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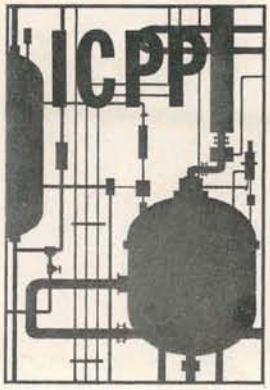

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A COMPARISON OF VARIOUS CALCINATION PROCESSES FOR HIGH-LEVEL RADIOACTIVE WASTES

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A B S T R A C T

On the basis of published information and data, the four principal radioactive waste calcination techniques, the fluidized bed, the pot, the radiant-heat spray, and the rotary-ball kiln, are examined and compared with respect to the principal process, operational, and product characteristics of each. An ultimate combined capacity of 1000 to 2000 gph is shown to be necessary to process generated and accumulated wastes between the years 1965 and 2000. The effects on product properties and on economics of ultimate waste disposal of the type of calciner selected are considered from many standpoints, including the composition, concentration, and activity level of the waste solution and the calcination conditions. Also discussed are creation of glass-like compounds from calciner products, personnel and equipment requirements, and the present status of development of each of the calciners. It is shown that one or more calciners may be suitable to process any particular waste, depending on the desired type of product and other circumstances.

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INTRODUCTION

The urgency of developing effective disposal processes for highly radioactive waste will intensify as the nuclear power industry matures. From the United States effort, four different calcination processes, fluidized bed[1], pot[2], radiant-heat spray[3], and rotary-ball kiln[4] are emerging. Product from any of these processes can be converted to glass-like materials in a step subsequent to calcination or can be dispersed in insoluble matrices to reduce the leachability of the activity by water and to increase end product thermal conductivity. Other techniques under development, but not as advanced as these calcination processes, include direct conversion of waste solutions to glass-like compounds[5], decomposition of waste and fixation of metallic salts therein in molten sulfur[6], and adsorption of radioactivity in solutions on clay type minerals followed by high temperature calcination[7].

Although considerable information has been published on waste disposal by the several techniques of calcination, the different processes cannot readily be compared, unfortunately, due to differences in reporting bases and in the states of development. A report[8], presently being printed, attempts to rectify partially the former situation by reducing much of the published data in over 120 references to common bases. This paper is a summary of the information in that report.

MAGNITUDE OF WASTE PROBLEM

Approximately 80 million gallons of high-level waste solutions have already been accumulated at various locations in the United States[9]. As the nuclear power industry matures, this volume of waste may mushroom, as shown on Figure 1, to levels as high as 500 million gallons by the year 2000; the exact rate of buildup will depend on various factors such as continued need for production fuel, rate of development of the nuclear power industry, types of reactors and fuel elements employed, the burnup levels of the fuels, and the technology

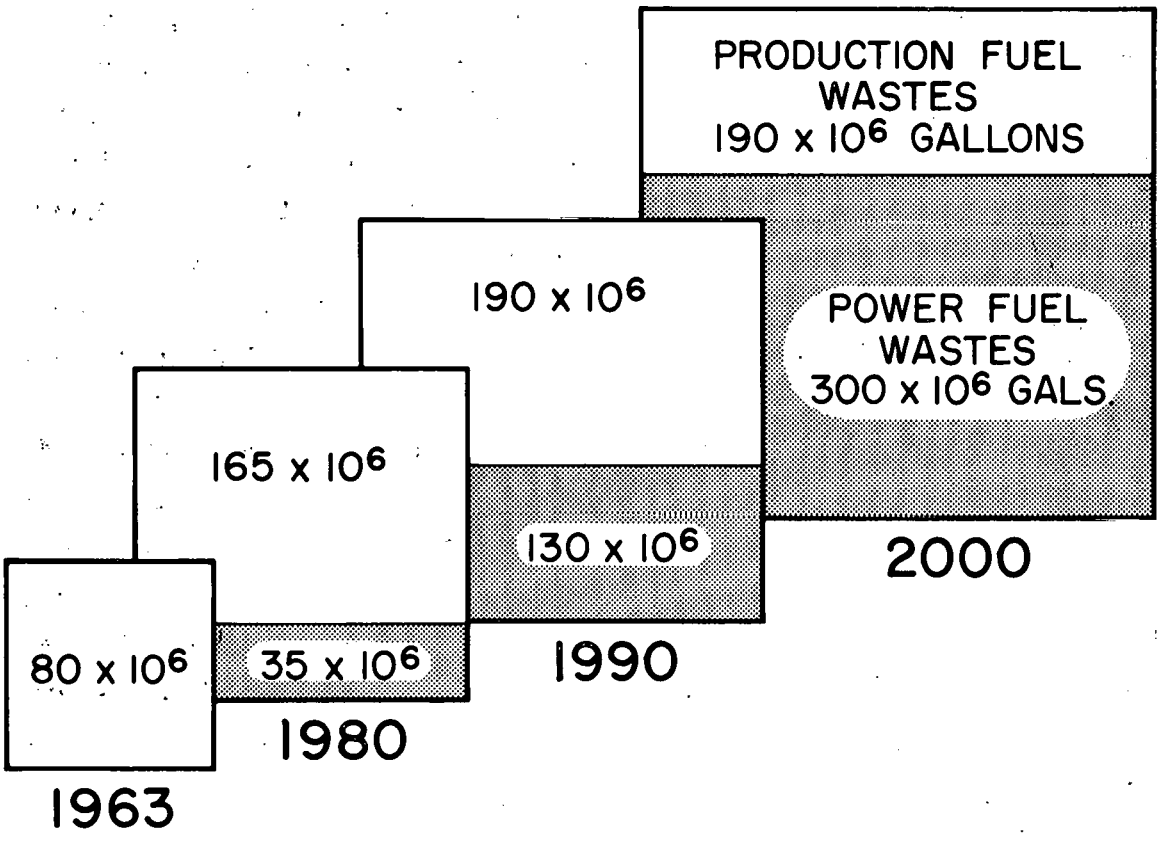

Fig. 1 The cans depict the relative amounts of highly radioactive wastes not in existence, together with those that may be generated by the year 2000. Arbitrarily it was assumed that five million gallons of production fuel waste would continue to accumulate annually through 1985, after which essentially all new wastes would be those from power reactor fuels.

of fuel reprocessing. Figure 1 is based on the Bruce estimate[10] of future volumes of power reactor fuel wastes and on an arbitrary assumption that five million gallons of production fuel waste will continue to accumulate annually through 1985, after which essentially all new high-level wastes will be those from reprocessing of power reactor fuels.

