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**Letter Report: Evaluation of Dryer/
Calciner Technologies for Testing**

G. Sevigny

February 1996

**Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest National Laboratory
Richland, Washington 99352**

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PACIFIC NORTHWEST NATIONAL LABORATORY

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UNITED STATES DEPARTMENT OF ENERGY

under Contract DE-AC06-76RLO 1830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
prices available from (615) 576-8401.

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161

The document was printed on recycled paper.

TABLE OF CONTENTS

INTRODUCTION	4
TECHNOLOGY DESCRIPTIONS	5
SPRAY CALCINER	5
FLUID BED CALCINERS	7
PLASMA CALCINATION	8
WIPED FILM EVAPORATOR	8
ROTARY CALCINER	11
ISSUES TO BE RESOLVED	13
ADVANTAGES AND DISADVANTAGES OF THE WFE OR CALCINERS	16
RECOMMENDATIONS FOR FUTURE TESTING AND RESOLVING ISSUES	17
CONCLUSIONS	20
REFERENCES	21
APPENDIX A - BIBLIOGRAPHY	

FIGURES AND TABLES

Figure 1 - Wiped Film Evaporator Schematic	9
Figure 2 - Rotary Calciner Components	12
Table 1 - Issues and Suggested Testing Scale	20

INTRODUCTION

This letter report describes some past experiences on the drying and calcination of radioactive materials or corresponding simulants and the information needed from testing. The report also includes an assessment of informational needs including possible impacts to a full-scale plant. This includes reliability, maintenance, and overall size versus throughput. Much of the material was previously compiled and reported by Mike Elliott of PNL "Melter Performance Assessment" and Larry Eisenstatt of SEG on contract to WHC in a letter to Rod Powell. Also, an annotated bibliography was prepared by Reagan Seymour of WHC and the bibliography is shown in Appendix A.

Descriptions of the drying and calciner technologies, development status, advantages and disadvantages of using a WFE or calciner, and recommendations for future testing are discussed in this report.

The vitrification of high level waste consists of various system designs. The designs in the United States of America have been centered around continuous slurry fed melters since the earlier 1980's. Other systems involving calciners or dryers and semi-batch melters were tested earlier, but abandoned in favor of the simple slurry fed melter with robust operation and good glass quality. The system designs were based on relatively small glass throughput compared to the present 10 to 20 ton/day throughput projected for the current high level waste plant. The calciner or dryer/melter system may provide a smaller footprint using more energy efficient processes than the simple slurry fed melter. The more complex system may provide advantages over a large slurry fed system that outweigh the disadvantages of a more complex system. The basic functions of the flowsheet are to provide a high quality vitreous product in a reliable, reproducible manner as cost effectively as possible. The basic requirements are to produce a vitreous product acceptable for storage and disposal at the high level repository while complying with all radioactive and chemical permits. The dryer or calciner function is to produce a dry easily handled product, increase significantly the melter production rate, and be less expensive than a simple slurry fed melter.

The flowsheet for the Hanford vitrification system includes an evaporator for concentrating the slurry from the pretreatment process, although other methods of dewatering are being considered. The current characterization information suggests the vitrification plant will receive a slurry containing about 5 to 15% solids. The solids will have been washed numerous times removing the majority of the soluble components. The concentration of solids is based on initial testing indicating the concentration level at which the material can be handled easily in agitated tanks and transfer lines. The evaporator system would concentrate the material to a higher level and probably include the addition of glass formers. This material is pumped to the drying, calcining, or vitrification unit for processing. The glass formers can be added before or after the drying or calcining unit. Control of the final product quality from the melter may be more difficult if the glass formers are added after calcination but the feed stream would be smaller and less abrasive.

TECHNOLOGY DESCRIPTIONS

Waste drying and calcining can be accomplished by using wiped film evaporators (WFE), screw dryers, filter dryers, tray dryers, rotary calciners, spray calciners, fluidized bed calciners, and plasma calciners.

Combustion fuel heated units were not considered because of the additional offgas produced and because of the need for additional safety requirements.

Small electric rotary calciners have many years experience being operated remotely in high-level waste vitrification facilities. The waste processed was acidic with small quantities of undissolved solids. Hanford waste is initially an alkaline stream with large quantities of undissolved solids. The rotary calciners require less building height and produce larger particles than spray calciners (Hull 1981). Therefore, for this report the rotary calciner is considered the basis for comparison.

Filter dryers are not included in this evaluation for removing liquids because existing data indicates the primary particles in the slurries are very small, and may form compressible flocs. These are very difficult to filter and dead end filtration is not presently considered the primary solid-liquid separation device. If a filter were to be used that caused the formation of a non-pumpable cake, filter dryers should be considered as a viable final separation step in the vitrification cells instead of having the pretreatment process separating the solids and sluicing them from the filter for transportation. No previous process experience with Hanford type waste was identified.

Screw dryers were also not included because the experience with large systems for this type of application were not found. Screw calciners have been used at Hanford for small acid streams in the Plutonium Finishing Plant. The experience was not directly applicable.

Tray and belt dryers typically use large quantities of air for drying which is considered undesirable for a radioactive system with rigid requirements on offgas cleanliness. The large quantities of air could be and are recirculated but this is a complication to the overall process. The standard use is for wet solids that do not flow well instead of pumpable fluid streams. Little experience was found on fluid or radioactive waste systems. Therefore, these technologies were not considered further.

Agitated drying is a batch system for drying material in an agitated vessel. It has long residence times and different methods of agitation as compared to a wiped film evaporator. The batch system has better processing flexibility. Disadvantages include not having the capability to be directly coupled to the melter and having periodic downtime for unloading that would decrease its availability. Therefore, it should not be considered further for pilot scale testing or plant operations. Laboratory testing information would be valuable to obtain basic drying properties.

SPRAY CALCINER

Spray dryer/calciners are efficient devices providing the material to be dried can be atomized effectively without clogging or abrading the nozzle, and solids carryover can be controlled easily. In comparison to the rotary calciner, spray calciners are bulky, with low energy efficiency, and produce a low density particulate product. There are high throughput designs that minimize some of the caking problems found in other calciners. Spray calciners have been used for calcination of simulated waste slurries (Dierks 1980, Holton 1981, Larson 1976) and for actual waste in a small demonstration system for Waste Solidification Engineering Prototypes (WSEP) project (Schneider 1969). A spray calciner consists of a spray chamber, cone section, vibrators, and gas filter assembly. A spray nozzle typically uses high velocity air to atomize the waste slurry flowing into the heated chamber where the water is evaporated and the solids dried. A combination of convective and radiant heat transfer from the heated walls is used to dry and calcine the waste. The walls can be heated by a number of methods, but past experience is based on electrically resistance heaters outside the chamber walls.

After calcining, a large percentage of the particles formed are entrained and need to be removed by cyclones and/or blowback filters. The calcine then flows into a cone section at the bottom for collection or directly into a melter. Glass formers can be added before or after calcining, but previous experience indicates the calciner operates better with the glass formers added after calcination.

Past testing at PNL has indicated the need for high efficiency corrosion resistant filters at the outlet to control the fine particulate produced. If the nozzle atomization does not work correctly because of partial plugging or improper operation the calciner will likely plug causing extensive maintenance problems. The waste slurry with glass formers added is very abrasive and causes operating problems for the spray nozzle although most abrasion problems were solved by using a ceramic spray nozzle. Recently, a private company has used a sonic horn to atomize low level waste simulant in a combustion fired calciner test. The atomization was efficient, and the particulate produced was very fine.

Radioactive acid waste was processed in a 2 m high by 0.56 m diameter spray calciner for the WSEP project. The furnace operated at 600 to 800°C with three zones of electric heaters. The calciner was directed coupled to an induction heated melter. The calciner was equipped with sintered metal filters that needed infrequent liquid cleaning in addition to air blowback. The calciner operated at 17 to 36 l/h with acid feeds and operated well except when sulfate levels were around 0.5M. The sulfate caused filter plugging problems and a high condensation point for sulfuric acid. As mentioned earlier a critical requirement was good atomization of the feed especially in a small system where the distance from the spray nozzles to the walls is not very large.

