly complete at that point. As the probe approached the nozzle the temperature dropped rapidly. Post-run inspection showed that the wall scale spot observed following run 3 had grown to about 2 ft diam. The atomizing nozzle was subsequently removed and inspected, then operated in a transparent calciner mockup; but no significant irregularities in the nozzle or spray pattern were observed.

DSS-5

The objective of this run was to determine the calcinability of waste containing large amounts of sodium. The waste tested contained 2M sodium and was representative of the then projected AGNS high-level waste designated

PW-6. During the 8-hr run the calciner feedrate was varied from 5 to 10 ℓ /hr. Feed to the calciner was very steady at feedrates greater than 5 ℓ /hr, but two feed nozzle plugging incidents occurred at the lower feedrates, necessitating use of the cleanout needle. Once after being completely plugged for 8 min, the nozzle cleared itself; but by this time the automatic control valve was wide open, allowing a momentary feed surge of over 50 ℓ /hr. These major process upsets produced no observable ill effects in the calcination chamber or the filters. Post-run inspection showed a 1 to 2-mm thick deposit on the upper half of the calciner wall. Furnace temperatures during the run indicate that the scale buildup reached dynamic equilibrium after 2 hr run time, and little change was observed during the last 6 hr of the run. Calcine from the run contained less than 1% moisture, and over 30% of the NaNO_3 was decomposed in the calciner. Samples of sodium-containing calcine are observed to be more cohesive and less dusty than calcine low in sodium.

The deentrainment of particulate solids effected by the sintered stainless steel filters progressively increased with aging of the filter precoat. Deentrainment factors measured by sampling calciner effluent streams were as high as 24,000 during the run.

DSS-6

High-sodium PW-6 waste was calcined at feedrates of 8, 12, and 15 ℓ /hr during a 42-hr run. During the run atomizing nozzle plugging occurred as often as hourly. Feed flow was restored by activating the cleanout needle. Frequent use of the cleanout needle necessitated frequent tightening of the packing gland around it. Eventually the packing net bottomed out, and the calciner was shut down for nozzle replacement. Subsequently a bellows seal for the cleanout needle was designed and built into a nozzle jumper. Loss of the caustic scrubber pump also required a shutdown. To get longer term operational data, the calciner wall scale established during run DSS-5 was not removed, and after run 6 no change in wall scale was observable. As indicated by furnace temperatures, the scale thickness did not change during the run. Samples of calcine taken at feedrates of 8 to 15 ℓ /hr show little if any difference in water and nitrate content.

During the run, hot off-gas from the filters was routed directly to a 35-cm (14 in.)-diam scrubber filled with 25-cm (1 in.) raschig rings. In the scrubber, upflowing off-gas was quenched and scrubbed with 6M NaOH. As evidenced by readings from thermocouples placed at 30-cm (12 in.) intervals in the packed column, nearly all heat transfer was made in the lower 30 cm (12 in.) of packing.

Decomposition products of the various nitrate compounds in the feed were observed to react with and neutralize the caustic. With PW-6 feed in runs 5 and 6 about 6 moles of caustic were neutralized per liter of feed with only 3M HNO₃ in the feed. With PW-4b feed (1M HNO₃) in runs 2, 3, and 4 about 1.5 moles caustic were neutralized per liter of feed.

DSS-7

This 40-hr run at 16 g/hr with PW-4b waste was uneventful. The feed-rate during the run seldom varied by more than 10% of set point, and the cleanout needle was not needed. Post-run inspection revealed a skirt of calcine deposited around the hole in the nozzle tip. The deposit was about the same size as one observed following DSS-3 but was heavier at the base and tapered to a summit in a volcano shape. The similarity in deposit size after 8 hr operation in DSS-3 and after 40 hr in DSS-7 indicates that the deposit observed was likely at steady state. Prior to the run both the spray chamber and filters had been water washed. After the run a 0.5-mm deposit was observed uniformly over the calciner interior. Furnace temperatures during the run indicated that deposit causes little resistance to heat transfer. Power consumption of 22 kW in the upper zone compared to 12 kW in the lower zone shows that most of the drying occurred in the upper half of the calciner.

Investigation of filter blowback effects was a major part of run 7. During the first 15 hr of operation the filter differential pressure increased to 25 cm (10 in.) of water, then remained at that level for the remainder of the run. Changing blowback conditions had only a temporary effect. It was observed that short 1/4-sec pulses of blowback air are just as effective as longer pulses and greatly reduce calciner pressurization during blowback.

DSS-8

This run was made to study the capacity of the 13-1/4-in. spray chamber using PW-4b waste at a reference concentration of 378 l/tonne of fuel. During the run over 580 liters of feed were consumed in 20 operating hours. Unfortunately, the calciner feed nozzle and filters were designed for 15 to 20 l/hr, and alterations were required to allow operation at high flowrates. The volume ratio of liquid to air in the atomizing nozzle was maintained constant to retain a mass median droplet size of about 75 μm . The necessary liquid pressure available from the feed pump was insufficient; thus two pumps were operated in series for subsequent tests. The filters were bypassed when the differential pressure became large enough to allow calciner off-gas to bubble through the emergency pressure release seal pot.

To determine the flowrate at which wall scaling becomes excessive, the water feedrate was increased hourly by 3 l/hr until calcine samples showed evidence of moisture or furnace temperatures indicated that scaling was occurring. At a wall temperature of 700°C this occurred at a flowrate of 38 to 45 l/hr. This value is conservative since at this flowrate insufficient pump pressure was available and the atomized droplet diameter was about 100 μm .

A short calcine production run was made at the same conditions as DSS-8 except that the PW-4b waste was concentrated to 225 l/tonne. The run was prematurely terminated at a liquid feedrate of 35 l/hr, before scaling became apparent. From this data, concentration appears to have little effect on calciner capacity.

DSS-9

The objective of this run was to determine the feedrate at which calciner wall scaling becomes excessive when calcining clean PW-4b waste at a wall temperature of 550°C. The run was very similar to DSS-8 in operational approach and in results except that the maximum feedrate at this wall temperature is 24 to 30 l/hr.

Calcine samples collected near the end of each flowrate step consistently contained less than 1% water and volatile nitrates. This data suggests that the 2-m (6-1/2 ft)-long calciner is longer than necessary. With Spraying Systems Setup No. 42 operating in the 33.6-cm (13-1/4 in.) calciner, the theoretical point of droplet impingement on the wall is 86 cm (34 in.) below the nozzle. At this point the calcine must be dry enough not to stick. Since this is less than half the calciner length, the lower zone apparently removes only a small residue of volatiles.

DSS-10

The objective of this run was to study the behavior of ruthenium in the calciner-melter system. Due to the high cost of ruthenium the waste contained only 10% of the as-defined value for PW-4b waste. The calciner was operated alone for 6 hr at wall temperatures of 700°C and 550°C, with the calcine being collected in a drum. The metallic melter was then connected, and operation continued at various melter conditions for 9 additional hours. Finally the melter was disconnected, and the calciner was operated for 1-1/2 hr to reconfirm the starting point. Isokinetic samples of vapor streams and dip samples of process tanks were taken throughout the run, then analyzed at the conclusion. Virtually all the ruthenium observed in the off-gas was in the condensate. During the "calciner only" portion of the run about 0.2% of the ruthenium was analyzed in the off-gas. However, after connection of the melter, the first condensate tank sample showed an inordinately large amount of ruthenium. A step ruthenium concentration increase also occurred coincident with melter disconnection. When these step increases are taken into account, about 2.4% of the total feedstock ruthenium was volatilized. Additional work is needed to determine whether 0.2% or 2.4% is the actual volatilization value during sustained operation.