The magnitude of the waste problem is related to the required throughput of future disposal plants on Figure 2 which compares cumulative amounts of wastes that can be processed between 1965 and any future year with plants having a combined capacity of either 100 gph or 1000 gph on 300-day-per-year operation. This figure clearly indicates that the combined capacity of waste disposal plants in the United States will have to be in the range of 1000-2000 gph to process by the year 2000, both the wastes presently in storage and those generated in the interim. The number of plants built, no doubt, will be dependent on the number of locations at which wastes are generated; however, it seems highly desirable to minimize this number because all radioactive materials will require some type of perpetual surveillance. In all liklihood, therefore, typical future plants for converting waste solutions to solids should have individual capacities exceeding 100 gph of waste solution.

Waste disposal plants should be developed rapidly since funds used for construction and later for perpetual surveillance of liquid tankage could be spent better for ultimate solids storage facilities. Calcination--by one of the four processes--is the only technology sufficiently developed today to meet the needs of the waste disposal problem; hence only the fluidized bed, the pot, the radiant-heat spray, and the rotary-ball kiln calcination processes are considered in this paper.

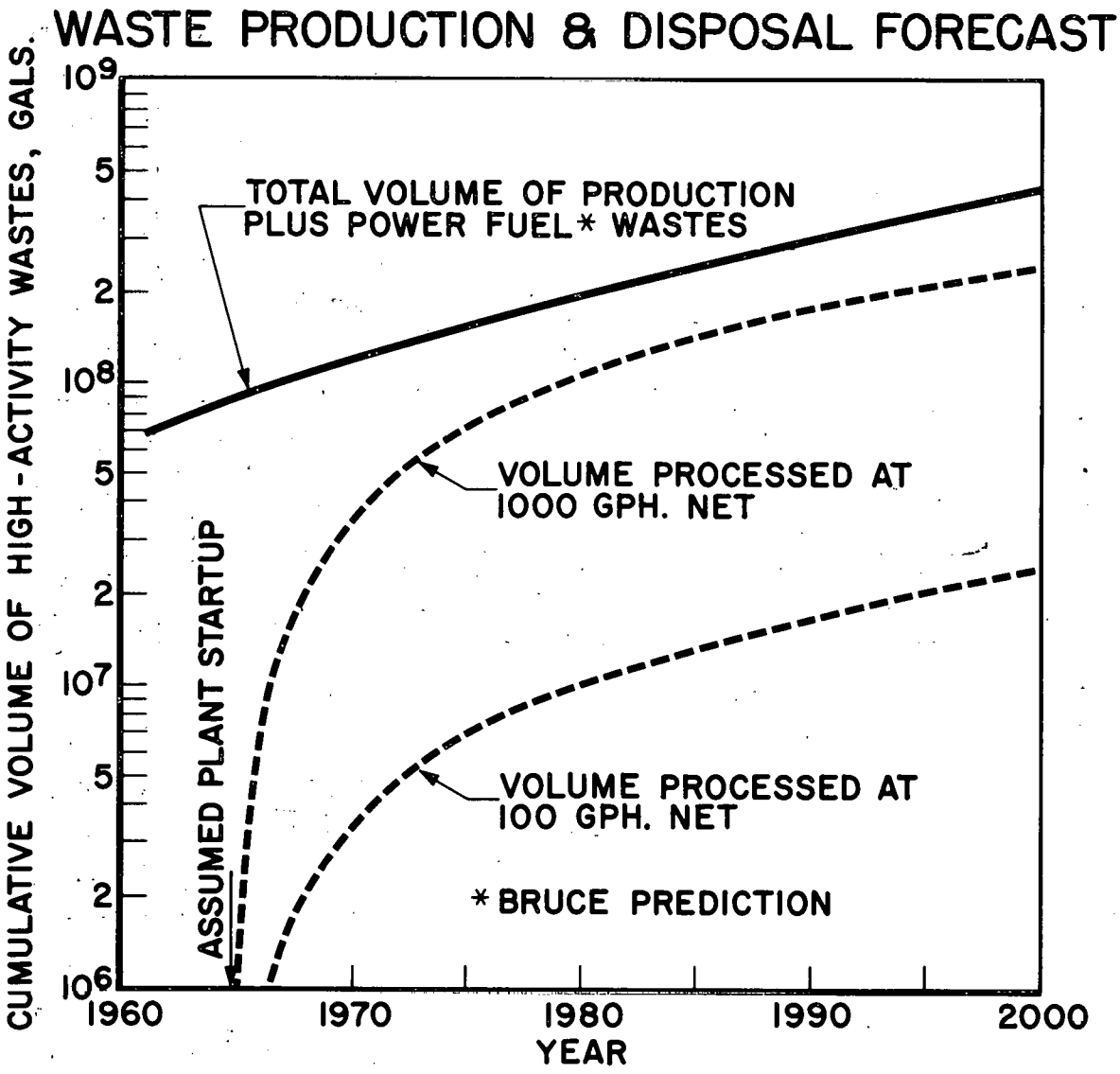

Fig. 2 Waste production and disposal forecast for the United States. Values of cumulative volumes of waste solutions are based on the Bruce prediction of future volumes of power reactor fuel wastes (10). The initial combined capacity of several solids conversion plants beginning operation in 1965 on a 300 day per year schedule would have to be in the range 1000 to 2000 gph to process all wastes during this period.

DESCRIPTION OF PROCESSES

The mechanics of waste decomposition are similar for all calcination processes; the fluidized bed, the radiant-heat spray, and rotary-ball kiln calciners are all capable of continuous operation while the pot calciner is inherently a batch unit in which the process vessel also serves as the final storage container. Figure 3 shows schematically a general radioactive waste calcination process. Waste solution entering the calcination vessel is evaporated and decomposed; volatile gases flash overhead to the off-gas system while the metallic salts remain behind in the calcination vessel. The off-gas is decontaminated in either a condensing or non-condensing system either of which can be used satisfactorily for all calcination processes. The type of off-gas system employed is dependent on the requirements and overall economics of a particular waste disposal plant. If there are local requirements for nitric acid, or if local air pollution control regulations prohibit the release of nitrogen oxides to the atmosphere, then a condensing off-gas system together with a conventional nitric acid decontamination system would be the most desirable system. On the other hand, if there is no requirement for slightly contaminated nitric acid, thus presenting a possible disposal problem, a non-condensing off-gas system may be the most desirable.