The large scale spray calciner tested at PNL had calcination chamber 3.2 m high, and 0.91 m in diameter. The calcination chamber had 9.15 m² of heat

transfer area with a 0.64 cm thick stainless steel wall. It used four zones of heaters with the capability of 150 kW each and a maximum temperature of 1000°C. The processing rate was about 300 l/h of slurry producing 21 Kg/h of calcine from acid waste. The blowback filters were 316 SS with a 10 μ m pore size. The calciner also used two vibrators to help prevent build-up of particulate in the chamber. The calciner was directly coupled to a joule heated melter and performed adequately. There was severe corrosion of the filters and nozzles which were believed to be controllable by selection of the proper materials of construction and better control of the operating parameters (Larson 1976).

FLUID BED CALCINERS

A fluid bed calciner consists of a heated chamber with a distribution screen on the bottom, and an inert bed (e.g., silica). The distribution screen is used to distribute the fluidizing air, collect large product particulate, and contain the bed during down times. The inert bed enhances heat transfer to the feed material and provides some control of the product particle size. The feed solution is sprayed into the bed where it is dried directly or coats the bed particles, agglomerates, dries, and is abraded off because of collisions with other particles.

Fluid bed calcination is a proven process using combustion fuels and air as the fluidizing medium and energy source. Many variations on the bed material and heating method are available, but have not been used for calcining simulated Hanford type waste. Allied Chemical Corporation Performed an evaluation of heating methods for a new calciner at the Idaho Falls plant and concluded direct combustion was superior to hot air fluidization, steam fluidization, or offgas recycle with hot air and in-bed electric heat (Freeby 1974). Extensive experience at Idaho National Engineering Laboratory exists for processing acid waste using combustion fuels. Interest from private vendors has been shown in providing a fluidized bed system using electric heat sources for processing high level waste supernate at Hanford.

The tests at Idaho indicate success with acid feeds containing up to 0.2 M Na and up to 1.1 M Na with additives such as iron to control sodium nitrate formation (Freeby 1975). The problems noted were feed nozzle plugging and excessive agglomeration in the bed. The calcination was performed using 4 and 12 in. diameter calciners. The calciner was heated using combustible fuel.

PNL tested a calciner vessel with a 1.7 m total height and a 17-cm square cross section below a 19-cm square section (Bjorklund 1976). The distributor plate had one hundred 0.12 cm holes on a 1.8 cm square grid pattern. An air atomized spray nozzle was supplied with feed from a recirculation loop with a centrifugal pump. The offgas flows through a cyclone chamber to the sintered metal filters. The processing rate was about 20 l/h with acid feed containing around 150 g oxide/l. The product contains a wide variety of particles sizes from <10 μ m to 210 μ m with the majority around 40 μ m. The equipment size versus processing rate is very good and the bed material can be used to absorb acid gases or catalyze reactions.

The fluid bed calciners can be operated with hot walls or a preheated air stream to provide energy, but detailed information on previous experience with nuclear waste was not found. Fluidized bed calciners should be considered because of its potential for high throughput, no moving parts, and particle sizes in a range that should be easy to handle.

PLASMA CALCINATION

The plasma torch provides a high temperature energy source from compact equipment without the use of combustion fuels by using electricity to create a high temperature plasma in an inert gas stream. The energy is transferred to the product by the flowing gas. It is typically used for high temperature applications such as cutting metal. A non-transferred plasma torch has been used as the heat source for a pseudo spray calciner test for unwashed Hanford type waste containing large quantities of Na (Goheen 1995). The goal of the test was to produce a calcined product with a different chemical form of aluminum hydroxide to enhance the dissolution of aluminum using sodium hydroxide. Plasma torches have also been used to directly boost the production rate of a joule heated slurry fed melter by installing them in the plenum space. The torch could be used to boost the melter production rate, but previous tests encountered numerous reliability problems. Commercial non-transferred plasma arc systems also need a lot of maintenance time for the electrodes and plasma heads. Therefore, the plasma torch is not recommended as part of the calcination system for high level waste at Hanford.

WIPED FILM EVAPORATOR

Wiped film evaporators can dry dilute liquids to powders and should be able to dry high-level waste feed (Westinghouse Hanford Co. 1994). A WFE is constructed of a straight or tapered large diameter pipe that can be oriented either horizontally or vertically (Perry and Chilton 1973). The inside wall of the pipe serves as the heat transfer surface. Liquid is spread on the inner surface by a rotating assembly of blades that has a close tolerance to the wall or actually rides on the film of liquid. High agitation from the assembly rotating at a tip speed of up to 12 m/sec (40 ft/sec) coupled with power intensities of 2 to 20 kW/m² (0.25 to 2.5 hp/ft²) gives it the capability to dry extremely viscous liquids. Residence times are of the order of only a few seconds.

LCI Corporation (formerly LUWA) recommended that Hanford waste be dried with a vertical WFE directly coupled to a melter. Figure 1 presents a schematic of LCI vertical evaporator. Vertical WFEs have less accumulation of dried phases than horizontal evaporators because the dried waste can break free and fall out of the exit. Also for a given diameter, vertical units dry faster than horizontal ones, and therefore, have a higher throughput per unit volume. The waste should be dried to a dry, flowable powder rather than to chunks or paste that could plug the discharge. If it is decided that the Hanford system will dry the waste to a paste, rather than to a powder (for example to reduce the carry-over from the melter), the evaporator design must not have any

obstructions in the exit. This is expected to be more difficult to control because of the radiant heat from the melter that would cause additional drying. Such designs are available but would require demonstration with waste types at Hanford (Glover 1994).

Figure 1 - Wiped Film Evaporator Schematic

For dilute waste streams an LCI WFE can remove 200 kg of water/hr/m² of heat transfer surface (40 lbs/hr/ft²) (Glover 1994). In vertical evaporators the heat transfer surface can be up to 40 m² (400 ft²). Horizontal systems can have a heat transfer surface up to 7 m² (80 ft²). If a wet granulated solid is fed to the WFE, the water evaporation rate drops to 50 kg/hr/m² (10 lbs/hr/ft²). According to the Tank Waste Remediation System Process Flowsheet, (Orme 1994) the melter feed after glass former addition (without an evaporator present) will be dilute, greater than 70 wt% water. For a glass generation rate of 400 kg/hr, about 2000 kg/hr of feed will be processed. Therefore, one vertical WFE would be sufficient to dry the high-level waste; one horizontal unit may be sufficient, but its capacity limit will be approached.

The reliability of WFEs should be good based on uses in industry and testing to date (Westinghouse Hanford Co. 1994). Wipe Film Evaporators are being used by commercial radioactive waste processing companies to dry sludge for disposal. However, the wiper blades need to be adjusted or replaced every six months, and mechanical seals have to be serviced at the same interval. The maintenance frequency needs to be investigated for abrasive feeds. Other items such as lubricated bearings also may limit the life of the unit or require automated lubricators. Remote maintenance is considered something that can be achieved with manipulators. A remote design for a small unit is being tested at Oak Ridge National Laboratory (ORNL) (Boring 1994). However a large scale remote unit design has not been completed and tested to determine the effect on process availability. The ability to maintain operations is an issue needing investigation and evaluation. The services required to operate the unit are instrumentation, steam, and electrical power.

Pacific Northwest Laboratory (PNL) and Oak Ridge National Laboratory (ORNL) have been involved in testing WFEs for drying liquid high-level waste.

PNL tested drying simulated PUREX solutions (1 to 3 molar nitric acid) in horizontal and vertical WFEs.

PNL's horizontal WFE had a heat transfer area of 0.5 m^2 (5 ft^2) and had a tip speed of 6.7 m/sec (22 ft/sec) resulting from the four paddle rotor operating at 450 rpm (Dierks and Bonner 1975). The waste feed entered the evaporator near boiling at the larger end of the drum that was tapered about 2° , and the dried feed exited out the smaller end. Water lubricated, graphite-to-stellite mechanical seals on each end of the rotor shaft permitted the evaporator to be operated at -250 mm (-10 inches) water. The paddles were straight, 3 mm ($1/8 \text{ inch}$) thick, and parallel to the rotor axis. The clearance between the paddles and the evaporator wall was kept at 0.8 mm ($1/32 \text{ inch}$). A steam jacket surrounded the drum.