Off-gas samples collected downstream of the caustic scrubber were analyzed and found to contain only 0.1% N₂O and 0.1% NO.

DSS-11

During this run the calciner capacity was investigated when processing high-sodium waste. The run plan was very similar to those for runs 8 and 9. The 11-hr run showed that with a 700°C calciner wall and the top-mounted vibrator, the 13-1/4 in. calciner capacity was 33 to 39 l/hr. Operation of the feed system is definitely improved at feedrates over 10 l/hr. Feedrate fluctuations were virtually nonexistent, and the cleanout needle was not used. Operation with a perpetual scale layer on the calciner interior renders the instrumentation less sensitive, and it becomes difficult to ascertain calcine dryness from internal temperatures. Sampling the calcine after operation at each feedrate was the only sure way to know when capacity had been exceeded.

DSS-12

Following run DSS-11 the 33.6-cm (13-1/4 in.) calcination chamber was removed and replaced with a 53-cm (21 in.) inside diameter unit. The calciner furnace is large enough to accept the larger unit, but the connection point on the existing base is not. The lower 30 cm (1 ft) of the larger chamber was thus tapered to avoid major modifications.

Run DSS-12 was intended to determine the capacity of the 53-cm (21 in.) calciner while processing clean PW-4b waste at a wall temperature of 550°C. During the 14-hr run, over 600 liters of simulated waste were calcined at flowrates up to 63 l/hr. At this flowrate the atomizing nozzle was unable to produce the normal small droplets. It was also observed that the furnace was unable to produce sufficient heat and furnace temperatures were lower at high feedrates. Thus the calciner chamber capacity at a wall temperature of 700°C is well above that possible with the existing feed system, furnace and the Spraying Systems Setup No. 42 nozzle.

While processing PW-4b simulated waste in runs DSS-8, 9 and 12, maximum capacity was sharply delineated since eventually a flowrate was reached at which wet droplets stuck to the normally clean wall, reducing heat transfer and producing more wet droplets. About 10 min from the time that furnace temperatures indicated wall scaling, calcine samples were wet.

DSS-13

During this run the 53-cm (21 in.) calciner capacity when processing high-sodium PW-6 waste was determined. The capacity was found to be 38 to 42 ℓ /hr at a calciner wall temperature of 550°C and 62 to 65 ℓ /hr at 700°C. As usual during operation, the calciner feedrate was increased hourly by 3 to 5 ℓ /hr until the point was reached at which the calcine moisture content approached 4%. The nozzle cleanout needle was used about hourly during the run to restore atomizing air flow. The run began at a wall temperature of 550°C. At a flow-rate of 40 ℓ /hr, calciner temperatures and calcine moisture content indicated that capacity was being approached. Thus the wall temperature was increased to 700°C and the run continued.

When calcining PW-6 reference waste composition, an equilibrium wall scale thickness is maintained which gradually increases with feedrate until an unacceptably moist calcine is produced. There is no well defined maximum capacity such as observed with nonsodium waste. While processing high-sodium wastes the amount of scale on the wall varies with many factors and can be decreased by:

1. increasing the vibration intensity
2. increasing the fraction of time the vibrator is acting
3. increasing the wall temperature
4. decreasing the droplet size
5. decreasing the feedrate.

A decrease in scale thickness is ascertained from:

1. increased calciner furnace temperatures (if furnace control is by wall temperature)
2. increased power consumption
3. increased off-gas temperature
4. decreased calcine moisture content.

DSS-14

This run was planned to confirm high flowrate operation prior to the long-term reliability run. The run was conducted with PW-4b waste and lasted 7.5 hr. A "hardened" atomizing nozzle tip was procured for the long run and tested during this run. As was later learned, the tip was type 404 stainless steel and was attacked by the nitric acid in the feed. Shortly after startup the feed pressure at the nozzle began to decrease, and after 1-1/2 hr the nozzle was removed to investigate. It was observed that the original 3-mm (0.125 in.) orifice had enlarged to 8 mm (0.3 in.). Surprisingly the calciner wall scale was no more than the usual thin film. A previously used type 303 stainless steel nozzle was installed, and the calciner was operated uneventfully for about 6 hr at 50 l/hr.

DSS-15

The objective of the run was to demonstrate the long-term reliability and capacity of the spray calciner coupled to the Inconel melter. During the run, 11,300 liters of PW-4b waste were calcined in 510 hr at flowrates of 15 to 55 l/hr. Over 1 tonne of calcine was produced, and although the melter was connected during only part of the test, 2.4 tonnes of borosilicate glass were produced.

The calciner feed system functioned well during the run with few interruptions. Only once was the nozzle cleanout needle used, and then only to remove calcine caked in the nozzle as a result of shutdown without a nozzle flush. Frequently solids would lodge in the control valve, causing feedrate spikes of up to 50 l/hr. Feed nozzle wear during the run was appreciable, and calciner wall scaling was found to be significantly affected by wear in the nozzle. The measurable wear occurred inside the air nozzle where liquid feed is atomized and ejected at near sonic velocity by the pressurized air stream. After 245 hr of operation at 15 l/hr the air nozzle orifice had enlarged by 0.25 mm (0.01 in.), corresponding to a 15% enlargement of flow area. Thereafter, air nozzles were changed at the first indication of nozzle wear. After 415 hr of run time a feed pump casing gasket failed, necessitating changeout of the pump. The leakage was started by insufficient tension on the holdown bolts.

The filter system on the EDL-102 spray calciner was designed for a feed-rate of 15 ℓ /hr. Since feedrates of 55 ℓ /hr were planned, a venturi scrubber was placed in parallel with the filters to carry the extra load. The scrubber was installed in such a way that water could seep into the calciner, causing the wall scaling and calcine moisture content to increase. Problems were also experienced with calcine settling in the 6-cm (2-1/2 in.) diameter piping to the venturi.

Long-term operation of the heated-wall spray calciner during run DSS-15 exhibited a slow buildup of wall scale which was not removed by the top-mounted wall vibrator. The cause of the scaling is not fully understood, but it appears that the buildup is very slow. Wall scaling was not excessive after 12 days of operation early in DSS-15. Replacing a worn nozzle appeared to decrease the rate of wall scaling. Apparently scaling is accelerated by improper flow patterns from a worn air nozzle.

The slow scale buildup during the run was observed by the slow decline in furnace power required to maintain the wall at constant temperature. Other wall scaling indications were decreasing calciner off-gas temperature and increasing nitrate content in the calcine.

Wall scaling severe enough to cause calciner shutdown occurred twice during the run. The first severe scaling occurred 336 hr into the run just after water from the venturi scrubber began dripping into the calciner. This water appears to have started rapid scaling, requiring calciner shutdown. The second wall scaling problem accelerated rapidly after beginning operation at 55 ℓ /hr. At this flowrate the feed nozzle is unable to maintain the usual 70- μ m droplet size, and droplets 100 μ m in diameter were produced, which have three times the volume of normal droplets.

Several areas for design changes were pointed out during the long run. Furnace control based on one wall thermocouple functions well when the wall has a uniform scale thickness but can lead to improper control when only part of the inner wall is scaled over. Two or more wall thermocouples located opposite each other or the furnace temperature should be used.