With the fluidized bed calciner schematically shown on Figure 4, the waste solution sprayed into the well fluidized heated bed of granular solids coats particles in the bed; water vapor and volatile gases flash from the spray droplets leaving oxides of metallic salts uniformly deposited on bed particles. At equilibrium conditions, the effect of particle growth is balanced by the formation of new seed particles and by the removal of product; bed temperature is maintained at a predetermined value in the range 300-500°C by internal heat exchange surfaces. Spheroidal granular particles

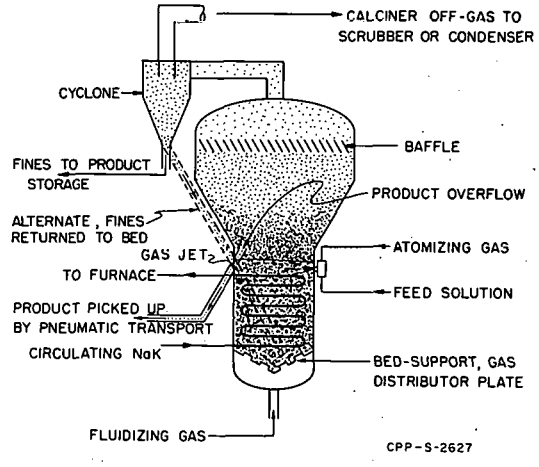

Fig. 4 Fluidized Bed Calciner Details.

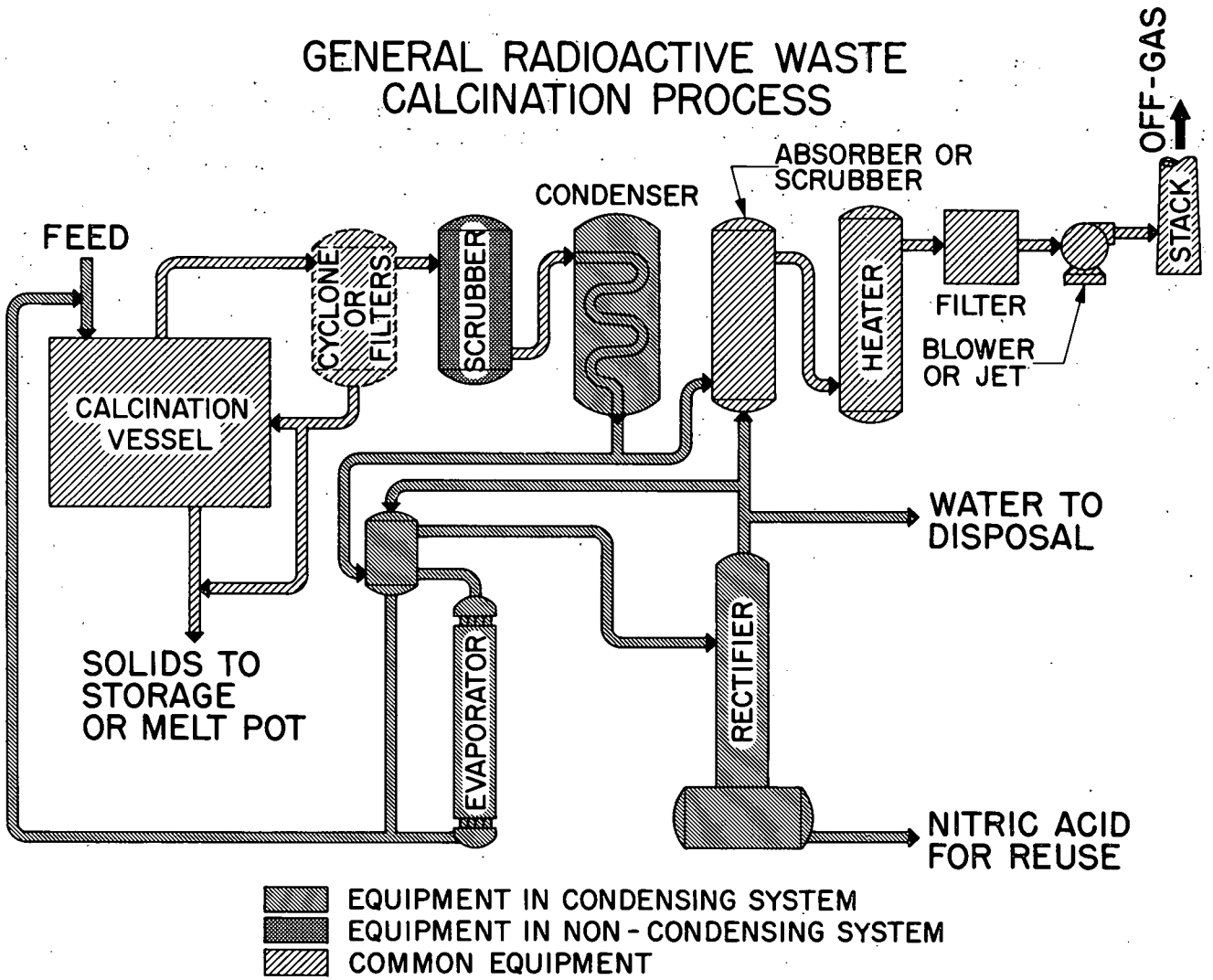

Fig. 3 General schematic diagram for processes used to calcine radioactive wastes. The type of calcination vessel and product handling system varies considerably, depending on the particular process; however similar off-gas decontamination procedures can be employed for all calcination processes.

ranging in diameter from 0.1 to 1.5 millimeters are continuously removed from the calciner and are transported pneumatically to storage facilities. The transport gas, after separation from the calciner product, is merged with the fluidizing gas and the gaseous reaction products in the calcination vessel. Solids removed in the off-gas system from the fluidizing gas may be returned directly to the bed or combined with product outside the calcination vessel; the latter represents current practice.

Waste solution introduced to an electrically heated cylindrical pot calciner, shown on Figure 5, is evaporated to dryness and calcined at temperatures ranging from 700-900°C. Metallic salts deposit in radial layers along the vessel walls and gradually fill the pot as a massive, porous solid. Water vapor and volatile decomposition products pass continuously at an ever diminishing rate around an overhead baffle in the pot and are introduced to the off-gas processing system. The pot calcination vessel, which serves also as the final storage container, is transported by conventional remote manipulation practices to its final repository.