The simulated acid waste solution could only be concentrated to 50 wt% solids, greater than 50% solids caused operating problems with the WFE. At less than 50% solids the concentrate was fluid, but beyond that it became more like a paste. As the 50% concentration level was approached, the torque required to maintain the set rotor speed increased sharply and scraping sounds were heard from within the evaporator. Examination showed that a hard scale collected between the paddles and the heat transfer surface from the midpoint of the unit to the discharge. The scraping sounds may have been the result of chunks of scale having become lodged between the blades and heat transfer surface as indicated by circumferential striations.

When the concentrate ($\leq 50 \text{ wt\%}$ solids) was discharged to an unheated container, there was no problem. However, when it was fed directly to a melter, the radiant heat caused further evaporation and caking of the discharge nozzle until it plugged. The % solids goal of greater than 50% is expected to be needed to be a significant benefit to melter operation.

An experiment was performed in which -325 mesh frit was added to the evaporator feed at a frit to metal oxide feed ratio of 2:1 (McElroy 1975).

The mixture was concentrated to 35 wt% solids when the concentrate became somewhat gelatinous and did not flow well out of the evaporator.

Other tests with the following horizontal and vertical evaporators were performed (McElroy 1976):

- Rototherm Artisan - 0.08 m^2 (0.88 ft^2) horizontal
- LUWA D-210 - 1 m^2 (10.8 ft^2) horizontal
- LUWA CP-150 - 0.3 m^2 (3 ft^2) vertical

Processing rates were 22 to 120 l/hr/ m^2 of evaporator heat transfer surface. The WFEs dried the waste to 10% to 20% liquid (17 molar nitric acid) giving a free flowing powder with 55 to 58 wt% oxide. Denitration was minimal. The vertical LUWA CP-150 had a higher solids buildup on the paddles of the rotor shaft than either horizontal WFE.

ORNL is developing a vertical WFE for concentrating radioactive waste composed of a 1M sodium nitrate and 1M potassium nitrate supernatant with 0% to 40 wt% solids consisting of 74% calcium carbonate, 18% magnesium hydroxide, and remainder aluminum hydroxide (Boring 1994). Tests are being performed to produce a sludge that solidifies on cooling and meets the requirements for disposal at Waste Isolation Pilot Plant (WIPP). At times a free flowing powder is obtained, but because this is not the desired product for the ORNL application, so the operating conditions were changed during testing.

The evaporator shell is a 0.6 m (2 ft) length of 25 cm (10 in.) schedule 40 pipe. It has a 0.5 m^2 (5.4 ft^2) heat transfer area. Heat is supplied to the WFE using 1.0 Mpa (150 psi) steam at 181°C (358°F). The inside wall of the evaporator has a set point of 177°C (350°F) which has maintained a flow rate of simulated waste up to 0.8 l/min (0.2 gpm). They use an agitated kettle heater to preheat their feed because sensible heat takes 2X the amount of WFE heat transfer area as does latent heat. At 3 l/min (0.8 gpm) the evaporator temperature is 154°C (310°F). At these temperatures there is no trouble with low melting salts. The wiper tip speed is 9 m/sec (30 ft/sec). The unit uses a 7.5 hp electric motor. The clearance between the blades and wall is 1.5 mm (0.060-in.), but the investigators want to lower it to 0.5 to 1 mm (0.020 to 0.040-in.). The blades vibrate more when the simulated waste has no solids, suggesting that the solid particles act as a lubricant. This WFE has no lower bearing allowing the blade assembly to be remotely removable.

ROTARY CALCINER

The rotary calciners used at the vitrification facilities in LaHague, France and Sellafield, England are 3 m long by 0.3 m diameter pipes fabricated from alloy uranium 2520 (Moncouyoux, et al. 1991). Figure 2 shows the components of the rotary calciner (Chapman 1983). They rotate at 30 rpm and are tilted about 3° from the horizontal such that the feed slowly flows down. A 2.5 m long rabble bar inside the tube breaks up the calcine and keeps it from sticking to the walls. A four zone 94 kW resistance furnace (two 32 kW and two 15 kW zones) heats the tube. The calciner has a reliable feed system for

liquid waste, but would not be suitable for high solids slurries. Once the waste has been evaporated, calcining takes place at 400°C for five minutes. Graphite sealing rings in each of the calciner end fittings provide leak tightness allowing it to be operated under a vacuum of -1 kPa. The evaporative capacity is 60 l/hr (70 l/hr with recycle), but larger ones could be designed and built. Waste is fed to the calciner through the upper end by a measuring wheel with the amount fed determined by monitoring the revolutions. Frit is added through an air lock at the calciner lower end fitting.

Figure 2 - Rotary Calciner Components

A melter that generates 200 kg/hr of glass would require a 250 to 500 l/hr calciner, depending on the waste loading. This is a five to ten times increase over the current design.

Two main parts need to be replaced every six months in the rotary calciner: the graphite seals and the rollers. Other rotary calciner parts usually last more than five years.

Rotary calciners have been used at Marcoule, France on a pilot scale in a radioactive environment starting in 1978, (Saverot and Laurent 1992). Also, they have been in use to treat acidic high-level waste at 50 l/hr in LaHague, France since 1989 and Sellafield, England starting in 1990 (Houghton 1992). The LaHague calciner is capable of 70 l/hr; treating 50 l/hr of waste generates 25 kg/hr of glass. Increasing the calciner diameter from 30 cm to 40 cm would increase the glass generation rate from 25 kg/h to 45 kg/hr using approximations based on the square of the diameter or directly proportional to the cross sectional area (Perrys 5th addition).

Hanford waste is alkaline and includes organic compounds. When alkaline metals constitute 50% of the waste, they can cause caking in the rotary calciner. This is probably due to the waste becoming sticky as it is heated through a temperature region lower than calcining temperatures. To prevent this caking aluminum can be added to the waste to achieve an aluminum to alkaline ratio of 0.3 (molar). The current blended waste has considerable amounts of aluminum although it may be in a mineralized form. In other acid waste pilot tests and laboratory hydroxide simulant tests, the addition of sugar has help break of caking during calcining operations and should be considered in future tests. A test on Savannah River High Level waste indicated the alkaline waste could not be calcined with frit addition before calcination (Hull 1981). The frit had a much lower melting point than frits currently proposed for the high temperature melters and lower then the proposed frit for the Hanford Waste Vitrification Plant 1150°C melter. The rotary calciner is a very good candidate for calcination as long as maintenance and caking do not severely reduce equipment availability. The effect on the typical canyon design would be minimal since the overall height would be within other equipment requirements.

In summary the systems described above have potential and some previous experience drying or calcining materials similar to the current proposed high level vitrification stream at Hanford. However the feed properties have some significant differences that have cause processing difficulties in the past. The main difficulties have been caking and/or plugging of the process equipment.

The processing systems have different processing issues. Many require atomization of the feed slurry for drying to avoid the formation of hard cakes. Others rely on mechanical forces to break of the crusty material being formed and often using chemical additives to assist in the process. The equipment ability to operate reliably over a range of conditions without plugging or corroding is a key issue in demonstrating an improvement over a single slurry fed melter in addition to processing rate enhancements.

ISSUES TO BE RESOLVED

Before drying or calcination equipment is used in a high-level waste vitrification facility the following concerns need to be considered. Most of the issues can be resolved by performing tests on simulated waste. Some of them can only be definitively addressed after the melter is selected.

DRYING AND CALCINATION EQUIPMENT ISSUES IN GENERAL

- Additional particulate entrainment from the melter caused by dry solids feeding needs to be determined. The off-gas and waste treatment systems would have to be designed to capture and recycle these particles directly using hot filters or indirectly using filters or wet scrubbers. For direct recycle, filter blinding and operating life are areas requiring information. For an indirect system, the handling of the solids, and the variations in the melter feed are issues as these recycle streams are returned to the process in batches.
- Melter production increases by feeding dried or calcined waste requires verification. The value has not been determined for blended Hanford wastes.
- Processability of Hanford waste needs testing over a wide range of expected Hanford waste compositions, generally up to pilot-scale. Almost all of the testing completed thus far has been on nitric acid waste; alkaline Hanford waste is untested. Tests might show that acid needs to be added to the Hanford waste which is a disadvantage overall because of the additional evaporation capacity needed and the increase in acid gas generation from the high temperature equipment.
- Space savings, facility design constraints, operational simplicity, reduced risk, and reduced overall cost for the optimum combination of calciner and melter need to be quantified.
- Remote design features for much of the drying and calcining equipment is needed or the impact of replacing and disposing of major parts needs evaluation. This evaluation would need to be performed in conjunction with the philosophy of remote maintenance (e.g., canyon remote versus hot cells serviced with robotic arms).
- Glass former addition before drying or calcining requires evaluation as to the potential impact on glass quality and equipment reliability. The information available would indicate the frit should not be calcined with the waste because of an abrasion and caking problems.
- Destruction of nitrates in the calciner and NOx emissions data from testing is needed to evaluate the technology.