Some problems were experienced with the calciner vibrator. Due to the heat at the top of the calciner where the vibrator was located, after about a week of operation the vibrator had to be removed and the piston cleaned and lubricated.

Performance of the sintered stainless steel calciner off-gas filters was generally good throughout the run. The filter differential pressure (DP) was adversely affected by increases in either vapor velocity through the filters or solids loading on the filters but returned to about 25 cm (10 in.) of water whenever the calciner feedrate was reduced to the filter design feedrate. 15 g/hr. At one point moist calcine wet the filters, but within an hour the differential pressure returned to normal. About 142 hr into the run the filter DP began to increase inexplicably and did not respond to blowback changes. Just before calciner pressurization, part of the off-gas was bypassed through the venturi scrubber. In less than half an hour the filter differential decreased and normal flow through the filters resumed. Whenever the solids loading to the filters was reduced for a short time the filters renewed themselves, and after resumption of normal filter loading the filter DP improved.

As determined from the total solids gained in the condensate, scrubber solution and scrubber effluent sampler, particulates passing through the off-gas filters were 0.5% to 0.05% of those contained in the calciner feed. As usual, higher decontamination was achieved after a steady-state, 2-mm (1/16 in.) coating of calcine was obtained on the filters. The off-gas decontamination function of the condenser and scrubber performed well, as described in previous reports. About 70% of the particulates collected in the scrubber, 30% in the condenser, and less than 1% in the scrubber off-gas.

Early in the run a differential pressure across the scrubber developed and steadily increased, eventually causing a system shutdown. The blockage was traced to NaNO_3 accumulations in the horizontal vapor inlet line to the scrubber. Improper design of the scrubber allowed NaOH from the scrubber to splash into the vapor inlet line where it reacted with incoming HNO_3 vapors, forming solid NaNO_3 . Periodically flushing the line with water eliminated the blockage.

Early failure of improperly tightened seals necessitated replacement of the caustic scrubber pump. Later pump overloading problems were eliminated by increasing the pump discharge pressure.

DSS-16 and 17

Runs 16 and 17 were made to produce the reference calcines, PW-4b and PW-6 respectively. The feeds for these two runs contained full levels of silver, cesium, ruthenium, rubidium, yttrium, and rare earth elements rather than the less expensive substitutes for these elements normally used when making process development runs (see Appendix B). Operational problems were not encountered during either run.

Because the purpose of these runs was the production of reference calcines, the runs were of short duration and testing of operating parameters was not a major consideration. However, a number of observations were made.

The air cap on the feed spray nozzle had an attached thermocouple, and the temperature of the cap was recorded during all phases of both runs. The recordings show that for feedrates of 16 to 17 ℓ /hr and calciner wall temperature of 680 to 775°C, the normal air cap operating temperatures were 325°C for PW-4b and 200 to 300°C for PW-6 feeds. The maximum temperature experienced by the air cap was 465°C. This temperature was seen during heatup and cool-down of the calciner when only atomizing air was flowing through the nozzle at a rate of 4 m^3 /hr (2.5 scfm). The nozzle air cap received thermal shocks when the feed was turned on and off. The greatest shock occurred when the feed was shut off and the cap temperature increased from 260°C to 420°C in less than 3 min.

Because of the potentially volatile nature of cesium, ruthenium, and tellurium, condensate and caustic scrubber solutions from the off-gas treatment system were analyzed for traces of these elements following both runs. In all instances the levels of these elements in the solutions were below detection limits. Thus less than 0.5% of the Ru and 0.8% of the Cs was volatilized from the calciner.

DSS-18

The objective of the run was to calcine simulated AGNS high-level waste for the first time. Also it was planned to evaluate for the first time each of the following: a spray nozzle with a B_4C insert, a bellows sealed clean-out needle assembly, and vibrators acting on the side of the spray chamber.

A total of 711 liters of AGNS HLLW was calcined in 39 operating hours. The spray calciner was operated for periods of 5 to 12 hr a day for 5 days. When the feed was not being pumped to the calciner, the calciner wall temperatures were reduced to $500^{\circ}C$, air was passed through the nozzle at a rate of $0.8 \text{ m}^3/\text{hr}$ (0.5 scfm), the filter blowback cycle was increased to 15 min, and the vibrator was turned off. No problems were experienced while running the calciner in this intermittent manner, and use of the nozzle cleanout needle was never required to restart feed flow. Daily startup and shutdown typically required 15 min.

The feedrate was increased from the usual 15 ℓ/hr to a maximum sustained rate of 23.6 ℓ/hr . The limiting factor was the filter pressure differential. In contrast to some previous experience, the pressure drop across the filters became constant within a few hours of the start of operation each day and remained constant as long as the feedrate remained unchanged. This stability permitted trouble-free operation of the spray calciner at feed flowrates which are considered high for the capacity of the off-gas filters. Examination of the filters following the run showed that they were uniformly coated with about 1 mm of soft, fine powder penetrated by pin holes. The solids deentrainment factor reported is low because during operation at high flowrates the seal pot was blown several times. When this occurs, calcine comes directly into the condenser. This increases the chromium, nickel, and iron content of the condensate and scrubber solution.

Several modifications to the spray calciner system were evaluated during the run. One modification was use of an air cap on the atomizing spray nozzle. The cap was made of 304 stainless steel and fitted with a B_4C insert in the critical wear area. Measurements were made before and after the run using a machinist's microscope with a precision of $8 \mu\text{m}$ (0.0003 in.). These showed

that the spray orifice diameter had increased 46 μm (0.0018 in.) at the exit and an average of 300 μm (0.0117 in.) at the internal mixing end. This wear data and that of the previously used 303 stainless steel air caps cannot be directly compared because no measurement data has been collected on the latter caps. However, the performance of the carbide insert is considered an improvement because no deterioration of the feed flow characteristics were noted during the 30-hr run. Indications of wear on the 303 stainless air cap were noted within 29 to 31 hr of run time at elevated feedrates during a previous run, DSS-15.

The B_4C insert was not affected by at least seven thermal shocks of 200°C temperature change in a few seconds when feed or water flow through the nozzle was turned on or off.

Due to previous problems with a packing gland seal around the nozzle cleanout needle, a nozzle was designed to replace the packing with a bellows. The cleanout needle worked well when tested at the beginning of the run, but was not used subsequently during the run. When inspected at the end of the run, signs of leaks were not observed.

Only one side-mounted vibrator was used during the run. Wall scaling was anticipated because of the sodium in the feed, but an examination of the calciner interior following the run showed less scale than usual during runs using low-sodium feed. Inspection of the spray chamber showed no measurable distortion of the barrel or impact pads due to the vibrators.

DSS-19

The objective of this run was to demonstrate direct coupling to the incan melter. The calciner operated uneventfully, producing a consistent flow of PW-7 calcine to the melter at a liquid feedrate of 18 ℓ/hr .

DSS-20

The purpose of the run was to produce "supercalcine" in engineering-scale equipment. "Supercalcine" is an advanced waste concept being developed as part of the WFP by Penn State University. The main objective is to add

to the waste selected components such that when the waste is calcined and subsequently heat treated at temperatures of $\sim 1050^{\circ}\text{C}$ stable, durable crystal-line products are formed.

