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W. F. BONNER AND J. L. McELROY

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UNITED STATES DEVELOPMENTS IN THE SOLIDIFICATION OF HIGH-LEVEL RADIOACTIVE WASTE

To be presented at Nuclear 1978, 5th International Fair and Technical Meeting of Nuclear Industries, at Basel, Switzerland, October 4, 1978

by
W. F. Bonner
J. L. McElroy

BATTELLE
PACKFIC NORTHWEST LABORATORIES
RICHLAND, WASHINGTON

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ABSTRACT

UNITED STATES DEVELOPMENTS IN THE SOLIDIFICATION OF HIGH-LEVEL RADIOACTIVE WASTE

by

William F. Bonner

and

Jack L. McElroy

A major waste solidification research and development program is being conducted by Battelle Pacific Northwest Laboratories under the sponsorship of the United States Department of Energy.

In the spring of 1977, three high-capacity processes for solidifying simulated high-level liquid waste became operational. The three processes are: the joule-heated, ceramic-lined continuous melter, the in-can melter, and the spray calciner. Recent operational experience with these and other processes are described in this report.

The continuous ceramic melter began operation in February 1977. Since that time, both liquid and calcined simulated high-level waste have been fed to the melter. Melting rates of over 100 kg per hour have been demonstrated while calcine feeding and liquid feeding rates of 100 liters per hour have also been demonstrated. A wide range of waste compositions has been converted to glass in the ceramic melter including compositions simulating defense wastes stored at Hanford and Savannah River in the United States. By May 1978, over 25,000 kg of glass had been produced and poured into mild steel or stainless steel canisters up to 3 ft in diameter by 9-1/2 ft tall. The tilt to pour drain mechanism worked very well, reliably stopping and initiating liquid melt flow as needed.

The in-can melting furnace in operation since April is capable of producing canisters of glass up to 28 in. diameter by 8-1/2 ft tall. The maximum melting rate of the in-can melting process has been found to be roughly a linear function of the canister diameter. Melting rates in a 24 in. canister can be over 100 kg per hour. Improved internal metallic fin designs have helped to bring about this capacity increase. A gamma emission technique capable of monitoring melt levels to within 1 in. during in-can melting has been

developed. The depth of unmelted material on the melt surface can be determined and selective or bulk depositions of radionuclides anywhere in the solidification system can also be monitored. Seventeen large-scale canisters have been filled to date of writing with simulated high-level waste glass in this unit.

The full-scale heated wall spray calciner, also started up in April, has been operated at liquid feed rates exceeding 300 liters per hour. All waste compositions tested are calcineable, even wastes containing over 95 percent sodium cations. The newly designed remotely replaceable atomizing nozzle has been fitted with a ceramic insert to avoid abrasion problems. Another type of nozzle compatible with air-lift liquid feeding has also been demonstrated. Particulates penetrating the filters are observed to be in the 0.5 to 5 micrometer range and over 99 percent of the particles penetrate the filters immediately following filter blowback.

Borosilicate glasses have been developed for most of the anticipated high-level radioactive waste compositions. Long-term thermal and radiation stability tests are underway. Glass devitrified during high-temperature storage has a modest factor of 2 to 10 increase in leach rate. Radiation doses equivalent to beyond 250,000 years have not shown any evidence of physical damage to the glass.

INTRODUCTION AND BACKGROUND

At Pacific Northwest Laboratory (PNL) processes are being developed for the vitrification of nuclear high-level liquid waste (HLLW). This work is being carried out by Battelle-Northwest (BNW) for the United States Department of Energy (DoE). Prior to 1977 much of this work was developed to be able to handle the anticipated HLLW that would arise from the commercial reprocessing of spent power reactor fuel. At that time, the equipment was designed to be capable of vitrifying liquid waste at a rate in excess of that required by a five ton per day nuclear fuel reprocessing plant. This choice of size has been fortunate because a major emphasis of the current program is directed toward providing the technology to convert existing wastes in the United States to glass. Because of the large volume of these wastes, high capacity processes are desirable. For example, if a decision were made to remove and vitrify HLLW from storage tanks at the Savannah River Plant in Aiken South Carolina, the calciner(s) would have to dry in excess of 500 liters per hour and the melter(s) would vitrify nearly five tons of glass per day. The equipment now being tested by PNL could meet these rates with approximately two parallel units.