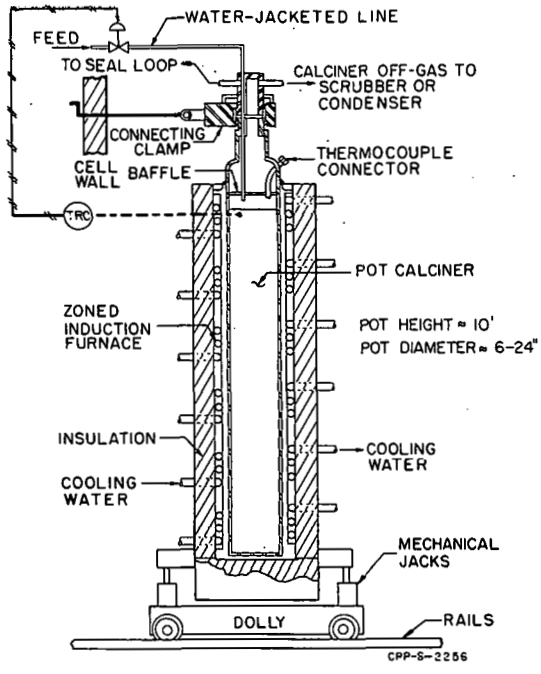

Fig. 5 Pot Calciner Details.

In radiant-heat spray calcination, the waste solution is atomized near the top of the calciner, shown schematically on Figure 6, from where it falls freely through the cylindrical vessel, which is usually electrically heated to temperatures ranging from 700-825°C. The suspension of feed droplets passes through zones of evaporation, drying, and calcination, and results in a finely divided powder ranging in size from 1-13 microns. Removal of the powdery product from the calcination vessel occasionally has required the use of a vibrating screw feeder.[11] Water vapor and volatile decomposition products, together with the gas used to atomize feed, are usually separated from the product by blow-back filters outside the calcination vessel, although the use of cyclones has also been considered. Product, because of its high porosity usually has been collected in pots below the calciner for subsequent melting if suitable additives have been used in the feed. Alternatively, product could be continuously melted and poured into pots. These pots in a plant facility would then be transferred by remote manipulation to a final repository.

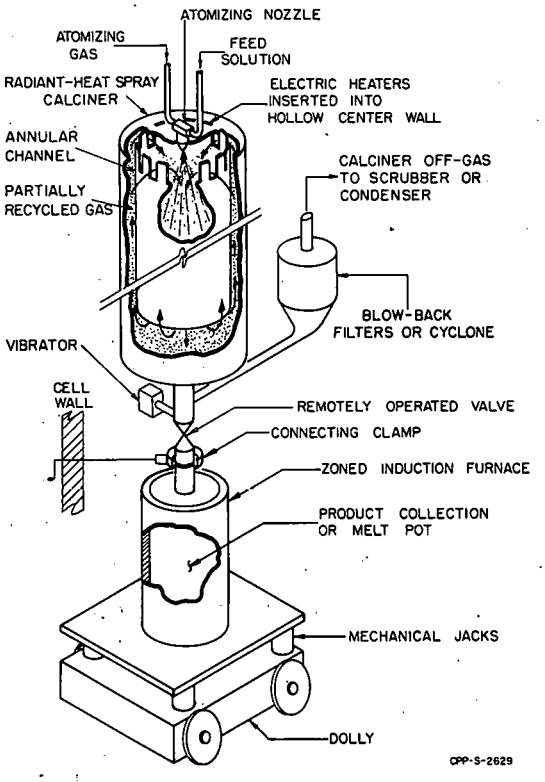

Fig. 6 Radiant-Heat Spray Calciner Details.

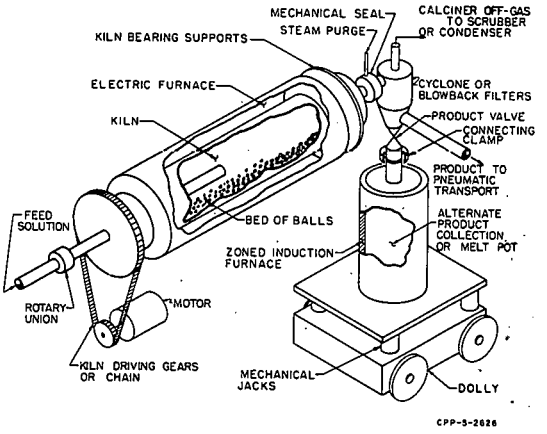

Fig. 7 Rotary Ball Kiln Calciner Details.

In rotary-ball kiln calcination, waste solution is dribbled or sprayed onto a bed of metal balls in a slowly rotating cylinder as shown schematically on Figure 7. The calciner is electrically heated to a temperature between 600 and 800°C. Product formed from deposition of metallic oxides on the moving balls is pulverized during kiln rotation into particles varying in size from 0.05 to 0.8 millimeters. Product overflows from the calciner co-current with the off-gases and enters a cyclone or metallic filters for product-gas separation. In development studies, product usually has been collected in pots below the calciner.

The composition of off-gas from a calcination vessel is dependent on the waste, feed rate, temperature, and mode of operation. Virtually all particulate matter and gaseous fission products must be removed from this gas prior to its release, Furthermore, off-gas scrubbing streams and condensate must be decontaminated by recycling at least a portion of them to the calciner or, less desirably, by putting them into separate storage. In a non-condensing system, the final off-gas

will contain essentially all gases--except those removed in scrubbers or adsorbers--resulting from the calcination reactions, together with any air or other gases employed in the process or leaking into the equipment. In a condensing system, the final off-gas will contain only those non-condensible, non-absorbable gases that pass through all equipment in the off-gas stream. The products of the condensing system will include, in addition to a gas stream, two or more liquid streams containing nitric acid, water, and perhaps various compounds of low volatility that cannot be retained by calciner products. The liquid streams would be produced from decontaminating the acidic condensates, possibly by continuous equilibrium vaporization.[12] In non-condensing off-gas systems, a primary cyclone is usually employed to separate the fines from the off-gas before it is introduced in turn to a venturi scrubber, silica gel adsorbers, and then to AEC-type high efficiency filters. In condensing systems, gas downstream from the condenser is usually introduced to an evaporator, a rectifier, and another condenser before introduction to the high efficiency filters. There appears to be no reason to favor either a condensing or non-condensing off-gas decontamination system since operating data[13,14,15] indicate that the activity released with a gas under either mode of operation is well below maximum acceptable limits. By employing proven techniques, the net volume of off-gas released per unit of waste can be similar for all calcination processes. If the release of off-gas from a plant ever must be reduced to a theoretical minimum, condensible or absorbable gases or perhaps recycled gases can be used for pneumatic instrumentation, for feed atomization where applicable, and for fluidizing in the case of the fluidized bed calciner.