WIPED FILM EVAPORATOR

- Do salts with low melting temperatures in Hanford waste cause plugging? Sodium nitrate/nitrite are such salts that are in the waste but in much lower quantities than the test described above; other salts may be present. Hanford HLW is not expected to have low melting salts.
- Tests of direct and indirect coupling to the melter are needed to allow for the most reliable, and cost-effective configuration of a WFE and melter
- Product characteristics (dryness, particle size, particle density, abrasiveness, etc.) that can be produced under various operating conditions need to be determined by pilot scale or larger tests.
- Remote design features are needed for adjusting the wiper blades and replacing seals
- Formation of cake on the blades and heat transfer surfaces that is not easy to remove is a likely possibility and testing is needed to determine if operating parameters can be adjusted to minimize the possibility.
- Corrosion/erosion rates of the blades and other materials contacting the waste slurries require quantification to estimate design life and life cycle costs.
- The production rate needs to be determined on a test system of sufficient size to allow scale-up calculations.
- Testing is needed to determine the effect on production rates when the typically used preheater is not used. The existing preheater design may not be reliable for alkaline feeds.

ROTARY CALCINER

- The production capacity of the calciner requires testing using Hanford type wastes including expected variations that could impact the calciner production rate and reliability.
- Quantity of entrained particulate leaving the calciner and the impact on secondary treatment systems requires evaluation.
- The scale-up capability of the calciner is undemonstrated for this type of waste. Many commercial plants exist with greater capacity but are not set up for remote maintenance. The Hanford melter is expected to have a capacity of 400 to 800 kg/hr of glass, whereas the maximum capacity expected (but not demonstrated) from current design concepts is 90 kg/hr.

- The configuration of the calciner and melter (calciner tilted 3° as at LaHague, direct or indirect coupling to the melter, glass formers added before or after the calciner, number of calciners per melter) needs to be evaluated for functionality and impact on plant operations.
- Testing is needed to determine the calciners ability to prevent scale formation by mechanically means and/or chemical additions.
- Maintenance requirements for the calciner and seals need to be determined based on past experience and comparison with shorter tests on Hanford waste.

SPRAY CALCINER

- Ability of spray nozzle design to operate reliably and control the product particle size needs to be tested with the simulated Hanford feed.
- Production rates for the calciner need to be tested with simulated Hanford feed and evaluated versus requirements that would be imposed on the cell height.
- Life of the spray nozzle and the require solids separation device (e.g., cyclones, filters) needs to be evaluated based on tests with simulated Hanford feed.

FLUID BED CALCINER

- Production rates using an electrically heated (includes induction heating) chamber and/or fluidizing air requires determination based on testing.
- Particulate size distribution of the product is needed
- Operating life of bed material (SiO_2 , recommended) needs to be determined based on testing to evaluate functionality.
- Testing of the systems under a range of conditions using Hanford type feeds are needed to ensure operating conditions can be maintained that prevent an excessive cake build-up.

ADVANTAGES AND DISADVANTAGES OF THE WFE OR CALCINERS

The main advantage of using a dryer or calciner is that it would increase the glass melt rate for a given melter size. Therefore, the number and/or sizes of melters that would be needed to vitrify the Hanford waste would be reduced. Operation of the melter may be simpler, because the temperature gradients within the melter would not be as great and the atmosphere may not be as

corrosive. Dry feed would allow the operation of some high temperature melters currently not considered viable for a slurry feeding.

The disadvantage for using a secondary device is the added monitoring and maintenance needed by another piece of processing equipment. If the equipment is directly coupled, the calciner/dryer reliability affects the availability of the entire vitrification system. For indirectly coupled equipment added lag storage is needed and the material would need to be reheated in the melter after storage.

The wiped film evaporator has advantages in the efficient heat transfer from an agitated surface and the lower operating temperatures typically allow for longer operating life. The lower operating temperature also allows for the use of steam in the cell that results in more reliable in-cell equipment than high temperature electrically heated equipment. The operation also allows for greater control over the moisture in the product that may allow easier handling than a very dry powder. The disadvantages are the blades and seal require considerable maintenance and a "dry" product may be difficult to produce for some feeds. The final product will have more unreacted chemicals than the calciners but this could be an advantage or disadvantage in the melter. The wipe film evaporator shows a lot of potential for processing Hanford waste rapidly in a small volume. The main concerns are the maintenance and reliability of the equipment.

Comparing the calciners with the WFE has relative advantages and disadvantages. Use of the calciner rather than the evaporator would place less of a thermal load on the melter, because less water would be sent to the melter, and the calcine would be preheated to a higher temperature. The difference is expected to be small because the difference in water content will likely be small. The additional latent heat would only be useful if the calciner were directly coupled to the melter. Also, the calciner would require more energy and operate at a higher temperature which may mean faster corrosion and shorter equipment life. The failed equipment will have to be disposed of as contaminated waste with costs varying greater depending on decontamination efforts and waste classification.

The rotary calciner has many years of experience in processing waste feeds of a different nature, but is well developed system for maintenance in cells with robotic arms. The system does produce large quantities of small particles that can be entrained but not as much as in the spray calciner. The rotary calciner has a rotating parts and an electric heater susceptible to failure although experience on the current system is good. A large remote system for use at Hanford has not been designed although commercial rotary calciners can be very large. The rotary calciner should be tested with simulated Hanford waste as a potential enhancement to the vitrification system.

Spray calciner advantages include the ability to prevent cake formation by drying in droplets. The droplets provide a high surface area with a short residence in the heated vessel to provide a high throughput. The disadvantages relative to the rotary calciner are the production of fine particulate that are easily entrained in the calciner and subsequently in the melter. This almost requires the system to be coupled to minimize the cost of

particulate removal equipment such as sintered metal filters. The short residence time of the droplets in the heating chamber also requires more precise control to prevent wet droplets for impacting the sides and causing build-up within the vessel. Extensive solids build-up on the wall has occurred in previous tests. The spray calciner also requires a higher pressure pump than the rotary calciner or use of another high energy device (e.g., centrifugal, sonic atomizer) to ensure adequate atomization of the feed slurry. The spray nozzle can be an unreliable device for slurry with high abrasive solids content. The spray calciner is a good process for testing provided the design considers reliable fluid atomization, high efficiency collection of particulate, direct coupling to the melter, and cell height is not a major concern.

The fluidized bed advantages as compared to the rotary calciner are fewer moving parts and may be less likely to form hard dry solids in the processing equipment. The fluidized bed is an efficient system with a lot of experience processing acid waste in combustion fired unit at INEL. However, experience with electrically generated heat and requirements for particulate capture are a disadvantage.

RECOMMENDATIONS FOR FUTURE TESTING AND RESOLVING ISSUES

Tests need to be performed to evaluate the technology and decide the specific type of equipment to use in the high-level waste vitrification facility, e.g., WFE, or rotary, spray, fluidized bed, or plasma calciners. Testing performed thus far on the use of a WFE or calciner to increase a glass melter throughput included too many varying parameters other than moisture in the feed to quantify the effect. Also, there is a dearth of data on the ability to calcine or dry Hanford waste, which is alkaline and has a broad range of characteristics. Previous testing was generally performed using acid feed. The small number of experiments performed using alkaline feed can be used to demonstrate feasibility although they were performed on waste with compositions significantly different from the feed presently projected for the Hanford high level vitrification plant. (e.g., see Allemann and Johnson, 1961; and Hull, 1981).

The test strategy should reflect that testing costs escalate as test size increases, and that radioactive testing is much more expensive than nonradioactive testing. Therefore, to the extent possible, the smallest scale testing will be used to resolve the issues identified above using non-radioactive HLW feed simulants. Radioactive tests should be limited to laboratory scale tests to compare the chemical and physical properties of the simulant and the actual waste material.