In addition to existing wastes, the program is beginning to assess problems that may arise if an alternative fuel cycle, such as thorium, is developed in the United States. Because of the presence of fluoride, the wastes from this cycle are expected to present materials problems that will require solutions, but the same processes that have been developed are expected to be applicable. Thus, the processes are expected to be able to handle a wide spectrum of waste compositions typical of those presented in Figure 1.

FIGURE 1. Typical High-Level Waste Compositions

Fe_2O_3 - 3.7%	Al_2O_3 - 8.0%	Al_2O_3 - 46.4%
P_2O_5 - 1.6	Fe_2O_3 - 6.3	CaO - 3.3
Fission Products - 88.0	F - 1.5	Fe_2O_3 - 31.6
U_3O_8 - 2.9	K_2O - 3.7	MnO_2 - 10.3
Others - 3.8	Gd_2O_3 - 6.7	NiO - 2.3
	ZrO_2 - 16.1	U_3O_8 - 6.1
	ThO_2 - 11.5	
	U_3O_8 - 1.2	
	Fission Products - 40.6	
	Others - 4.4	

Currently, the system comprised of the spray calciner and continuous ceramic melter is receiving the most emphasis. This system is preferred by most because of its combined features of high capacity and broad adaptability to waste compositions and the potential for producing a high quality glass. The ceramic melter also is potentially capable of direct liquid feeding, thus eliminating the need for a calciner. The in-can melting system tested during the WSEP program[(a)] is being developed as a backup to the ceramic melter. Some additional development work is being carried out with a fluidized bed calciner, a modification of the system used at the Idaho National Engineering Laboratory to solidify existing HLLW. Finally, a small portion of the U.S. program is continuing to look at advanced waste forms such as glass marbles, ceramic pellets and metal matrices.

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a. J. L. McElroy, et al., Waste Solidification Program, Volume II, Evaluation of WSEP High-Level Waste Solidification Processes, BNWL-1667 (June 1972).

SPRAY CALCINATION

The heated wall spray calciner has been developed mainly at PNL. Pilot-scale radioactive testing as well as full-scale nonradioactive testing has been conducted. Significant improvements have been accomplished in the calciner components in recent years that affect operating performance.

PROCESS DESCRIPTION

The spray calciner consists of an externally heated vertical cylinder into which liquid waste is sprayed. See Figure 1. Pneumatically atomized liquid waste is dried and calcined as it falls through the 700°C calcination chamber. Heat is provided by an external multizone furnace. Entrained calcine collects on porous stainless steel filters and falls directly into the attached vitrification process after being removed by a periodic pulse of blowback air. Operation of side-mounted vibrators prevents accumulation of calcine at any point in the calciner.

OPERATING EXPERIENCE

In April, 1977, the spray calciner shown in Figure 2 was started up. The calciner is 3 ft in diameter by 10 ft tall and contains ft^2 filter area. At the time of this writing, liquid feedrates of over 300 liters per hour have been demonstrated in this unit during 400 operating hours. Modifications are currently being performed to further increase the capacity.

To reach flow rates of this magnitude, atomizing nozzles with a minimum orifice of 1/4 inch are routinely used. The need for a flow control valve in the feed system has been eliminated. The atomizing nozzle can act much like an orifice flowmeter being calibrated against liquid pressure, air pressure and air flowrate to indicate the liquid feedrate. Liquid feedrate thus known can be readily adjusted by adjusting only atomizing air pressure. Elimination of the requirement for a pressurized feed system has also been demonstrated by use of external mix nozzles. Spraying systems, setup No. 70, has been routinely used in the new calciner. Standard air lift techniques may thus be used with a spray calciner.