The required product handling systems present striking contrasts among the various calcination processes. Granular materials produced in the fluidized bed, radiant-heat spray, and rotary-ball kiln calcination processes can be conveyed pneumatically from a calciner to a storage facility in pipelines, can be transported in pots, or perhaps can be conveyed with the aid of vibratory equipment. Cellular materials or glasses, on the other hand, such as are created in pot calciners or in

melt pots adjacent to the radiant-heat spray calciner, must be transported in the pots to a repository using remote handling equipment. Transportable pots are limited in size by consideration of remote manipulation, handling and transport to move them from the processing area to storage as well as by considerations of maximum storage temperature.

THROUGHPUT CAPACITY

The presence of several indeterminate factors makes it impossible to set a capacity now for future waste disposal plants. The immediate need for several large capacity plants has already been shown; still there may be circumstances justifying one or more low capacity plants, but only for the next few years. Such circumstances need not impede planning for the future because no calciner must be operated at its design capacity. All can be operated at rates ranging from their design rate down to one tenth of the design rate, and in some cases with no loss in efficiency and only a small increase in operating cost. Operation at low percentages of design capacity may require dilution of the waste feed with a large recycle water stream requiring additional furnace heat; however, this is not a significant factor in the overall economics of waste disposal. If the investment costs of a continuous operating calcination facility increase with the capacity to a power of only 0.1 to 0.2, as is the case for most nuclear processing plants, spare capacity can be provided with only a small increase in investment cost. A waste processing plant designed on this basis could thus adapt to increasing demand without incurring additional capital cost; in effect, a large capacity calcination unit would be operated at less than design capacity during early years with a gradual shift to higher throughput levels as demand increased. An attractive alternative, if the waste processing unit is built in connection with a fuel reprocessing plant, is to operate the calciner part time in its early years alternating the operating crew with chemical processing assignments which require similar talents. If the ultimate capacity requirement of a waste calcination plant is uncertain, it would appear advisable to err on the side of providing excess initial capacity.

The capacity of a calciner is limited by those variables which govern the amount of heat that can be transferred into the zone of waste decomposition and calcination. The capacity of each of the calcination processes will be considered in turn.

The capacity of the fluidized bed calciner has been found from pilot plant studies with various feed compositions to be dependent only on the heat transfer area, the bed temperature, the temperature of the heating medium, the bed particle size, and the fluidized bed density, the last two being those factors influencing the controlling heat transfer coefficient. Figure 8 shows the capacity per unit heat transfer area as a function of the mean temperature of the heating surface for several values of bed temperature, assuming a heat transfer coefficient of 50 BTU/(hr)(ft^2)(°F) selected from the range of experimentally observed values of 40 to 100 BTU/(hr)(ft^2)(°F)[16]. During normal operation, the heat transfer coefficient has easily been maintained above 75 BTU/(hr)(ft^2)(°F) by keeping the average size of the particles in the bed below 0.6 mm[16]. No test unit used to date has employed as large a heat transfer area as its volume would permit. The range of throughput capacities of a single calciner can vary from bench scale rates, below one gph, to an extrapolated maximum capacity of about 1500 gph of aluminum nitrate waste for a single 60-inch diameter calciner. With Purex type wastes, a 100°C lower heating surface temperature required to prevent any product fluxing on the tubes would result in a 20 percent lower capacity. Other factors which affect the capacity of a calciner need not be extrapolated beyond proven pilot plant performance to achieve capacities up to 1500 gph in a 60-inch diameter unit. More spray nozzles would be needed than employed in any unit to date; however, tests have shown that nozzles can be installed

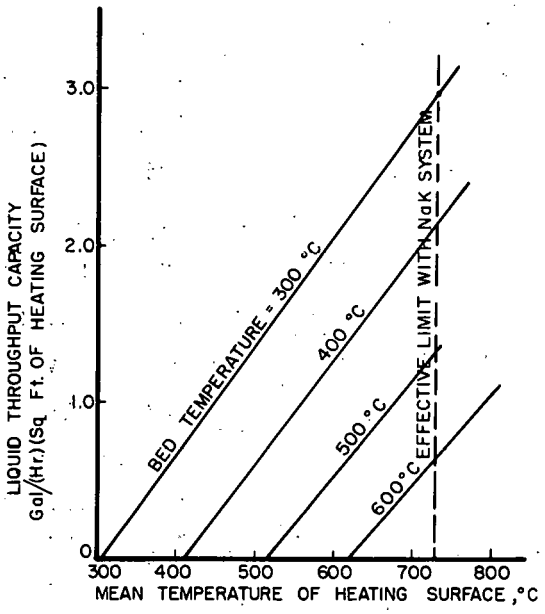

Fig. 8 Capacity of fluidized bed calciners based on a surface-to-bed heat transfer coefficient of 50 BTU/(hr) (ft^2) (°F) selected from the experimentally observed range 40 to 100 BTU/ (hr) (ft^2) (°F), dependent inversely on bed particle size. Operation with a small bed particle size could result in even higher capacities than shown in the figure. The limiting temperature of the heating surface allows for a 50°C differential between it and the boiling point of a eutectic sodium-potassium heating fluid.

both above and below the heating bundle, requiring no increase in spray density per unit volume.

The average feed rate to a 7 1/2-foot long, eight-inch diameter pot calciner[17], over one cycle, excluding necessary turn around time, has been found to vary between 20 and 30 liters per hour depending on the composition of the waste; it appears that an average rate including an 11-hour turn-around time for plant-scale units may be about 26.7 liters/hr[18]. Based on this value it appears that the maximum capacity of a single calciner about 24 inches in diameter and 12 feet long (ten feet of heated length) is about ten gallons per hour for calcination of aluminum nitrate type waste and about eight gallons per hour for Purex type wastes. Figure 9 shows the total capacity of a pot calciner rather than capacity per unit area as for the other calciners to avoid misleading impressions; since the average feed rate to a pot calciner is almost independent of diameter[18], the capacity per unit area varies inversely with pot diameter.