The spray calciner operated very smoothly. The cleanout needle was not used, and the spray chamber showed no signs of fouling. The run was made with feedrates ranging from 16 to 25 ℓ/hr for a total run time of 7 hr.

DSS-21

The objective of the run was to evaluate vibrator effectiveness under off-standard conditions and produce calcine for glass melt studies. Fouling conditions were introduced by decreasing the atomizing air flowrate to about half the normal value. This tripled the feed droplet size and allowed moist particles to strike the hot calciner walls. During this time the vibrators were deactivated to assure accumulation of wall scale. The scale buildup was visually monitored through a viewport installed in the calciner top flange. In two sets of runs, the vibrators were off for about 6-1/2 hr. The scale accumulation was up to 6 mm (1/4 in.) thick in places, but still the calcine product was dry. When the vibrators were activated, a single 3-sec pulse from one vibrator was sufficient to remove all scale.

A series of runs was conducted in which the vibration cycle was varied from 1-1/2 to 30 min under fouling conditions. The spray chamber was maintained clean at both time cycles.

A total of ~ 800 liters of AGNS simulated waste was calcined in about 45 hr at feedrates ranging from 16 to 21 ℓ/hr . After the run, microscopic examination of the ceramic air cap failed to show any wear (less than $13\ \mu\text{m}$ [0.0005 in.]). Adverse effects of thermal shock during startup or shutdown of the spray calciner were not observed.

DSS-22

The objective of the run was to produce supercalcine and further investigate the vibrators and effects of the supercalcine on the filters. During the run the spray chamber was operated at a feedrate of 17 ℓ/hr for 4 hr.

Run startup was delayed momentarily by a plugged nozzle resulting from failure to water flush the nozzle at the end of the previous run. The nozzle blockage was removed by pressing the cleanout button which activates the remote pneumatic cleanout needle. Thereafter, operation was uneventful. Following the run the spray chamber was free of scale, and only the normal dust film coated the filters.

DSS-23

The objective of the run was to confirm the operability of the spray calciner with NFS simulated HLLW. During the run the spray calciner was coupled to the in-can melter. Due to the demonstration nature of the run, operation was at 15 ℓ /hr for 3.5 hr. The only unusual event was that filter differential pressure increased slightly from 12.5 to 14 in. of water during the run.

Preparations for the run began about 1 week before the visit of NFS personnel. In this short time, the waste and melt compositions were developed and the equipment was readied. Because of the confidence in the process the first test was conducted during their visit. As usual the process performed without problems.

DSS-24

The objective of the run was to evaluate an atomizing nozzle with a 6-mm (1/4 in.) orifice (Spraying Systems Company Setup No. 72) during long-term operation of high feedrates.

To allow operation at these feedrates, the filters were bypassed and the calciner off-gas was allowed to directly enter the condenser tubes. To preclude plugging of the condenser with calcine, a spray nozzle was fitted into the condenser and used to flush solids from the tubes during operation.

During the test, the calciner was operated at 50 ℓ /hr for 7 hr without difficulty. The feedrate was then gradually increased to 76 ℓ /hr and held for 40 min. At this feedrate the existing calciner furnace could not maintain the wall temperature at 700°C. Although thermocouples were not attached to the wall, previous data indicates that the wall temperature was well below

500°C at these conditions. Also, at 76 ℓ /hr the building vacuum system could not maintain the desired vacuum of 25 cm (10 in.) of water in the spray calciner unit. The run was thus terminated.

The piping installed to bypass the filters contained a short horizontal section. Early in the run calcine deposition in this section required shutdown. The problem was eliminated by installing a pressurized air line at the problem area and blowing with air every 10 to 15 min for about 1/2 min.

The new feed atomizing nozzle performed very well, routinely producing calcine containing less than 1% moisture. According to the manufacturer, to obtain a droplet size of less than 70 μ m the ratio of atomizing air pressure to liquid pressure should be greater than 2. At 76 ℓ /hr a liquid pressure of 1.5 atm (20 psig) and an atomizing air pressure of 3 atm (40 psig) were effective.

The side-mounted vibrators prevented accumulation of calciner wall scale, even after the power to the furnace in zone 2 was tripped off twice, causing the furnace to be down a total of $\sim$ 20 min due to a faulty alarm system. Each vibrator was set to alternately vibrate the chamber with a 3-sec pulse every 1-1/2 min. Visual inspection after the run showed the chamber was very clean, but small patches of scale buildup ranging up to about 3 mm (1/8 in.) thick were observed in the cone. These deposits probably formed during the furnace outage.

DSS-25

The objective of the run was to evaluate the spray calciner's ability to process simulated AGNS ILLW containing mainly sodium cations. After an initial mishap the run proceeded smoothly. At the conclusion of the 3-hr, 15 ℓ /hr run the calciner interior was very clean. The spray calciner product contained 1.8 to 8.3% moisture and was of nonuniform size, ranging from the usual powder to crusty 2-mm (1/16 in.)-diam agglomerates. The calcine nitrate content was about 10%, corresponding to decomposition of about 90% of the NaNO_3 during processing.

A mishap occurred at the beginning of the run: the atomizing air was accidentally overlooked, allowing a stream of feed to dribble into the calciner for ~10 min. Normally the atomizing air keeps the nozzle cool enough to prevent thermal shock of the ceramic nozzle insert when the cool liquid waste is introduced. In the absence of atomizing air the nozzle was near 700°C when the liquid was introduced. Following the run the ceramic tip was observed to have fractured into three pieces, which were held in place by the retaining ring. Future nozzles should be designed to minimize possible thermal cracking, and measures should be incorporated to preclude loss of atomizing air.

Prior to the run the ceramic nozzle had accumulated about 48 hr on the spray calciner and over 900 hr on the nozzle test station without measurable wear (<13 μm).

During the short run, a gradual buildup of filter differential pressure was observed, which may or may not be significant. This may have been a result of poor waste atomization caused by the cracked nozzle. It may also have been due to sodium nitrate melting of the filters. The filter powder coating contained a significant fraction of sodium nitrate, and the filter chamber temperature during the run was well above the sodium nitrate melting point. Future high-sodium runs will be conducted with filter temperatures of less than 300°C.

DSS-26

The objective of the run was to investigate the possibility of locating the filter blowback valves out of the cell and producing calcine for glass melt studies using simulated AGNS HLLW. The spray calciner was operated at 18 ℓ/hr for 10 hr, producing ~40 kg of calcine. Results were encouraging, and testing will be continued for long-term operational data.

DSS-27

This short run was intended to study the in-can melter and to continue evaluation of the filter blowback system. The spray calciner was operated at 20 ℓ/hr for 3-3/4 hr using AGNS simulated waste.

During the run, filters were allowed to accumulate calcine for 75 min before being cleaned by filter blowback. To provide more regular calcine discharge, 20% of the filters were pulsed every 15 min. As anticipated, the filter differential pressure was slightly higher than when pulsed more frequently, but the results of the test were very encouraging.

DSS-28

The objective of the run was to evaluate the spray calciner's ability to calcine simulated reprocessing plant startup and shutdown waste. In this waste composition 94% of the cations are sodium.

The drying chamber temperature was set at 480°C to assure about 250°C at the filter housing and thus avoid melting of sodium nitrate on the filters.

A 4-1/2 hr run was made at 15 ℓ /hr with only a few minor problems. The vibrators were not operating properly during the first half of the run. One of the vibrators was not aligned properly and was malfunctioning. The other vibrator cam switch was accidentally set such that it did not activate. The vibrator problems were discovered and corrected about halfway through the run.