FIGURE 1

SPRAY CALCINER — CERAMIC MELTER SYSTEM

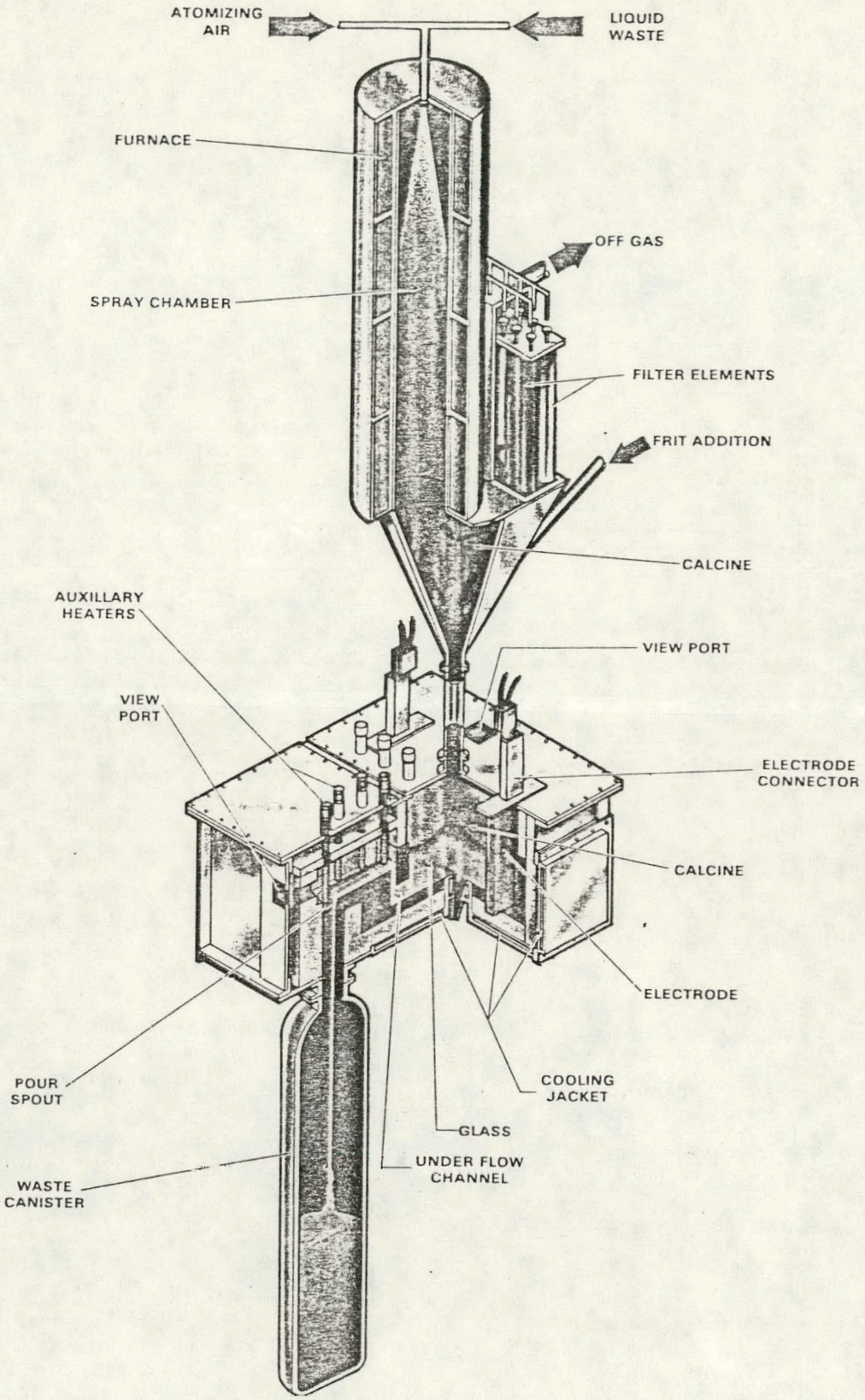
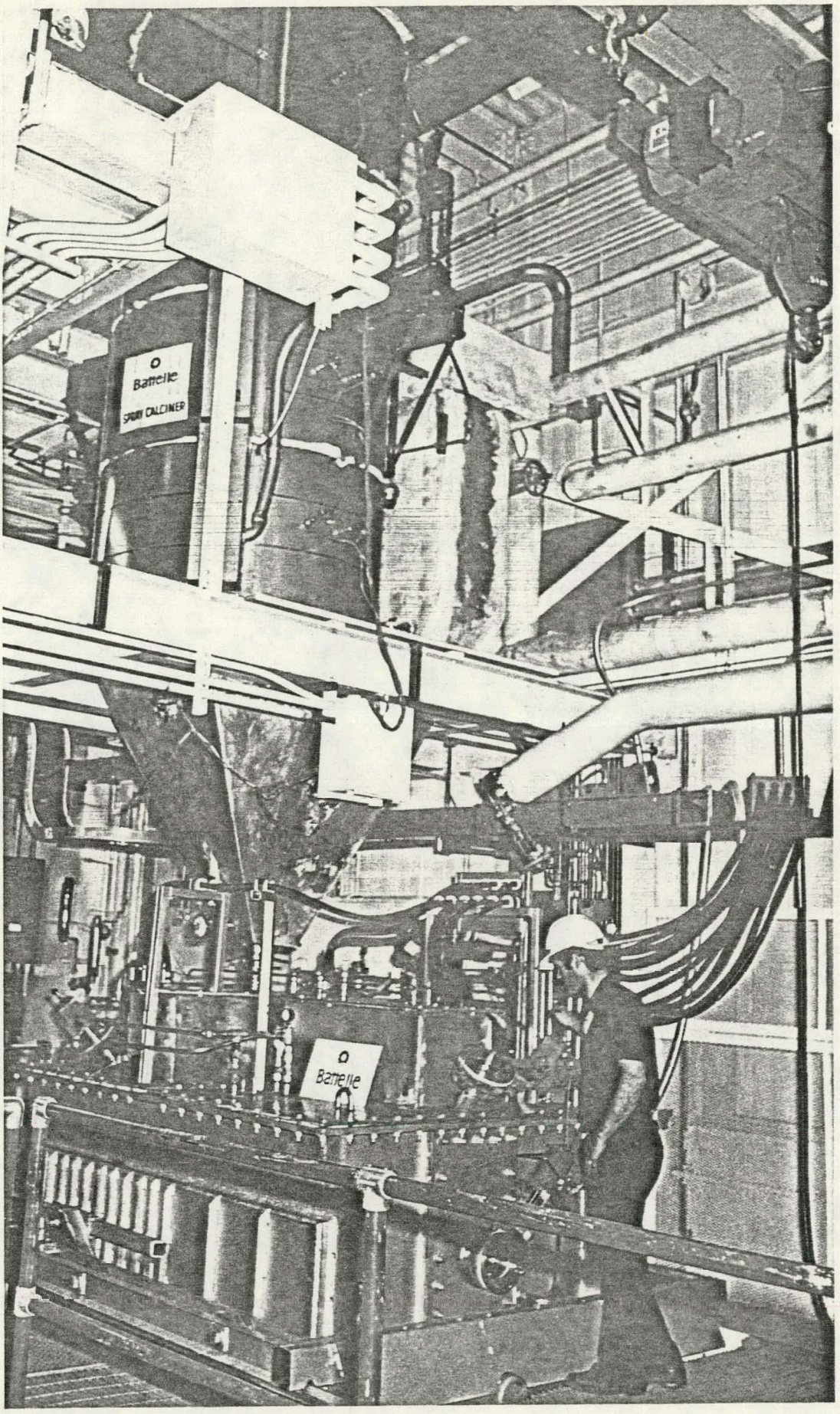