Laboratory and bench-scale testing generally focus on process chemistry and effects of changes in variables over a relatively wide range. Pilot-scale typically investigates the process considerations and identifies process and equipment problems. Because costs per data point escalate with size, tests with the larger-scale systems are generally limited to verifying scale-up behavior and at a relatively small number of conditions.

The objective of the testing is to confirm that small-scale radioactive testing can be extrapolated to full-scale plant operation by performing laboratory, pilot, and full-scale testing on simulants. Once this is demonstrated, other HWVP feeds need only be tested on scale sufficient to evaluate equipment operating parameters.

Drying and calcining tests, some coupled with the melter, need to be performed to respond to these matters. Some of the confirmatory testing needs to be performed at pilot to full scale as shown in Table 1 to substantiate that there are no problems with scale-up. Full scale testing could be preformed in the actual plant melter and the results would not be required for the next round of evaluations. Design of the WFE and/or calciner systems needs to be initiated after initial bench or pilot scale tests are performed. The early design work is needed so the integrated process system can be evaluated. Some of the pilot scale tests can be performed by the potential equipment vendors.

The results of these tests will be used to evaluate and select the technology for drying or calcining the waste. As the testing program progresses, preliminary evaluations should be performed from time to time to help set the direction for remaining tests and focus the limited funds to the most promising technologies and address the most significant issues.

Future evaluation criteria should be based on providing a system that increases melt rate, minimizes maintenance and facility needs. The expected increase in waste processing rate in the melter has the highest ranking, because it is the main reason for considering this equipment. Operating, maintenance, equipment disposal costs, followed by capital costs are next in importance, due to the need to keep the cost as low as practicable. Operating complexity and ease of interfacing with other systems measures the ability to provide a reliable process. The next decision point for the technologies should be based on information up to the Engineering Development stage as defined by demonstrating cost/benefit advantages, pilot scale testing success, and design features for a full scale unit.

Without performing any additional tests, the rotary calciner appears the best choice for a secondary system because of low height requirements; maintenance is not expected to be as intensive as the wiped film evaporator; process flexibility is good; and the particle size is not expected to be exceptionally small. The wipe film evaporator is the recommended highly because the processing is fast, the processing conditions are milder than the calciners and has a lot of flexibility. If hard cake formation is a problem, the spray calciner is a good choice with previous radioactive experience.

Table 1 - Issues and Suggested Testing Scale

Potential issue	Lab/Bench	Pilot	Full Scale
Effect of low melting salts	X	X	
Corrosion/erosion rate of material		X	
Maximum processing rate		X	X
Range of acceptable operation		X	X
Reliability of process with and without glass formers in the feed		X	
Remote design verification		X	X
Product carryover in offgas		X	X
Product characteristics (e.g., percent moisture, size distribution, nitrate decomposition, stickiness, density)	X	X	
Energy efficiency		X	
Processing rate range (maximum/minimum)		X	
Effect of coupling to melter with or without countercurrent melter offgas flow		X	
Process Control testing for Waste Form Qualification		X	X

CONCLUSIONS

The rotary calciner, wiped film evaporator, fluidized bed, and spray calciner show promise for enhancing cost effective production of large quantities of glass. Tests should be performed with a simulated Hanford waste blend to determine processing rates for the dryer/calciner and a dry fed melter. Faster waste processing rates per equipment cost and cell space requirements may be sufficient to justify the extra equipment operations and maintenance activities that would be required for a calciner or dryer. Additional testing is needed with Hanford waste types to be able to perform the evaluation. Minimal calciner tests should be performed until production rate enhancements for a dry fed melter are determined.

Previous experiments indicate dry feed would increase melter throughput significantly and the total capital and disposal costs would be less.

However, operating costs maybe higher dryer/calciners than the melter because of maintenance requirements. Calciners provide a dryer product than WFEs. Therefore, the product from calciners should process faster in the melter although the difference is not expected to be significant.

Several experiments on drying simulated radioactive waste have been performed with WFEs. They have indicated that they can remove a large amount of moisture and generate a product that should be able to be delivered to the melter. Although before a dryer/calciner is used, some testing and/or effort in designing the interface between the WFE and melter will be required. Also, additional information on the operating life of components is needed to ensure the maintenance requirements do not significantly affect availability.

Particulate carry-over from the melter was a problem with dry feed to the melter (McElroy 1975). During the performance of some of the PNL tests, additional off-gas treatment equipment was needed and may be required for an uncoupled system (e.g., cyclones, sintered metal filters). Additional testing is needed to determine the required equipment.

Based on testing to date on alkaline feeds, no drying/calciner system currently developed has shown enough reliable operation to justify its use to reduce the melter size.

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Appendix A

CALCINER\DRYER ANNOTATED BIBLIOGRAPHY

1. Sasaki, N., H. Sasaka, M. Ohba, Y. Hasebe, H. Nagaki, and N. Tsunoda. "Solidification of High Level Waste (5) - Fluidized Bed Calcination of Simulated High-Level Waste by the Continuous Inert Bed Concept". Tokai Works Semi-Annual Progress Report (Jan.-June, 1978). PNCT-831-78-01, February, 1979, pp. 124-128.

Summary

This paper from a semi-annual progress report discusses fluidized bed calcination of high sodium bearing waste using the inert bed concept. In this study simulated high level waste was fed into a 4 inch diameter fluidized bed calciner.

The major constituents in the simulated waste were Na, Fe, Ni, Cr, K, Sr, Ba, Zr, Mo, Co, Te, Y, and a rare earth mix. Fused silica was used as the inert bed and aluminum nitrate was introduced as an additive to promote calcination.

The major findings of the paper in relation to composition and the additives were that:

1. The fluidized bed calcination under continuous inert bed concept in which aluminum nitrate is used as an additive and fused silica as a fluidized bed particle would be recommendable for the operating procedure of calcination of high level liquid waste containing high sodium nitrate.

2. Aluminum nitrate should be added to the feed at greater than 0.1M while operating the calciner at $>600^{\circ}\text{C}$.

2. Sasaki, N., H. Sakata, M. Ohba, N. Tsunoda, Y. Hoshino, and Y. Hasebe. "Solidification of High Level Waste (4) - Fluidized Bed Calcination of Simulated High-Level Liquid Waste by the Attrition-Elutriation and Particle Growth Concepts". Technical Report - Tokai Works Semi-Annual Progress Report (July-Dec. 1977). PNCT-831-78-02, Tokai, Japan, July, 1978, pp. 95-97.

Summary

This paper from a semi-annual progress report discusses fluidized bed calcination of high sodium bearing waste. In this study, simulated high level waste was fed into a 4 inch diameter fluidized bed calciner.

The composition of the simulated feed was not available, but because this study was carried at the same facility it is likely that the composition is similar to reference one. Iron nitrate and aluminum nitrate were used as additives to suppress the effects of sodium nitrate on the fluid bed calcination.

The major findings of the paper in relation to composition and the additives were that:

1. Simulated high level waste with a 1M sodium concentration is feasible when more than 0.7M iron nitrate is added to the feed and the calciner is operated at $>700^{\circ}\text{C}$.
2. Particle growth concept is more appropriate than the attrition-elutriation concept in the operation of the fluidized bed.
3. Simulated high level waste with 1M sodium concentration is feasible when more than 0.40M aluminum nitrate is added to the feed and the calciner is operated at $>650^{\circ}\text{C}$.
4. Severe feed nozzle plugging was observed in the operation of the fluidized bed calciner.

3. Abrams, C.S. and L.C. Witbeck. "Sodium Waste Technology - a Summary Report". Technical Report - Argonne National Laboratory. ANL-86-50, Argonne, Illinois, January, 1987.

Summary

This report discusses, in part, the MEDEC (melt-drain-evaporation-calcination) as it relates to the calcination of sodium by a rotary drum calciner. Pure sodium was injected into a rotary drum calciner to assess the possibility of calcining sodium bearing wastes in this calciner as part of the MEDEC process.

The major findings of this study in relation to the rotary calciner and the sodium content were that:

1. At approximately 20% bed volume or higher, it was observed that the large batch wetted the entire bed and formed a large cohesive mass which eventually overloaded the machinery.
2. The drum seals performed well for awhile, but eventually leaked particulates into the process cell atmosphere.
3. Finely divided product carry over in the calciner off gas caused major plugging problems.