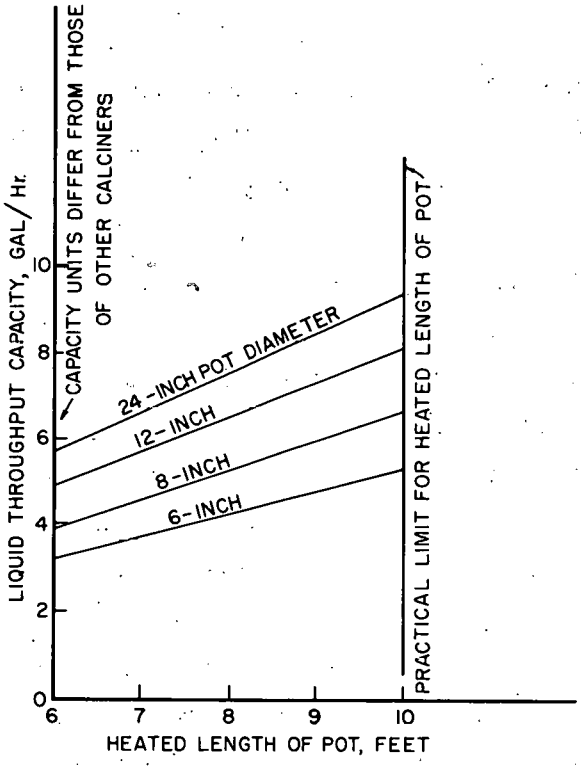

Fig. 9 Capacity of single pot calciners based on a pot wall temperature of 900°C, aluminum nitrate waste solutions, feed rates independent of pot diameter, feed rates observed during development studies, and a pot turn around time of eleven hours. The salt concentration of the waste being calcined will have a marked effect on capacity with this calciner.

The capacity of the radiant-heat spray calciner is difficult to predict, but according to Allemann, et al,[19] the maximum capacity is reached when incompletely dried particles deposit excessively on the calciner wall. On Figure 10, the capacity has been related to nominal residence time of particles and to vessel diameter with limitations imposed by the heat flux. These limitations were established during development studies[20] using water feed both before any deposition of solids had occurred on the calciner wall and after a run in which the deposits were maintained

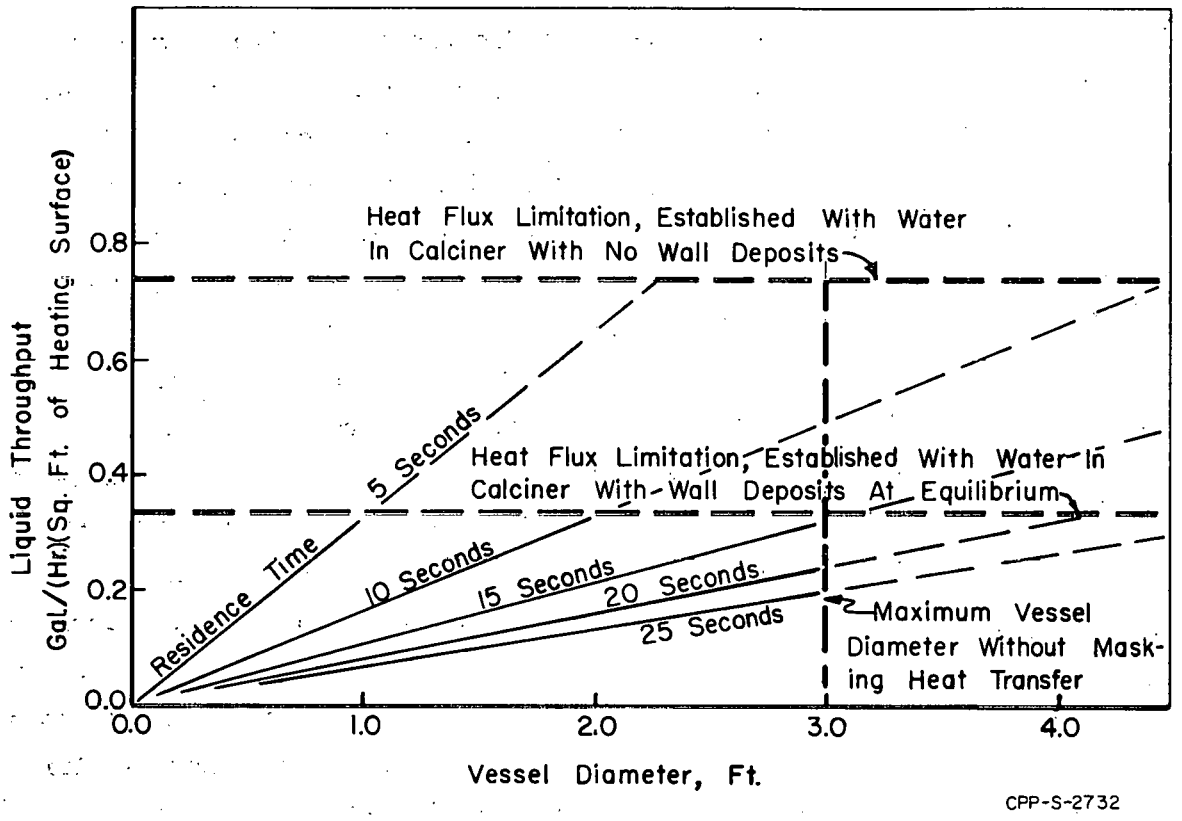

Fig. 10 Capacity of radiant-heat spray calciners based on 800°C furnace temperatures and outlet gas at 400°C and 12 psia. Heat flux limits were experimentally established [20] with water feed before and after formation of normal wall deposits in the calciner. Capacity of single calciner may be limited by residence time, vessel diameter, vessel length, or heat flux. Required residence time (nominally based on outlet conditions), which is dependent on the degree of calcination sought, may vary over a wide range.

at an equilibrium value by rapping. On later runs somewhat higher throughputs were achieved for brief periods of operation. The necessary residence time to insure desired drying and calcination in a reactor is uncertain. For similar apparatus, Gauvin, et al[21], report satisfactory residence times varying between 16 and 126 seconds; Allemann, et al, cite satisfactory residence times varying from 5-15 seconds[19] with waste. However, with the latter work, it was reported that incompletely calcined powders decomposed further to oxides of iron and aluminum when heated to 900°C. The three-foot diameter limitation shown on the figure indicates the upper size at which Allemann, et al[19], and Johnson[22] believe that heat transfer into the center of the vessel will not be

masked and result in uneven temperature distribution. The range of capacities for a single radiant-heat spray calciner can vary from bench scale rates to an extrapolated maximum capacity of about 65 gph of aluminum nitrate waste, assuming for the latter a three-foot diameter calciner 20 feet long. The vessel length, together with the length of necessary appurtenant equipment below the calcination vessel, would be fixed by cell depth considerations.