Figure 2



The spray calciner is exceptionally flexible to waste composition. Wastes containing over 95% sodium cations have been calcined by the addition of silica to the feed stream. Drastic, instantaneous changes in feedstock concentration or composition have little, if any, affect on calciner performance.

Calcine mass mean particle diameter can be controlled in the 15 to 220 μm range by varying the nozzle type, the liquid-to-air ratio, and the furnace temperature.

Tests performed with cyclone dentrainment rather than filters have been sucessful. Removal efficiencies of 95% are routinely achieved with a low-pressure drop cyclone separator. The user thus has a choice of cyclone or filter.

Particulates passing through the sintered stainless steel filters between blowbacks have been analyzed and found to be less than 0.5 μm in diameter. Over 99% of the particulate mass passing through the filters does so immediately following blowback. These particles range from 0.5 to 5 μm in diameter. Maximizing time between filter blowbacks is thus desirable. Blowback times of over one hour have been tested. Under these conditions, less than 0.005% of the calcine penetrates the filters.

CERAMIC MELTER

Development of the joule-heated ceramic melter for vitrification of radioactive waste began at PNL in late 1973. Since that time, this technology has been incorporated in many radioactive waste vitrification facilities around the world. The spray calciner and ceramic melter is being developed as the primary system for vitrification of the neutralized waste stored at Savannah River.

PROCESS DESCRIPTION

Energy is supplied to the joule heated ceramic melter by passing alternating current through molten glass between immersed electrodes. As shown in Figure 1, calcine and frit flow from a calciner directly onto the surface of the molten glass forming a relatively cool layer or cold cap on the melt. The mixture continuously settles and melts into the molten pool. After a given residence time, the melt flows up through a riser into the overflow trough and discharges into the receiving canister. Discontinuation of melt flow to allow canister changeout is accomplished by simply tilting the entire melter back

two to five degrees. During canister changeout, glass is accumulated but otherwise the melter operates normally. After changeout is complete, the melter is tilted back to operating level. The canister is then cooled, capped and seal-welded, leak checked, decontaminated and removed to storage.