4. Newby, B.J. "Calcining Sodium-Bearing Waste by Blending with Zirconium Fluoride Waste". Technical Report - Exxon Nuclear Idaho Company. ENICO-1006, Idaho Falls, Idaho, November, 1979.

Summary

This report covers the pilot plant work performed to develop a flowsheet for calcining sodium bearing waste based on blends with zirconium wastes. Calcining runs were carried out in ten and thirty centimeter diameter fluidized bed calciners. DTA-X-Ray was also carried out in support of the calcination runs.

Two different concentrations of the constituents in the simulated first cycle zirconium waste were blended with one composition of simulated sodium bearing waste. The two different zirconium wastes were representative of waste tanks WM-182 and WM185 at Idaho Chemical Processing Plant (ICPP). The major constituents of the zirconium wastes were Zr, Al, B, Fe, NO_3 , and F, while the major constituents of the sodium bearing waste were Al, B, Na, K, Mn, Hg, Fe, NO_3 , Cl, PO_4 . Calcium nitrate was added to the feed to reduce Cl and F volatility. Technically speaking, the Zr wastes were also introduced as additives to promote calcination.

The major findings of this study in relation to composition and the additives were that:

1. Sodium bearing waste can be effectively calcined with blends of Zr and Na wastes containing up to 5.3 mol% Na. Fluidized bed operability decreases substantially above this limit.
2. Introduction of calcium nitrate to the feed substantially reduces F and Cl volatility during calcination of the waste blends. An optimum mole ratio of 0.70 Ca/F is recommended.
3. The undissolved solids content of Zr-Na waste blends containing a Ca/F mole ratio of 0.7 is sufficiently low so that plugging of calciner feed equipment is less of a problem.

5. Bjorkland, W.J. "Fluidized Bed Calcination Experience with Simulated Commercial High-Level Nuclear Waste". Technical Report - Pacific Northwest Laboratories. BNWL-2138, Richland, Washington, November, 1976.

Summary

In this report calcination of simulated high level wastes representative of those to be generated by commercial fuel reprocessors has been tested in fluidized bed calciner using an inert material. The inert material improves

the operation of the bed since particle size control is not required, a low inventory of fission products is maintained in the bed, high sodium bearing wastes can be calcined, and high feed rates are possible.

Several compositions of simulated waste were used in this study. However, each composition contained concentrations of Na, Fe, Cr, Ni, PO_4 , Gd, fission products, actinides, and HNO_3 . The sodium concentration was the only species that was varied widely, since the primary objective of this study was to show that high sodium wastes could be calcined by this method. No additives were used to effect calcination in this study.

The major findings of this study in relation to composition were that:

1. Continuous inert bed calcination provides a significantly improved operating technique when applied to commercial HLLW solidification.
2. Sodium levels up to 1M are calcinable with fluidized bed calcination using an inerts.

6. Newby, B.J. "Laboratory Flowsheet Development for ICPP WM-183 Waste". Technical Report - Idaho National Engineering Laboratory. ICP-1124, Idaho Falls, Idaho, October, 1977.

Summary

This report describes flowsheets that were being developed to calcine waste stored in Idaho Chemical Processing Plant (ICPP) waste tank WM-183 without fluidized bed agglomeration or excessive corrosion of the off gas system caused by the presence of sodium nitrate and chloride respectively. Two flowsheets were being considered: (1) adding calcium nitrate to a blend of WM-183 waste with zirconium fuel waste, (2) adding powdered iron and silver nitrate to WM-183 waste. DTA-X-Ray was used to evaluate the calcinability of the waste in each flowsheet.

The major constituents of the WM-183 waste are Al, Na, K, F, Cl, NO_3 , SO_4 , PO_4 , Ca, Cr, Cu, Fe, Mg, Mn, Ni, and B.

The major conclusion drawn from this study in relation to composition and the additives were that:

1. DTA-X-Ray studies show that calcination of WM-183 waste without additives would cause agglomeration of the fluidized bed particles.
2. DTA-X-Ray studies show that the addition of powdered iron or blending of zirconium waste with WM-183 waste shows promise for eliminating agglomeration during calcination. In addition, adding iron powder to

commercial waste shows much greater promise for eliminating fluidized bed particle agglomeration than adding iron to WM-183 waste.

3. Gas evolved from adding powder to WM-183 waste does not contain enough hydrogen to constitute an explosion hazard.

4. The addition of aluminum nitrate to WM-183 waste to which iron has been added has potential for keeping the chloride in the calcine.

7. Newby, B.J. "Calcining Sodium-Bearing Waste Using Aluminum Nitrate". Technical Report - Westinghouse Nuclear Idaho Company. WINCO-1026, Idaho Falls, Idaho.

Summary

In this report methods were studied for converting the sodium bearing wastes at the Idaho Chemical Processing Plant (ICPP) into granular, free flowing solids by fluidized bed calcination. Test runs were carried out in a 10 and 30 cm diameter fluidized bed calciners in which sodium bearing waste was blended with aluminum nitrate and various additives. Aluminum nitrate represents Fluorinal waste, which is anticipated to be blended with the sodium bearing waste.

One composition of simulated sodium bearing high level waste was used. The major constituents of the simulated waste were Na, Al, B, K, Mn, Fe, NO_4 , Cl, PO_4 , SO_4 , and acid. Various additives were added to the waste to obtain desired calciner operation, fluidized bed characteristics, properties of calcined solids and chloride volatility. The calcination feed compositions were blends of the sodium bearing waste and: (1) aluminum nitrate and boric acid, (2) boric acid and magnesium nitrate, (3) iron metal, (4) boric acid and sugar, (5) boric acid and calcium nitrate, (6) phosphoric acid and calcium nitrate, (7) calcium nitrate, (8) phosphoric acid, (9) hydrofluoric acid-boric acid-calcium nitrate, (10) aluminum powder.

The major findings of this study in relation to the composition and the additives were that:

1. A blend of sodium bearing waste and 2.2M $\text{Al}(\text{NO}_3)_3$ (2:1 vol.) with 0.10-0.20M boric acid added to the feed is readily calcinable. Blends with 0.20-0.25M boric acid resulted in difficulty in controlling particle size. Blends with 0.40M boric acid tended form clinkers in the bed.

2. Too small of a nozzle in the fluidized bed will cause frequent plugging of the nozzle.

3. Decreasing the 2:1 volume ratio of $\text{Al}(\text{NO}_3)_3$ to sodium bearing waste with 0.20M boric acid resulted in frequent nozzle plugging.

4. The addition of magnesium nitrate to a blend of $\text{Al}(\text{NO}_3)_3$ and sodium bearing waste with 0.20M boric reduced particle size control, increased chloride volatilization, and decreased total alumina and crystalline sodium aluminate concentrations in the calcined solids.

5. A blend of 2.2M $\text{Al}(\text{NO}_3)_3$ and sodium bearing waste (2:1 vol.) with 0.52M iron powder is readily calcinable. However, iron addition to the acidic waste results in a vigorous chemical reaction. Caking of this calcined product occurs in storage vessels over long periods of time.

6. Decreasing the volume ratio of $\text{Al}(\text{NO}_3)_3$ and sodium bearing waste with iron additive results in a decrease in particle control. In addition, the same amount of nitrate that is decomposed by the iron in lower volume ratios is replaced by the nitric acid needed to stabilize the solution and dissolve the iron powder.

7. Blends of 2.2M aluminum nitrate and sodium bearing waste (2:1 vol.) with 0.20M boric acid and one mole of sugar for each 10-20 moles of nitrate present were calcined without bed agglomeration or product size control problems.

8. Plugging of the off gas filters when calcining solutions containing sugar may be a problem with certain types of filters.

9. Blends of 2.2M aluminum nitrate and sodium waste with 0.24M calcium nitrate resulted in good retention of chloride in the calcine, but difficult to control particle growth and high nitrate concentration in the calcine. Decreasing or increasing the calcium nitrate concentration substantially resulted in severe agglomeration.

10. Blends of 2.2M aluminum nitrate and sodium waste containing 0.20M phosphoric acid is readily calcined. However, difficulty in particle growth control and low retention of chloride in the calcine solids was observed.

11. Blends of 2.2M aluminum nitrate and sodium waste with 0.15M phosphoric acid and 0.52M calcium nitrate resulted in doubling the percentage of chloride retained in the calcine solids when only calcium nitrate is added.