An unusual scale buildup around the feed nozzle was observed during this run. The nozzle plugged 2 hr into the run, and use of the pneumatic cleanout needle was necessary to clear it. A gradual temperature decline observed at the feed nozzle tip thermocouple indicated scaling. However, after the vibrators were functioning normally, a periodic descaling of the nozzle occurred every 20 to 30 min, as was shown by the recorded temperature profile of the spray nozzle tip. A sharp nozzle temperature increase of about 25°C indicated that the buildup had been dislodged.

The spray calciner ran smoothly for the last half of the run. The calcine produced was a buff, dry product. However, post-run inspection revealed a glossy brown scale on the upper half of the chamber while the lower half showed indications of molten material trickling down to the cone area. The cone area was covered with a layer and drippings of a hard yellowish-green material. It was judged that long-term operation would not be practical with this feed composition and these operating conditions.

The filters showed an accumulation of powder, but only a slight filter pressure drop increase to 38 cm (15 in.) of water was noted. There was also an accumulation of calcine in the cone area below the filters.

DSS-29

The objective of the run was to obtain information on the amount of ruthenium lost during calcination either by volatilization or simply carried over by calcine that penetrated the sintered stainless steel filters. Simulated NFS HLLW (PW-8a) was spiked with 0.0065M of Ru (11% of the as-defined concentration).

A 13-1/2-hr run was made at 15 l/hr without problems. The spray chamber was maintained between 750 and 800°C, and the filters were blown every 30 min. Condensate and scrub solution samples were analyzed for ruthenium.

Less than 0.7% of the ruthenium metal was observed in the scrub and condensate tanks. However, analysis of the calcine fails to account for about 4% of the ruthenium metal. Visual inspection of the condenser showed signs of calcine agglomerating and forming some tiny spheres about 0.3 mm (0.01 in.) in diameter. The spheres have the same chemical composition as the calcine.

DSS-30

This run was a continuation of run DSS-28 in developing a method for calcining high-sodium feed solutions such as startup-shutdown waste. Laboratory tests were conducted using SiO_2 to react and decompose sodium nitrate to form a water glass as shown in the following equation:

Thermogravimetric studies indicate that complete decomposition is achieved at 720°C. Thus for the run the spray calciner chamber was maintained between 720 and 750°C.

Diatomaceous earth (89 wt% SiO_2) was added to the sodium nitrate feed solution on a 2 to 1 weight ratio. The amount of SiO_2 is enough for the conversion of liquid waste to a borosilicate glass. A positive-displacement pump was used to pump the very abrasive feed solution. The feedrate varied considerably due to problems with the pump.

An average flowrate of 15 l/hr was maintained throughout the 4-hr spray calciner run. The spray calciner operated very smoothly; however, the filter pressure drop steadily increased to 46 cm (18 in.) of water but suddenly dropped 10% near the end of the run. The filters were blown every 20 min. The off-gas temperature at the filters was $\sim 450^{\circ}\text{C}$. At this temperature the high NaNO_3 content of the powder caused it to adhere and accumulate on the filters. A 5 to 10-mm calcine layer accumulated on the filter and was not removed by blowback.

When the spray chamber was visually inspected, it was observed to be covered with a white-green glassy scale. The glassy scale was not removed by the vibrators.

Thermogravimetric analysis of the product and scale indicates that the scale contained very little nitrate (about 2.5 wt%) but that the calcine product contained 19 wt% nitrate.

DSS-31

Due to the formation of water glass on the chamber during run DSS-30, run 31 was made under similar conditions except that the spray chamber temperature was dropped from 750 to 575°C , decreasing the off-gas temperature at the filters from 450°C to 290°C .

DSS-31 was discontinued, however, after 2 hr due to a high pressure drop across the filters. The filters were heavily coated with calcine from the previous run which was not removed even after several blowback cycles. DSS-31 run was attempted with the coated filters, anticipating improved performance at lower temperatures. However, the pressure drop gradually increased, thus forcing to shutdown. Visually inspected, the spray chamber was seen to be free of scale but with the usual film coating.

DSS-32

The objective of run DSS-32 was to study the effects of the high-sodium feed during calcination. It was a continuation of run 31. Before run DSS-32 was made, the filters were removed from the spray calciner and cleaned by soaking in dilute nitric acid.

The run proceeded smoothly for 4 hr, at which time problems with the feed pump forced a shutdown. During the run wall scaling and filter blinding were not indicated. Post-run inspection confirmed the same. The spray chamber contained only the usual calcine film, and the filter coating was also normal. Since the vapors entering the filters were 290°C, which is below the NaNO_3 melting temperature, the calcine was not sticky and appeared to release from the filters easily.

Table A-1 summarizes the data from the 32 developmental spray solidification runs.