Due to its efficient heat input capabilities, feeding of liquid waste to the ceramic melter, without prior calcination, is an attractive option. In this process, liquid waste and slurried glass formers flow into the melter covering the melt surface with a boiling liquid layer. Melter off-gas treatment is thus that of an evaporator. As liquid waste is added, equilibrium is established with solids from the liquid waste precipating and eventually melting in the molten pool. Two sets of horizontal electrodes, one above the other, are used in the liquid fed melter. During liquid feeding, power can be increased to the upper electrodes near the surface of the glass melt when most energy is needed to vaporize the liquid. Otherwise, the melter is constructed and functions similar to the calcine fed melter.

OPERATING EXPERIENCE

In February of 1977, a continuous melter termed the liquid fed ceramic melter capable of processing over 100 liters per hour of liquid waste was started up. In April 1978, a melter coupled to the plant-scale spray calciner and capable of producing glass at over 100 kg per hour was started up. Since startup, both melters have been maintained at operating temperature. At the time of this writing, over 25 metric tons of glass have been produced in the liquid fed melter during 500 operating hours.

The tilt-to-pour concept in which melt discharges through an overflow has proven reliable. The entire melter is tilted ±2° to start or stop the drainage of glass. Flexible connections are required but judicious locating of joints relative to the pivot point can minimize the difficulty. Heating of the overflow area with globar heaters has been successful.

Inconel ^{R} 690 electrodes continue to exhibit superior properties for high-level waste glass use. After two years operation, only minimal attack has been observed. Monofrax K-3 refractory chosen for its outstanding corrosion resistance and its low electrical conductivity has performed well. Even though subjected

to repeated thermal shock when malfunctions occur during liquid feeding, small cracks are observed in the refractory but significant spalling has not been observed.

Foaming in the melter was observed using simulated Savannah River waste. While melting this composition, carbonates in the waste decomposed at a temperature where the glass was quite viscous. This caused the material to foam and substantially reduce the processing rate. Subsequent operations have shown that foaming can be avoided by proper selection of glass former's physical and chemical properties along with appropriate melt formulations.

Melt is normally drained into carbon steel canisters that are up to 3 ft in diameter by 9-1/2 ft tall. Several metric tons of glass are contained in each canister. During an extended test with simulated Hanford neutralized waste, canisters were filled in air at an average rate of 95 kg/hr. Although filled without external heating or cooling, incompelte filling or significant thermal distortion of the canisters was not observed. The highest canister external surface temperature was 475°C.

During operation, wall mounted electrode temperatures remain significantly below that of the melt. Temperatures in the bulk of the melt are as high as 1300°C while electrodes remain at 1000 - 1050°C. Temperatures at the top of a 10-in. thick cold cap are below 200°C. This selfcooling feature is attractive for assuring long melter life.

IN-CAN MELTING

The in-can melting process has been demonstrated both radioactively on a pilot-scale and nonradioactively with canisters over 2-ft in diameter. It is an extremely simple and well developed process.

PROCESS DESCRIPTION

In-can melting utilizes the waste canister as the melting crucible. A canister is placed inside a vertical multizone furnace, coupled to the output of a calciner, then heated to 1000 to 1050°C. Calcine and glass-forming frit flows into the canister where it is melted and slowly fills the canister. Temperatures in all furnace zones are controlled simply by thermocouple output.

When a canister is filled, the calcine/frit stream is diverted to the other canister in an adjscent furnace. Clean frit or other materials may be added at this point to immobilize any unvitrified material in the unfilled portion of the canister. After filling is complete, the canister is held at melting temperature for two to four hours to complete melting.

OPERATING EXPERIENCE

The PNL plant-scale in-can melter became operational in April of 1977. This melting furnace is capable of producing canisters 8 ft tall by up to 28 in. in diameter.