12. Blending aluminum powder, nitric acid, and sodium waste produces a violent reaction. In addition, the amount of nitrate the aluminum powder destroys in the sodium waste ends up being added by the amount of nitric acid need to maintain stability of the solution.

8. Domish, R.P., and L.P. Hatch, "Continuous Calcination of High-Level Radioactive Wastes by Rotary Ball Kiln". Technical Report - Brookhaven National Laboratory. BNL-832, Long Island, New York, November, 1963.

Summary

This report studied the feasibility of using a rotary ball kiln in calcination of simulated HLW. A two kiln process was used to reduce corrosion of the calciner materials. Steel balls were introduced into both kilns to aid in heat transfer and break up the calcine. This study was particularly interested in parameters such as corrosion and best materials to prevent corrosion, dust control, and leaching. However, typical operating parameters were also studied but in lesser detail.

This study only involved one feed composition, in which the main constituents were NO_3 , Al, Na, Cl, and acid. Sodium content was less than 0.036M.

The only major finding in relation to the composition was that cake formation was observed when inadequate wall temperatures for decomposition of the salts occurred. Cake formation was not a problem over most of the runs.

9. Bonner, W.F., H.T. Blair, and L.S. Romero. "Spray Solidification of Nuclear Waste" Technical Report - Pacific Northwest Laboratory. BNWL-2059, Richland, Washington, August, 1976.

Summary

This report summarizes the findings of the Waste Fixation Program (WFP) on spray calcination of simulated high level wastes. This study utilized a heated wall spray calciner fitted with top mounted vibrators. The primary purpose of this study was to demonstrate the spray calciners' ability to handle a variety of different waste types and investigate key processing variables.

Spray calcination of six different types of simulated high level waste were investigated in this study, including "clean" HLLW (a G.E. type waste from a plant wherein no chemical salts were added during reprocessing), "dirty" HLLW (an Allied General Nuclear Services (AGNS) type waste, moderately high in salts), AGNS waste (a relatively clean ILLW containing 0.1M Fe and PO_4), Combined HLLW and ILLW, Nuclear Fuel Services Waste (NFS), and combined NFS HLLW and NFS sodium waste. The major constituents of the simulated waste were K, Mo, Fe, Co, Ni, rare earth mix, didymium, HNO_3 , Na, Cr, Ni, and PO_4 . Silica was used as an additive to enhance calcination of high sodium wastes.

The major findings of this study in relation to composition and the additives were that:

1. Encrustations of calcine regularly form around the nozzle exit, but seemed not to significantly hinder atomization or calcination.
2. Significant abrasion of the 303 SS nozzle was observed, but mostly corrected by using a 96% alumina nozzle.

3. Wastes containing up to 2.0M sodium maybe calcined, but calciner capacity must be decreased as more sodium in the wastes is introduced into the feed.

4. Top mounted vibrators cannot effectively remove calcine buildup on the wall when high sodium content wastes are being process at high capacity. However, it is felt that side wall vibrators may overcome this problem.

5. Scaling on the walls maybe caused by 1) partial melting of the particle on contact with the wall, 2) sufficient particle moisture or acid content to cause stickiness but insufficient to cause descaling as vaporization occurs at the hot wall, 3) sintering.

6. Powdered silica may be added to the feed to promote calcination of high sodium wastes. This run was carried out with simulated feed other than the six primary simulated feeds used in the majority of the study. This run was not entirely successful since a glaze formed on the inside of the calciner walls.

7. Feed nozzle plugs were common among high sodium feeds.

10. McElroy, J.L., C.R. Cooley, W.V. DeMier, and J.E. Mendel. "Pot Calcination Performance During First Radioactive Tests in Waste Solidification Engineering Prototypes: Waste Solidification Program, Volume 4". Technical Report - Pacific Northwest Laboratories. BNWL-814, Richland, Washington, December, 1968.

Summary

This report presents results and analyses of the first six radioactive demonstration runs with the pot calcination system in waste solidification engineering prototypes (WSEP). Solidification of high level aqueous radioactive wastes containing approximately 4 million curies was successfully completed in the six demonstration runs. The principal variables investigated in these runs were fission product power, pot size and waste chemical composition.

Two types of waste (low sulfate, high iron and high sulfate, low iron) were prepared from Hanford Purex Plant acidic waste (Purex 1WW) and $^{144}\text{Ce-Pr}$ solutions from the Hanford Fission Products Processing Plant, and some inert chemicals. These two types of waste were named PW-1 and PW-2. Primary constituents of the waste were Na, Al, Fe, Y and rare earths, NO_3 , SO_3 , and fission products. Ca, SO_4 , and Na were added to the feed to either promote calcination, substitute for other constituents, or reduce volatilization of ceratin species.

The major findings of this study in relation to composition and additives were that:

1. Foaming of the PW-1 waste during feeding is a potential problem. Foaming did not occur when using PW-2 waste.
2. The presence of sulfate tended to decrease foaming.
3. Solutions high in nitric acid tended to foam more readily.
4. Aluminum concentrations above 0.5M tended to aggravate the foaming tendency.
5. High solids content in PW-2 waste caused severe plugging of the equipment.
6. Some scaling was observed in processing both wastes.

11. Bond, W.R., J.N. Hartley, J.E. Mendel, J.L. McElroy, K.J. Schneider and M.R. Schwab. "Waste Solidification Program, Volume 6 - Spray Solidification Performance During First Radioactive Tests in Waste Solidification Engineering Prototypes". Technical Report - Pacific Northwest Laboratories. BNWL-1391, Richland, Washington, August, 1970.

Summary

This report presents results and analyses of the first six radioactive demonstration runs with the spray solidification system in waste solidification engineering prototypes (WSEP). Solidification of high level aqueous radioactive wastes containing approximately 7.8 million curies was successfully completed in the six demonstration runs. The principal variables investigated in these runs were the heat generation rate in the solidified waste and the two waste types.

The two types of waste (sulfate free and sulfate containing) were prepared from Hanford Purex Plant acidic waste (Purex 1WW) and ^{144}Ce -Pr solutions from the Hanford Fission Products Plant, and some inert chemicals. These two types of waste were dubbed PW-1 and PW-2. Primary constituents of the waste were Na, Al, Fe, Y and rare earths, NO_3 , SO_3 , and fission products. Al, Ca, Li, and Na were added to the feed to either promote calcination, substitute for other constituents, or reduce volatilization of ceratin species.

The major findings of this study in relation to composition and the additives were that:

1. Deposition of partially dried calcine on the walls and at the bottom of the spray calciner chamber was observed. This problem could be partially corrected by using a different feed nozzle. Long term operation of the spray calciner revealed significant calcine buildup on the walls and bottom of the feed calciner. This problem was attributed to inadequate atomization of the feed.

2. Plugging of the feed nozzle occurred many times when high salt, high solids content feed (PW-2) was solidified. This problem can be overcome by sufficient periodic washing of the feed nozzle.

3. A wall vibrator can effectively be used to prevent calcine buildup on the walls of the calciner. However, the wall vibrator was subject to occasional failure.

12. Kulichenko, V.V., V.F. Savel'ev, V.A. Prokhodtsev, and A.A. Ryabova. "Calcination of Model High-Level Wastes in a Horizontal Apparatus". Soviet Atomic Energy. Volume 56, NO. 5, May, 1984, pp. 314-318.

Summary

This study describes the use of a rotating horizontal worm conveyor calciner in solidifying acidic high level radioactive waste. It is stated that a horizontal plant is much less sensitive to the waste composition than is a fluidized bed or sprayer. However, the design of a horizontal plant is more complicated due to moving mechanisms in the worm conveyor and the low surface area in which to transfer heat. The calcinator is 27 cm in diameter and 3.6 M long.

Various compositions consisting of primarily $\text{Al}(\text{NO}_3)_3$, NaNO_3 , and molasses were solidified in the calciner. Some runs contained $\text{Fe}(\text{NO}_3)_3$, $\text{Cr}(\text{NO}_3)_3$, $\text{Mn}(\text{NO}_3)_2$, and $\text{Ni}(\text{NO}_3)_2$. Molasses was added to accelerate decomposition of the nitrates.

The major findings of the study in relation to composition and the additives was that:

1. The horizontal calciner could solidify high aluminum and sodium wastes with and without additives. However, very high sodium wastes were observed to stick to the walls of the tube.