TABLE A-1. Operating Data and Results from Spray Calcination Tests

Run Number	1	2	3	4	4B	5	6	7	8	9	10	11	12	13	14	15A	15B	15C
Date	6/28/73	7/11/73	7/20/73	8/3/73	8/3/73	8/21/73	9/12-14/73	10/9-11/73	11/2/73	11/12/73	12/6-7/73	12/13/73	1/4/74	1/10/74	1/30/74		2/11-3/4/74	
Feed																		
Type	Distilled water	PW-4b	PW-4b	PW-4b	PW-4b	PW-6	PW-6	PW-4b	PW-4b	PW-4b	PW-4b	PW-6	PW-4b	PW-6	PW-4b	PW-4b	PW-4b	PW-4b
Specific gravity	1.0	1.17	1.15	1.15	1.15	1.4	1.38	1.17	1.16	1.16	1.16	1.39	1.14	1.38	1.14	1.15	1.15	1.15
Temperature, °C	25	46	47	49	57	50	52	37	48	36	40	35	40	50	45	38	40	40
Nozzle pressure, psig	NA	16	18	16	18	17	22	24	(f)	(f)	35	(f)	(f)	(f)	(f)	35	41	72
Feedrate, l/hr	18	6.6	16.4	15.5	14.4	9.2	9.6	16.0	<47	<36	26	<38	<63	<70	50	15	30	45
Total feed consumed, l	32	38.1	91.6	90.4	37.8	63.8	393	637	451	120	281	267	600	405	283	5135	2070	2903
Number of unplanned interruptions	0	0	1(a)	0	0	1(b)	2(a,c)	0	1	0	0	0	0	0	1(d)	2(e)	1(e)	3(e)
Operating time, hr	2	5.6	5.6	6.5	2.63	7.9	41	39.8	14.5	4.2	16.2	11	14.2	11	7.4		Total 510	
Atomizing Feed Nozzle																		
No. 42	No. 42																	
Nozzle description	303 SS																	
Atomizing air flow, scfm	6.4	6.6	5.7	5.1	4.8	4.6	5.4	5.5	(f)	(f)	10	(f)	(f)	(f)	14	5.6	10	12
Atomizing air pressure, psig	40	40	40	40	40	40	40	40	(f)	(f)	60	(f)	(f)	(f)	100	35	60	100
Atomizing air temperature, °C	NA	45	47	50	56	61	55	51	(f)	(f)	32	31	29	28	36	38	40	40
Calclner (p)																		
Furnace temperature, °C																		
Upper zone	790	690	720	725	725	740	745	785	(f)	(f)	820	(f)	(f)	(f)	835	765	810	840
Lower zone	675	700	675	670	670	725	730	720	(f)	(f)	765	(f)	(f)	(f)	712	750	700	695
Internal wall temperature, °C																		
Upper zone	700	665	640	650	650	700	700	700	700	550	700	700	550	(f)	700	700	700	700
Lower zone	700	688	650	650	650	700	700	700	700	550	700	700	550	(f)	700	700	700	700
Power consumption, kW																		
Upper zone	NA	9.9	20.3	17.7	17.7	13.6(g)	11.4	22.0	(f)	(f)	29	(f)	(f)	(f)	37	16	24	31
Lower zone	NA	10.9	13.3	11.4	11.4	16.2(g)	12.3	12.1	(f)	(f)	20	(f)	(f)	(f)	31	16	21	25.5
Heat Flux, BTU/hr ft ²	2600	950	2400	2200		1300	1400	2300	6700	5200	3700	5500	5700	6400	4600		4100	
Spray Chamber ID, in.	13																	
Vacuum, in. of water																		
Normal	13.0	12.8	10.0	10	10	9.0	10	10	6	10	5	(f)	(f)	(f)	8	10	10	10
During blowback	11.0	8.0	5.6	6	6	4.4	5.5	2	1	2	1	(f)	(f)	(f)	4	5	5	5
Calclne																		
Moisture content, wt%	-	NA	NA	0.81	0.81	NA	1.66	0.66	0.91	NA	NA	<1	<1	<1	NA	0.5	0.7	0.4
Nitrate content, wt%	-	NA	NA	0.041	0.041	0.32	34.7	0.61	0.15	NA	NA	39.5	NA	42.2	NA	1.1	1.8	3.8
Calclner Vibrator																		
Model	Not used	VM-1200(w)																
Cycle time, min	2	2	2	2	2	1	1	2	5	5	5	1	5	5	5	5	5	5
Pulse time, sec	-	2	2	2	2	2	2	2	1	1	1	1	2	1	2	2	2	2
Air supply pressure, psig	-	40	40	40	40	60	60	60	40	40	40	60	40	70	40	40	60	60
Calclner Off-Gas Filters																		
Blowback air temperature, °C	400	265	350	425	425	400	400	400	350	400	450	295	400	300	420	350	350	350
Blowback air pressure, psig	30	30	30	30	30	30	30	100	100	60	60	60	60	60	60	60	100	100
Blowback cycle, min	2	2	2	2	2	2	2	2	5	5	2	1	2	3	2	3	3	3
Blowback pulse, sec	1	1	1	1	1	1	1	1	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Final filter pressure drop, in. of water	0.25	1.0	2.5	2.5	2.5	2.4	3.7	10	20(i)	12.5(j)	21	26(k)	24(k)	22.5(l)	NA	10	16	12
Total gas flow to filters, acfm	41.6	25.2	39.0	44.6	42.5	28.0	37.2	33	82(i)	64(j)	85	90(k)	86(k)	87(l)	NA	45	57	52
Filter chamber temperature, °C	300	320	360	360	380	350	400	425	(f)	(f)	460	360(k)	280(k)	125(l)	375	420	410	320
Filter face velocity, ft/min	2.7	1.6	2.52	2.87	2.74	2.25	2.40	2.2	5.3(i)	4.14(j)	5.5	5.8(k)	5.6(k)	5.6(l)	NA	2.9	3.7	3.4
Final permeability, ft/min-in. of water	11	1.6	1.0	1.25	1.10	0.95	0.64	0.22	0.28(i)	0.33(j)	0.26	0.22(k)	0.23(k)	0.25(l)	NA	0.29	0.24	0.27
Solids deentrainment factor(n)	NA	140-1300	1000-4000	1000-4900	1000-4900	2400-24,000	1000-4900	140-320	150-300	NA	340-770	180-920	NA	1200-1450	NA	400-2000	NA(m)	NA(m)

NA Not Available

a. Feed interruption due to leakage around atomizing nozzle cleanout needle.

b. Feed interruption due to loss of melter furnace control thermocouple.

c. Feed interruption due to failure of an effluent treatment pump.

d. Feed interruption due to failure of hardened 400 series stainless steel nozzle.

e. Feed interruption for changeout of worn atomizing nozzle.

f. Parameters systematically changed during capacity runs.

g. Greater power consumption in the lower zone due to partial scaling of the upper calcine interior wall.

h. New side mounted vibrators operating.

i. At time gas flow through seal pot began.

j. At 40 l/hr calciner feedrate.

k. At 39 l/hr calciner feedrate.

l. At 60 l/hr calciner feedrate.

m. Part of the calciner off-gas bypassed the filters.

n. Based on analyses of K, Cr, and Ni.

o. Based on analyses of Cs and Ru.