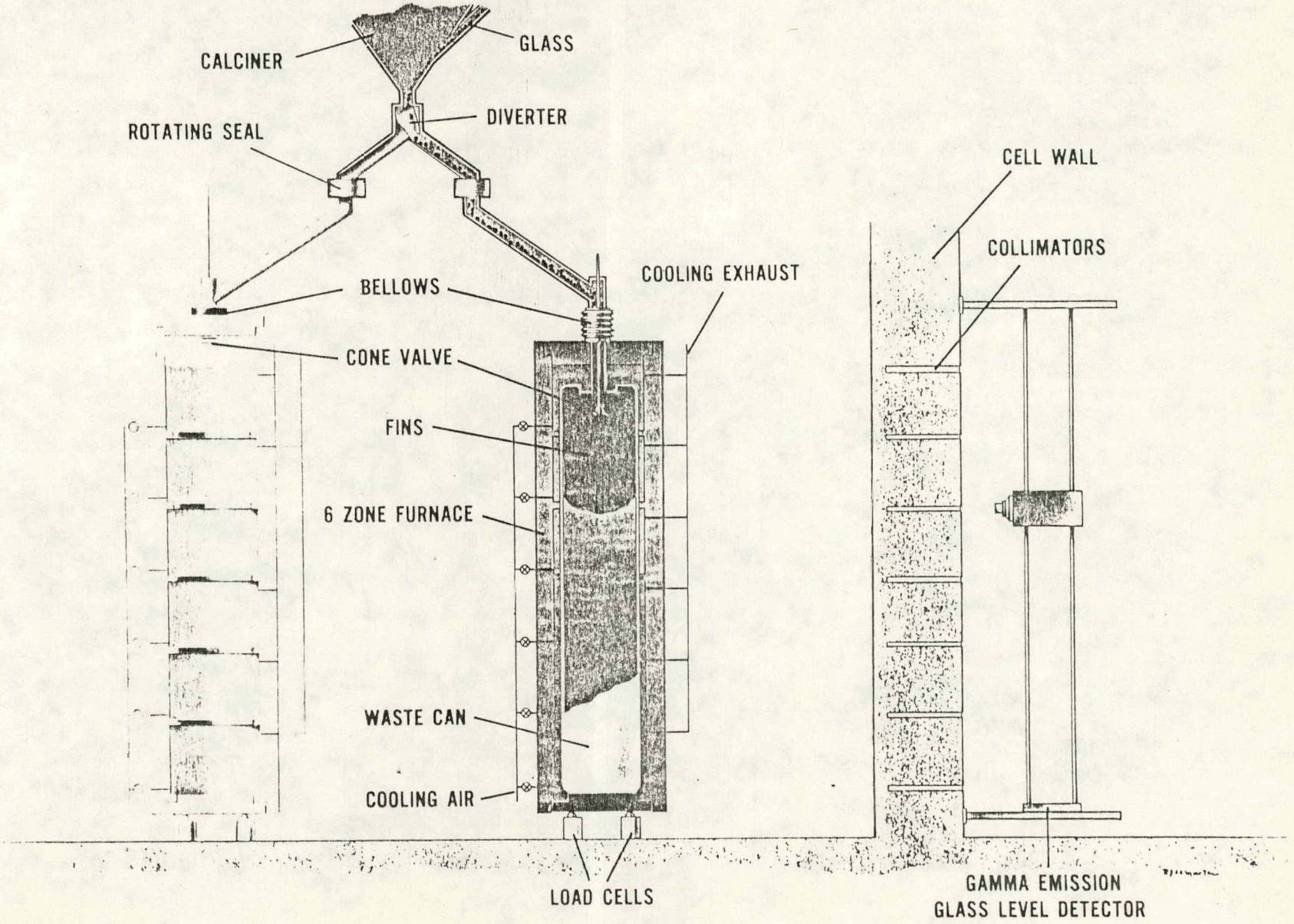
Forty-two engineering-scale canisters of simulated radioactive waste have been produced by the in-can melting process. During a recent 10-day continuous operation test with the spray calciner/in-can melter, 12 canisters of glass were produced. Since it is desirable that a commercial canister not be encumbered with thermocouples either inside or on the surface, all canisters during this run were filled without reliance on temperature or visual monitoring. In fact, two of the canisters were filled with viewing windows and temperature indicators totally obscured. In all cases, the canisters were filled properly.

A gamma emission technique has been developed for monitoring in-can melting progress. This system, diagrammed in Figure 3 , relies on gamma radiation from the radioactive waste to indicate the melt level in the canister. Tiny holes in the cell wall act as collimators to level monitoring even though the canister may be several meters from the wall. Tests with radioactive canisters show the melt-air interface can be monitored to within one inch quite readily. Holdup of a radioactive material anywhere in the canister (or processing equipment) can be detected by its gamma emissions.