2. Up to 260 g/l of sodium nitrate could be calcined in the worm conveyor with the molasses additive.

3. Nitrate content in the calcinate was directly related to the amount of molasses added to the feed.

13. Cameron, W.A. and S. Merlin. "An Evaluation of the AVM Process and its Applicability to West Valley". Technical Report - SGN/Numatec. pp. 542-546.

Summary

This report describes the operating experience of the AVM vitrification plant in France for the last three years. A comparison of the AVM and West Valley wastes is made and the applicability of the AVM technology to the West Valley high level waste is partially assessed.

The AVM plant has been in hot operation for the past three years, processing a wide range of compositions. AVM high level waste is acidic and primarily contains Al, Na, Mg, Fe, Ni, Cr, F, P, Gd, actinides, and fission

products. Sodium levels in the feed range from 1 to 23 g/l. The major problems that have occurred during hot operation have been:

1. Contamination of a work area due to both a failure of the automatic feed valve supplying glass frit to the rotary kiln, and excess pressure in the calciner.
2. Contamination of the calciner lubrication oil recuperation circuit.
3. Replacement of the two parts of the dust scrubber for corrosion problems. Fluorine contained in the feed is to blame.
4. Replacement of the driving motor of the calciner tube.

Comparing the AVM waste with WVDP waste, the primary differences are that the WVDP waste is neutralized and contains a very high sodium content. It is stated that the one clear advantage of adopting the AVM process at the WVDP is the availability of significant data accumulated during hot operation.

14. Hull, H.T. "Trip Report on Rotary Kiln Test at Envirotech in Salt Lake City". Trip Report - Technical Division at Savannah River Laboratory. DPST-81-270, Savannah River, Georgia, January 8-9, 1981.

Summary

This trip report details the findings of a DWPF rotary kiln test at Envirotech in Salt Lake City, Utah. This study investigated the feasibility of using a rotary calciner to calcine simulated Savannah River alkaline high level waste.

A 6.5 inch diameter three foot long rotary calciner was used to perform the experiments. A steel bar was inserted inside the calciner to break up the calcine.

Two alkaline solutions were prepared to simulate DWPF alkaline waste sludge. The first solution contained 19 wt% solids and 81 wt% water and the second contained 40 wt% solids and 60 wt% water. However, the solids in the second solution contained 35 wt% simulated sludge and 65 wt% Frit 211 (80 mesh). Common to both solutions was the composition of the waste sludge, which included $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, MnO_2 , $\text{Ca}(\text{OH})_2$, NaNO_3 , and Na_2SO_4 . Azodicarbonamide was added to the feed to prevent decomposition outside of the kiln.

The major findings of the study in relation to the composition and additives was that:

1. First feed solution calcined easily to a free flowing granular product. No scaling was observed on the inside of the kiln.

2. Second feed was uncalcuable due to frit melting in the kiln. A sticky bed and abundant scaling were observed.

15. Freeby, W.A. "Interim Report - Fluidized Bed Calcination of Simulated High-Level Commercial Wastes". Technical Report - Idaho National Engineering Laboratory. ICP-1075, Idaho Falls, Idaho, June, 1975.

Summary

The purpose of this study was to develop and verify process flowsheets for converting Allied-General Nuclear Services (AGNS) and Nuclear Fuel Services (NFS) aqueous wastes to granular solids using the fluidized bed calcination process. Tests were made using a four and twelve inch diameter calciner.

Four different simulated compositions were studied, including a combined high level and intermediate level AGNS waste, concentrated AGNS waste containing specified concentrations of sodium, dilute AGNS waste containing minimal amounts of sodium, and NFS high level acid waste. The major constituents in the waste were Na, Fe, Al, Cr, Ni, NO_3 , K, Mo, Co, Cd, Te, Ba, Gd, PO_4 , and a rare earth mix. Iron powder was added to promote calcination and/or modify the properties of the calcined waste. The major findings of this study in relation to the composition and the additives were that:

1. Concentrated AGNS HLLW can be successfully solidified using fluid bed calcination without additives, if the sodium concentration is below 0.20M feed nozzle plugging and moisture in the calcined product occurs with wastes containing more than 0.20M sodium and no additives.

2. Concentrated AGNS HLLW containing up to 1.1M sodium can be successfully solidified using fluid bed calcination, if iron is added to the waste to suppress sodium nitrate formation.

3. Dilute AGNS HLLW can not be calcined successfully by conventional fluid bed methods since particle size and bed inventory cannot be controlled in the desired operating range.

4. Fluid bed calcination of combined AGNS HLLW-ILLW and NFS acid waste is feasible.

5. NFS waste containing 1M sodium and no additives has a tendency to agglomerate.

16. Alford, M.D. "Fluidized Bed Calcination of Simulated Purex High-Activity Level Wastes - Interim Report". Technical Report - General Electric Hanford Laboratories. HW-66384, Richland, Washington, September, 1960.

Summary

The Hanford eight inch square fluid bed waste calciner was operated for six months in this report, processing simulated Purex-type acidic waste. This report was aimed at defining and improving major operational problems and qualitatively defining the effect of various operating variables.

Four feed compositions were tested, including compositions that represent a low-acid, high salt waste from the formaldehyde-kill process, high sulfate, high iron waste, and two variations on the Purex first cycle waste. The primary constituents in the simulated waste were Na, Fe, Al, Cr, Ni, SO_4 , PO_4 , and NO_3 .

The major findings of the study relating to composition were that:

1. High sodium and high sulfate wastes have a tendency to fuse in the bed, deteriorously affecting the fluid bed operability by scaling of the heat transfer surfaces above 600°C . Thus, feeds of this type must be calcined below 600°C .
2. The most serious problem encountered in fluid bed calcining of Purex wastes was that of solids build-up and particle agglomeration at and/or near the feed nozzle. Modification of the nozzle was necessary, but did not yield optimum results. High sulfate wastes severely agglomerated at the nozzle.
3. Inadequate fluidization results when a sufficiently large number of agglomerates collect in the bed ($> 5 \text{ wt}\%$).

17. Allemann, R.T., and B.M. Johnson. "Radiant-Heat Spray Calcination Process for the Solid Fixation Waste". Technical Report - General Electric Hanford Laboratories. HW-65806 Pt 1, Richland, Washington, February, 1961.

Summary

The spray calcination of simulated wastes has been studied in a relatively small scale reactor eight inches in diameter and ten feet tall. A wide variety of compositions were handled, including Darex, Zirflex, TBP-25 and acidic and basic Purex wastes. Many process variables were studied, including feed composition, additives, thermal conductivities, atomization, feed rate, reactor temperature, volatilization, etc..

Of particular interest is the applicability of spray calcination for high-level wastes containing sodium, such as the Purex wastes. Six different

compositions of simulated acidic and basic Purex waste were studied. Principle species present in most of the simulated Purex wastes were Na, Fe, Al, Ni, Cr, NO_3 , and SO_4 . Several additives were used to promote calcination and/or modify the properties of the calcined waste. The additives used were sugar, phosphate, boric acid, combinations of sugar and phosphate, combination of sugar and boric acid, and calcium.

The major findings of the study relating to composition and the additives were that:

1. Feed high in Na, NO_3 , SO_4 , particularly basic feeds, were not calcinable without additives.

2. Incompletely calcined powders, notably the product from high-sulfate Purex wastes, were difficult to handle because of their tendency to cake in the filter system and cyclone. This difficulty occurred principally with the acidic waste and to a lesser extent the neutralized waste. Build-up of calcine on the walls of the calciner was also a problem, but could be removed by occasionally tapping on the walls of the calciner.

3. The addition of sugar to the acidic waste effectively overcame the caking problem, but lumps still tended to form in the cyclone with the neutralized waste. Sugar, added to decompose sulfates and nitrates, was shown to be very effective in promoting calcination of all Purex wastes. Sugar further improves the characteristics of phosphate treated feeds, neutralized wastes, and wastes containing high NaNO_3 and sulfate compounds cannot be calcined with out sugar additions.

4. Phosphoric acid was added to the feed in an attempt to lower the melting temperature of the calcined product to 800-900°C. Results show that the phosphate not only lowered the melt temperature of the calcine to 820°C, but also changed the calcine properties such that the calcine is more dense and free flowing.

5. Boric acid was added to high aluminum containing wastes in attempt to produce true glass matrices in the calcine. Results of this addition were successful.