16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34
5/17/74	5/22/74	10/4-8/74	2/6/75	7/16/75	7/30,31/75 8/1,5,6,7,9/75	9/15/75	10/8/75	11/3-5/75	12/18/75	1/7/76	2/10/76	4/15/76	4/28/76	6/16/76	7/1/76	7/12/76	7/22-8/4,6/76	8/11,12/76
PW-4b 1.19 38 24 16.6 85 0 5.5	PW-6 1.40 40 24 17 58 0 3.7	PW-7A 1.28 24-47 24-28 14.8-23.6 712 0 39	PW-7 1.21 NA 26 16 104 n 5.75	Super Calcine 1.09 NA 24 16-20 140 0 7	PW-7A 1.27 NA 14-26 16-20 80n n 43	Super Calcine 1.12 NA 20 17 ~70 n 4	PW-8 1.3 NA 20 15 ~55 n 3.5	PW-7A 1.25 NA 8-27 20-76 ~750 n 16	AGNS ILLW 1.0 NA 21 15 18 ~70 1(s) 4.5	PW-7A 1.29 NA 21 18 ~180 0 10	PW-7A 1.26 NA 21 20 ~90 0 4.5	PW-8E 1.06 NA 21 15 67 0 4.5	PW-8A 1.23 NA 22 15 115 0 13.2	PW-8E 1.14 NA 22 15 80 0 5.1	PW-8E 1.10 NA 22-18 15 30 0 2	PW-8E 1.10 NA 22-18 15-7 55 1(x) 4	PM-8A 1.35 NA 40-35 25-20 300 1(y) 10.25	Super Calcine 1.29 NA 35 20-22 300 0 7.5
6 35 19	6 35 20	No. 42 B ₄ C Insert 6.5-7.3 40-45 16	6.5 4n Ambient	6.6 35	No. 42 Ceramic Air Cap 3.5-7.0 16-35	6.0 35	6.75 35	No. 72 SS Air Cap 12-17 28-54	No. 42 Ceramic Air Cap 6.25 35	6.0 35	6.5 35	7.0 35	6.0 35	3.0 35	~5 35	4.5 35	5.0-4.0 40-35	4.0 35
780 710 700 700	735 700 700 700	780-820 710-725 700 700	785 715 NA(q) NA	NA NA NA(q) NA	795 785 NA(q) NA	780 775 NA(q) NA	740 735 NA(q) NA	770-750 765-650 NA(q) NA(q) NA	780 795 725(v) 715(v) 740(v) 720(v) NA NA NA	790 790 725(v) 715(v) 680(v) NA NA 1600	785 775 720(v) 710(v) 675(v) NA NA 1800	500 540 475(v) 460(v) 425(v) NA NA 1400	850 835 785(v) 805(v) 775(v) NA NA 1400	800 795 750 755 720 NA NA 1400	650 660 595 580 550 NA NA 1400	615 625 590 518 490 NA NA 1400	825 860 715 710 650 NA NA 2200	785 765 690 680 625 NA NA 1800
9.2 4.2 NA 2.7	9.6 3.6 NA 31	9.2-7.6 4.4-0.8 NA NA	9.2 4.0 NA NA	NA NA NA NA	10 6 0.24-3.9 1.9-12.2	10-8.4 6.0-3.2 NA NA	10.8 6.8 NA NA	10.8 2.0 0.1-4.4 4.3-13	8.0 6.8 1.8-8.3 9.75	11.2 2.8 & -0.8 NA NA	10-6.8 2.0 NA NA	9.2 0.4 NA NA	10.0-7.2 0.0 0.0 ~1 18	5.2 0.0 NA NA	2.0 -5.2 NA NA	10.0 7.6 NA NA	6.8-8.0 28 ~1 16.1	6.0 2.0 NA NA
VM-1200AC(h) 2(h) 2 60	2(h) 2 6 100	VM-1300AC(h) 2 3 44	2 3 44	1.5 3 44	1.5-6n 3 44	1.5 3 44	1.5 3 44	1.5 3 40	1.5 3 40	2 3 40	2 3 40	1.5 3 40	2 3 40	1.5 3 40	VM-1300AC 1.33 3 40	VM-1300AC (hbw) 1.5 3 40	VM-1300AC (w) 2.5 3 40	2.5 3 40
275-310 60-30 342 0.25 5-10 46 420 3.0 0.30-0.59 >20n(o)	250 60 2 0.25 5.6-7.6 44 365 2.8 0.3 -0.5 >130(o)	265 60-80 3 & 2 0.25 9-15.8 37-50.6 290-310 2.4-3.3 18-.27 20 to >19n	305 6n 2 0.25 9.25 46 41n 3.0 0.32 NA	NA 6n 2 0.25 NA NA NA NA NA	300 6n 2 0.25 12.5-15 50 41n 3.2 0.22 NA	300 6n 2 0.25 14.5 50 450 3.2 0.22 NA	300 6n 2 0.25 13.75 44 405 2.9 0.2 NA	300 6n 2 0.25 NA(r) Up to 157 NA(r) NA(r) NA	260 60 2 0.25 16.5 43 405 2.78 0.17 NA	-(t) 80 2 & 60 0.25 14 & 12 52 450 3.3 .24 & .28 NA	-(t) 75 0.25 19.25 59 450 3.8 0.20 NA	(t) 90 30-45 0.25 21 42 510 2.8 0.13 NA	(t) 90 20 0.25 17.5 38.3 460 2.5 0.14 NA	(t) 90 30-3 0.25 19.5 ~33 290 ~2.2 ~0.11 NA	(t) 90 15-30 0.25 8.25 NA 305 NA NA	(t) 90 15-10 0.25 13.75 62-48.6 440-425 4-3.1 0.29-0.23 NA	(t) 90 10-5 0.25 15.0 48.5 425 3.1 0.21 NA	

p. Calciner ID was 13-1/4 in. during runs 1-11 and 21 in. during runs 12-27.
q. No internal thermocouples.
r. Off-gas bypassed from filters.
s. Temporary shutdown occurred ~10 min after the run began due to atomizing air turned off.
t. Nonheated blowback air.
u. 20% of filter blown every 15 min with a total cycle of 75 min.
v. Thermowell located inside the chamber measuring temperature at 4 in., 22 in. and 44 in., respectively, from top to bottom of spray chamber.
w. Top-mounted vibrator.
x. Feed pump problems.
y. Blew seal pot, thus contaminating off-gas coupling.

APPENDIX B: WASTE FIXATION PROGRAM SIMULATED WASTE COMPOSITIONS

The compositions of simulated wastes used in development and demonstration of the heated-wall spray calciner are based on past and current estimates of high-level and intermediate-level radioactive waste compositions expected to be generated at various proposed fuel reprocessing plants in the U.S. These compositions depend on the type of fuel, burnup, power level, and the process flowsheet. The fission products in the waste were determined using the ORIGEN code and the assumptions that the high-level waste originated from the reprocessing of light water reactor fuel having a burnup of 33,000 megawatt days per tonne of fuel and a specific power level of 30 MW. These fission products and their molar concentrations at 378 ℓ /MTU (100 gal/MTU) are shown in Table B-1. They are assumed to be the same for all waste compositions simulated.

The significant differences in the various high-level waste compositions occur in the amounts and types of inerts and the amounts of the actinides present as a result of the variations in the reprocessing flowsheets at different plants. To account for these variations, two waste compositions were originally selected that would bracket the anticipated range of compositions. One end of the range is represented by a composition designated PW-4b, which is based on the G.E. process flowsheet and contains no sodium. At the other end of the range is composition PW-6 which represents the maximum anticipated sodium content in a blend of high-level liquid waste and intermediate-level waste. The current AGNS process flowsheet indicates waste compositions PW-7 and PW-7a may be produced. These compositions can be compared in Table B-1. The significant differences between the G.E. and AGNS compositions are the gadolinium and increased uranium and plutonium contents in the AGNS wastes. The gadolinium is added during reprocessing to serve as a neutron poison. The PW-7a composition represents a blend of HLLW and ILLW and thus has an increased sodium and phosphate content. Recently, NFS has defined waste compositions that may be produced during their future operations. It is designated in the table as PW-8.

To simulate these waste compositions, aqueous solutions are prepared with the nitrates, carbonates, and oxides of the desired elements. For economic reasons and to avoid working with radioactive materials, substitutions are made for some elements including all the actinides. The elements used as substitutes are selected to be as chemically similar to the elements they represent as possible and are substituted on a per mole basis. The substitute elements used are also presented in Table B-1. The naturally occurring mixture of rare earths is used when preparing the simulated waste solutions rather than using the relative amounts of lanthanides defined by the ORIGEN code. Didymium carbonate, the natural rare earth mixture with most of the cerium removed, is used to simulate the gadolinium. Cerium is used as a substitute for uranium because CeO_2 is known to behave like UO_2 in glass melts, and the calcine produced by the calciner studies is used in the melter development studies.

All the constituents except the MoO_3 used to prepare the simulated wastes go into solution. The small MoO_3 crystals are kept in suspension in well agitated tanks, but they tend to settle in horizontal lines and in poorly agitated tanks. The addition of didymium carbonate to a simulated waste composition increases the solution viscosity and helps suspend the MoO_3 .

Simulated High-Level Nuclear Waste Compositions
Used in the Spray Calciner Development Studies

TABLE B-1.