To avoid unmelted material being left in the unfilled portion of the canister, the entire canister is placed in the heated zone of the furnace. At completion of melting, all material clinging to the surface of the canister has been observed to be sintered or melted to form a material with leach resistance similar to that of the glass in the bulk of the canister. Approximately 0.05 % of the glass is loose in the neck of the canister. Should future criteria require that the loose material in the canister neck be eliminated, a clean frit or other material may be added on completion of the melting step before cool-down.

FIGURE 3

IN CAN MELTER



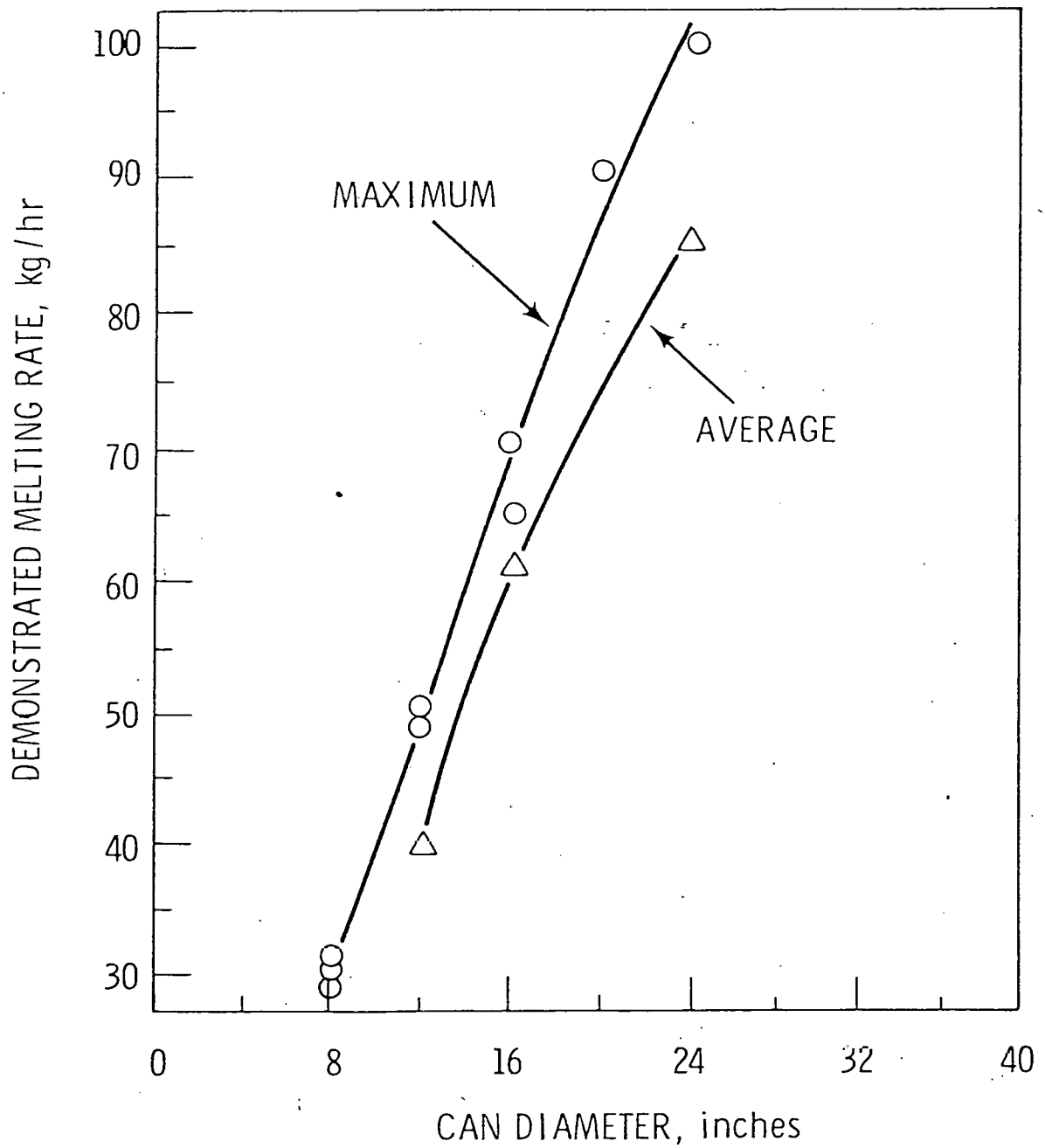
Melting rates of over 100 kg/hr have been demonstrated in the in-can melter. Melting rate is a strong function of canister diameter as shown in Figure 4. These canisters contain internal unattached stainless steel fins for increasing the melting rate. Canisters from 12 inches diameter to 24 inches diameter have been filled in the same melting furnace. A broader size range is possible in a properly designed furnace. The melting rates shown are greater than that required for a 1500 ton/year fuel processing facility and are about the rate required for vitrifying defense waste at both the Savannah River and the Hanford sites.