The capacity of rotary-ball kiln calciners thus far has been limited by the effective rate of heat input into the kiln.[4] During pilot plant studies with an eight-inch diameter, seven-foot heated length calciner, the feed rate has varied between three and five gallons per hour. The correlation on Figure 11 shows the estimated capacity per square foot of heating surface based on an overall heat transfer surface coefficient of 30 BTU/(hr)(ft^2)(°F) which was calculated from limited data from runs in which the operating conditions were not varied significantly. The maximum capacity of a single rotary-ball kiln calciner, 2 1/2-foot diameter 20-foot long, although difficult to estimate, may be as high as 200-300 gph, based on Figure 11, provided the feed--and hence the demand for heat--can be effectively dispersed throughout the length of the calciner. An engineering feasibility study[23] (assumptions unstated) indicated a rotary-ball kiln calciner 2 1/2 feet in diameter 20 feet long would have a capacity of about 100 gph.

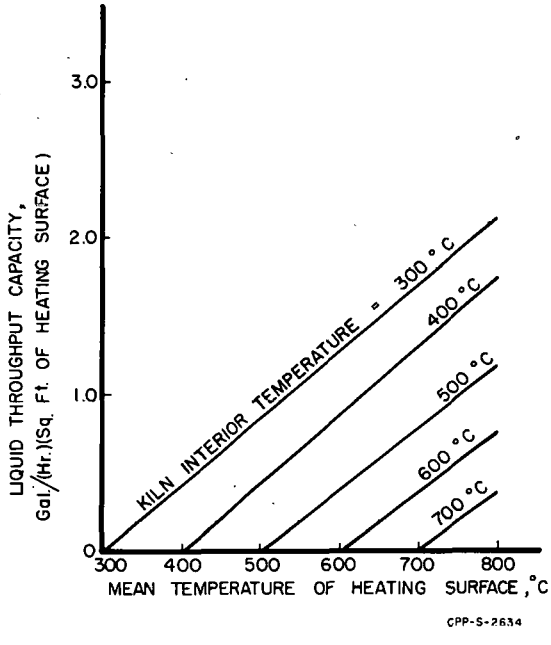

Fig. 11 Capacity of rotary-ball kiln calciners based on a surface-to-bed heat transfer coefficient of 30 BTU/(hr) (ft^2) (°F) calculated from meager data. Further development work is desirable to substantiate the calculated heat transfer rate, and to establish that feed can be dispersed effectively over long sections of a heated kiln.

The potential throughput capacities of the various calcination processes are compared on Figure 12 which shows the number of calciners along with the volume of storage facilities that would be required for

each of the processes to handle 1,000 gph of acidic Purex wastes. This task could be accomplished either by a single fluidized bed calciner, five feet in diameter by 20 feet high, by four rotary-ball kiln calciners each 2 1/2 feet in diameter by 20 feet long, by 15 radiant-heat spray calciners three feet in diameter by 20 feet high, or by 100 lines of pot calcination equipment using pots two feet in diameter by 12 feet long. Because of the high porosity of radiant-heat spray calciner product, investigators[19] believe that additives should be used so that the product can be melted to a glass-like material in a pot and thus significantly reduce the overall material volume.

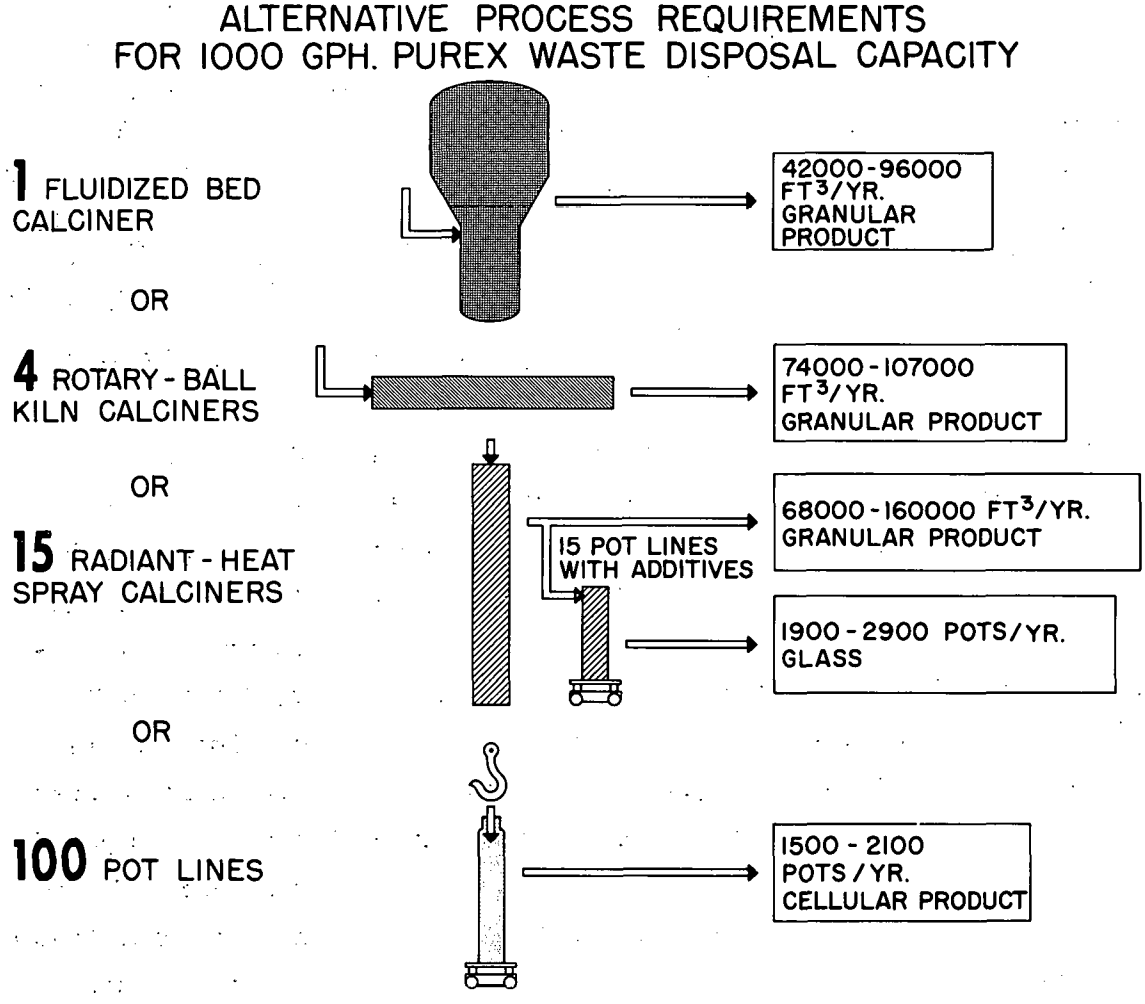

Fig. 12 Alternate Process requirements for disposal of 1000 gallons per hour of Purex type wastes. Calciner vessels and storage volumes are shown approximately to scale with respect to each other. Required volume to store end products are based on the range of porosity exhibited by experimentally obtained material from each process.