Elements In Reference Wastes	PW-4b			PW-6			PW-7			PW-7a			PW-8			Chemicals Used To Prepare Simulated Waste
	As Defined Molar Concentration at 378 g/MTU	Simulated Composition Substitute Elements	Molar Concentration	As Defined Molar Concentration at 378 g/MTU	Simulated Composition Substitute Elements	Molar Concentration	As Defined Molar Concentration at 378 g/MTU	Simulated Composition Substitute Elements	Molar Concentration	As Defined Molar Concentration at 378 g/MTU	Simulated Composition Substitute Elements	Molar Concentration	As Defined Molar Concentration at 378 g/MTU	Simulated Composition Substitute Elements	Molar Concentration	
Fission Products:																
Rb	0.010	K	0.064		K	0.064		K	0.064		K	0.064		K	0.064	KNO ₃
Cs	0.054	-	0.106		-	0.106		-	0.106		-	0.106		-	0.106	CsNO ₃
Zr	0.106	-	0.117		-	0.117		-	0.117		-	0.117		-	0.117	ZrO(NO ₃) ₂ ·2H ₂ O Solution
Mo	0.095	Mo	0.059		Mo	0.059		Mo	0.059		Mo	0.059		Mo	0.059	MoO ₃
Tc	0.022	Fe	0.010		Fe	0.010		Fe	0.010		Fe	0.010		Fe	0.010	Fe(NO ₃) ₃ ·9H ₂ O
Ru	0.059	Co	0.032		Co	0.032		Co	0.032		Co	0.032		Co	0.032	Co(NO ₃) ₂ ·6H ₂ O
Rh	0.010	Ni	0.002		Ni	0.002		Ni	0.002		Ni	0.002		Ni	0.002	Ni(NO ₃) ₂ ·6H ₂ O
Pd	0.032	Omitted	0.002		Omitted	0.002		-	0.002		-	0.002		-	0.002	AgNO ₃
Ag	0.002	-	0.012		-	0.012		-	0.012		-	0.012		-	0.012	Cd(NO ₃) ₂ ·4H ₂ O
Cd	0.002	-	0.027		-	0.027		-	0.027		-	0.027		-	0.027	TeO ₂
Te	0.012	-	0.027		-	0.027		-	0.027		-	0.027		-	0.027	Sr(NO ₃) ₂
Sr	0.027	-	0.0006		-	0.0006		-	0.011		-	0.011		-	0.011	Ba(NO ₃) ₂
Ba	0.027	-	0.050		-	0.050		-	0.150		-	0.150		-	0.150	
Y	0.014	-	0.010		-	0.010		Rare Earth (a) and Didymium (b)	0.011		Rare Earth (a) and Didymium (b)	0.011		Rare Earth (a) and Didymium (b)	0.011	
La	0.024	-	0.034		-	0.034		-	0.109		-	0.109		-	0.109	Rare Earth Nitrate (a)
Pr	0.023	Rare Earth Mix (a)	0		Rare Earth Mix (a)	0		-	0		-	0		-	0	and Didymium Carbonate (b,c)
Nd	0.071	-	0.006		-	0.006		-	0.018		-	0.018		-	0.018	
Pm	0.0019	-	0		-	0		-	0		-	0		-	0	
Sm	0.014	-	0.004		-	0.004		-	See Inerts		-	See Inerts		-	See Inerts	
Eu	0.003	-	0.095		-	0.095		-	0.161		-	0.161		-	0.161	
Gd	0.002	-			-			Ce	-		Ce	-		Ce	-	
Ce	0.051	-			-			Rare Earth (a) and Didymium (b)	-		Rare Earth (a) and Didymium (b)	-		Rare Earth (a) and Didymium (b)	-	
Actinides:																
U	0.011	Omitted	0	0.054	Omitted	0	0.110	-	0.110	0.110	-	0.110	0.052	-	0.052	
Np	0.0085	"	0	0.0085	"	0	0.0085	-	0.0085	0.0085	-	0.0085	0.0085	-	0.0085	HNO ₃ Solution
Pu	0.0001	"	0	0.0005	"	0	0.001	-	0.001	0.001	-	0.001	0.0005	-	0.0005	NaNO ₃
Am	0.0018	"	0	0.0018	"	0	0.0018	-	0.0018	0.0018	-	0.0018	0.040	-	0.040	Fe(NO ₃) ₃ ·9H ₂ O
Cm	0.0004	"	0	0.0004	"	0	0.0004	-	0.0004	0.0004	-	0.0004	0.020	-	0.020	Cr(NO ₃) ₃ ·9H ₂ O
Inerts:																
HNO ₃	1.0	-	1.0	3.0	-	3.0	2.0	-	2.0	2.0	-	2.0	7.0	-	7.0	
Na	0.0	-	0	2.0	-	2.0	0.01	-	0.01	0.586	-	0.586	0	-	0	
Fe	0.05	-	0.05	0.5	-	0.5	0.10	-	0.10	0.10	-	0.10	1.32	-	1.32	
Cr	0.012	-	0.012	0.045	-	0.045	0.012	-	0.012	0.012	-	0.012	0.040	-	0.040	
Ni	0.005	-	0.005	0.020	-	0.020	0.005	-	0.005	0.005	-	0.005	0.020	-	0.020	
PO ₄	0.025	-	0.025	0.025	-	0.025	0.10	-	0.10	0.236	-	0.236	0.050	-	0.050	
Gd	0.0	-	0	0	-	0	0.151	Didymium (b)	0.013	0.151	Didymium (b)	0.013	0	-	0	
H ₂ O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	

- a. Commercial rare earth mix nominal oxide composition: 0.2% Y₂O₃, 24% La₂O₃, 48% CeO₂, 5% Pr₆O₁₁, 17% Nd₂O₃, 3% Sm₂O₃, 2% Gd₂O₃, and 0.8% other rare earth oxides.
- b. Commercial didymium nominal oxide composition: 4% Y₂O₃, 39% La₂O₃, 2% CeO₂, 10% Pr₆O₁₁, 37% Nd₂O₃, 5% Sm₂O₃, 4% Gd₂O₃, 2% Dy₂O₃, 0.2% Ho₂O₃, 0.4% Er₂O₃, and <0.1% of each other rare earth oxides.
- c. Sufficient HNO₃ was added to convert all carbonate to nitrate.

APPENDIX C: Pre-WFP Simulated Waste Composition

Waste Type	Darex	Neutralized Purex	FTW	1MW No F.P. with F.P.	1MW with F.P.	1MW with F.P.	NFS 1st Cycle	NFS 1st & 2nd Cycle Mixed	PW-2	Pedox	Pedox
Component (M)											
H	1.0		0.7	3.9	4.0	4.94	3.8	4.0	0.38	0.2	0.52
Fe	1.5	0.5	0.19	0.56	0.11	0.12	0.79	0.57	0.50	0.05	0.012
Al		0.12	0.048	0.12	0.056	0.045			0.001	1.6	2.2
Cr		0.07	0.019	0.07	0.025	0.018	0.003	0.001	0.024	0.001	0.004
Ni		0.03	0.01	0.029	0.012	0.009	0.001	0.001	0.01		
Na		6.0	0.33	0.63	0.49	0.40	0.114	0.35	0.93	1.85	1.28
Mn											0.04
Li											
Mg											
Co										0.01	0.14
Cs					0.025	0.014	0.04	0.015	0.042		
K											
Sr											
Ba					0.012	0.011	0.056	0.015	0.035		
Ca											
Y+R.E.											
Zr					0.094	0.045	0.112	0.055	0.12		
Mo						0.021		0.031	0.065		
NO ₃					0.007	0.0035	0.100	0.024	0.065		
SO ₄											
To Balance		1.0	0.40	0.73		0.137		0.35	0.87	0.02	0.04
Si			0.01			0.006			0.01		
PO ₄			0.005	0.01					0.006		
Concentration (g/ltU)	8700	95	190	190	300	300	420	950	390	~6500	~6500

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