The in-can melter is relatively insensitive to waste composition. Since the melting crucible is removed with each canister of glass, accumulations in the melter can not occur. Reducing agents such as silicon metal to control second phase formation can be readily handled. Waste compositions simulating defense wastes at Savannah River and Hanford as well as numerous wastes representative of processing spent fuel have been vitrified in the in-can melter.

Canisters filled using the multizone in-can melting furnace have shown that little effect is observed from multizone operation. Canister wall temperatures are controlled by monitoring furnace temperature. It has been found that adequate heating of the canister wall can be readily achieved; however, with a furnace designed to receive variable size canisters, cooling one zone of the canister while heating an adjacent zone to 1050°C has not been successful. Vertical heat transfer within the canister and furnace preclude differences of more than about 200°C between adjacent zones of the furnace.

FIGURE 4

IN-CAN MELTER CAPACITY



GLASS PROPERTIES

High-level waste glass produced in these processes is high quality. An extensive program is underway evaluating the durability of the large-scale canisters of glass.

Potential dispersion mechanisms for radionuclides have been evaluated and found to be low. Resistance to water leaching is similar to pyrex glass. Even when devitrified, the waste glass leach rate is similar to common bottle glass. Resistance to dispersion in air is high due to the small amount of respirable particles even after thermal or mechanical shock. Dispersion by volatilization from hot glass would occur only during an accident condition. At glass temperature of 670°C, the volatility rate is low, equivalent to a leach rate of 10^{-5} g/cm^2 day.

Exposure of the waste glass to the effects of high temperatures (650 - 900°C) can produce crystal growth termed devitrification. The largest effect of devitrification was observed after one year at 700°C--a leach rate increase of one order of magnitude. Normally, leach rate increases after devitrification is on the order of a factor of 2 to 5. The overall performance of glass appears good in potential leaching environments.

Significant progress has been made evaluating the effects of alpha radiation damage in the glass. Changes in glass density and stored energy, due to accumulated alpha radiation dose, have been observed to stabilize after doses equivalent to about 1000 years. Some representative date for HLW glass at 25°C is shown in Figure 5. These data are anticipated to be indicative of other property changes resulting from radiation damage.

Accelerated alpha radiation damage is obtained by substituting ^{244}Cm for chemically similar rare earth materials in the glass. Thousands of years of alpha damage can thus be simulated in a few weeks. Density changes occur due to rearrangement of atoms within the glass matrix as a result mainly of nuclears recoil during alpha particulate emission. The density increases observed are not anticipated to be detrimental. Some waste glasses have been observed to densify less than shown and others actually expand under alpha radiation. Stored energy occurs when atoms dislodged from the silicate matrix come to rest

in a higher energy state. On heating, energy is released as atoms return to their latice position. Due to the selfhealing nature of glass, stored energy decreases with increasing temperature.

RADIOCHEMICAL ENGINEERING REMOTE ASPECTS

The spray calciner and in-can melter have been operated previously with radioactive wastes in the WSEP remote engineering cells.[a] At that time high levels of radioactivity and fission product heat were attained from blending fresh Purex defense waste and fission product solutions. The spray calciner and in-can melter are currently being prepared to operate again with various types of high-level radioactive wastes. New design features are being incorporated that will improve the equipment reliability. These include a side-mounted calciner vibrator and an abrasion resistant feed atomizing nozzle.

A remotely operable and maintainable continuous ceramic melter is currently being designed for operating in the WSEP cells. This will be the first melter of this type to be tested with all of the remotely operable features. The melter will be coupled to the existing spray calciner. It will employ several alternative draining techniques and Inconel-690 electrodes. The melter lining will be K-3 refractory bricks. Cold testing of this melter is scheduled for early 1979.

One of the final steps in completing the technology for the spray calciner and in-can melter will be the generation of a technical design manual. This manual will include a detailed architect-engineer design of this equipment as it would be operated in an actual plant. This design is just recently underway. The technical design manual will be completed in late 1979.

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a.

FIGURE 5

RADIATION EFFECTS IN VITRIFIED HIGH-LEVEL RADIOACTIVE WASTE