CALCINER PRODUCTS

Required volumes of storage facilities for the calcination processes shown on Figure 12 are based on values of the properties of calciner product given in Table 1 and on the composition of an acidic Purex waste used in an economic study made by Oak Ridge National Laboratory.[18]

TABLE I

PROPERTIES OF PRIMARY CALCINER PRODUCTS

	Fluidized Bed	Pot	Radiant-Heat Spray	Rotary-Ball Kiln
Average size, mm	0.25-1.20[24]	-------	0.002-0.013[27]	0.13-0.16[28]
Type	Granular	Cellular	Granular	Granular
Bulk Density, g/cc	0.5-3.0[24,25]	0.4-1.6[2]	0.18-1.1[27]	0.65-0.95[28]
Gross Porosity, %	44-76[24]	51-86	67-94	69-79
Typical Volume Reduction Factors	7-20	5-9	2-4	7-10
Thermal Conductivity	0.08 @ 40°C[26]	0.06 @ 100°C[2]	0.05 @ 40°C[27]	0.098[29]
BTU/(hr)(ft)(°F)	0.27 @ 800°C	0.6 @ 900°C	0.13 @ 200°C	(temperature not reported)
Nitrate Contest, wt.%	5-12 @ 300-500°C[24]	0.006-3.40 @ 400-1000°C[2,30]	Not reported	Not reported

The values in Table 1 are the range of values observed for various wastes processed during experimental work with each of the calciners. Unfortunately identical wastes have not been processed in each of the calciners, which prevents a direct comparison. This is primarily a problem in calculating comparative volume reduction factors. For comparisons made in this paper, experimentally obtained values of bulk density were used to calculate porosity and volume reduction factors wherever possible. Where experimental data were not available, a best estimate of bulk density or porosity was employed, based on a range of experimentally obtained values from wastes that were calcined. Volume reduction factors shown herein may differ from those in other publications due to a difference in definition. The volume reduction factor used herein is defined as the ratio of the volume of concentrated waste normally expected in tankage to the final volume of the end product.

The properties of a calciner product significantly affect considerations of long term storage and at times the calcination process itself. Both the physical and chemical properties of calciner products can vary over wide ranges depending on the waste calcination processes, mode of operation, processing subsequent to calcination and other factors. With respect to physical properties, sharp demarcation exists in appearance, viz, products may be either granular or cellular. Granular products are produced in the fluidized bed, the radiant-heat spray, and rotary-ball kiln calcination processes. Cellular product, but not necessarily vitreous material, is produced in the pot calcination process.

Through use of proper fluxing agents, the final products of all calcination processes can be made into vitreous or glass-like materials at practical temperature levels, 800-1000°C, having a relatively low water leachability and a high thermal conductivity. Because the properties of the glass-like material are essentially independent of the calcination process employed to generate the initial product and because the use of fluxing agents in all cases will result in an end product of greater material volume than that minimum volume theoretically obtainable otherwise, glass-like products will be considered separately later in this paper.

Water leachability of a granular product will be higher while thermal conductivity (and with high porosity material, the liquid-to-solid volume reduction factor) will be somewhat lower than those of the corresponding cellular product. Thermal conductivity and specific activity of a product together with the diameter of a storage vessel and rate of heat dissipation therefrom govern the temperature of product in storage. This temperature must be limited to avoid volatilization of radioactive isotopes or corrosive compounds. Economically, it is highly desirable to use the largest containers possible--those that result in maximum allowable temperature at the time of product internment----for storage of radioactive materials because vessel costs increase approximately linearly with vessel diameter while the useful storage volume increases with the square of vessel diameter. Even though a cellular material may have a higher thermal conductivity than does a granular

material, the granular material offers other important economic advantages independent of transportability. A granular material may be stored in annular bins of greater length than a transportable pot, the cost of an annular bin per unit volume is about 70 percent of that of a corresponding cylinder; also, granular solids can be stored for an interim period in relatively small, cooled bins and later transferred to larger, less expensive bins, but this can not be done with a cellular material.

Some investigators[31] have suggested that a period of interim storage of liquid wastes precede calcination for the decay of activity to allow the use of large economical storage containers. An alternative procedure, which does not involve storage of the liquid waste during its period of greatest hazard, is possible with granular calciner products since they can be placed in interim storage and later be moved pneumatically--after the decay of activity--either to less expensive permanent storage or to a final processing step for vitrification or investment in a heat conducting matrix. With such interim storage of the solids, the difference in thermal conductivity between the granular and cellular materials loses its economic importance.

While these advantages of the easily transportable product are obvious, there is another less obvious but perhaps significant point. A retrievable product meets in part the suggestion of those in the scientific community[32,33] who believe no present or near future treatment should irrevocably remove radioactive waste from accessibility to future generations. Interim storage of these wastes as granular solids offer a greatly reduced hazard over liquid storage, but retains much of the accessibility. Thus, preparation of a granular waste product today represents a reasonable compromise between the extremes of permanent tank storage as liquid and immediate production of small volume pots of vitreous materials, both with respect to present safety aspects and with respect to flexibility for future utilization of any economic value in the waste. This also avoids the permanent economic penalty associated with storage of waste in small containers.

VITRIFICATION OF CALCINER PRODUCTS

By use of proper fluxing agents, the products of all calcination processes can be made into vitreous or glass-like materials at practical temperature levels; the properties of glass-like materials are essentially independent of the calcination process employed to generate the initial product. All processes will require use of fluxing agents to produce glasses, the nature of which will depend on the initial waste composition; in most cases this will result in a material of greater volume than that minimum volume theoretically obtainable otherwise as shown on Figure 13. On this figure the expected volume of glasses is compared to those of corresponding solutions and calciner products for several wastes. The figure is based on the amount of waste oxides incorporated into glass-like materials by investigators at ORNL[31] and the relative volumes of calciner products calculated from best estimates of porosity observed for similar type products obtained during experimental operation. To be attractive economically, the increased expense (combined chemical, operating, and capital costs) of producing a glass-like material must be offset by savings either due to a further decrease in volume or through the use of larger cheaper storage vessels because of a higher thermal conductivity of the final product. Most glasses, because of their relatively high thermal conductivity, probably can be contained in vessels whose upper limit of size is determined only by considerations of remote manipulation; however, ultimate storage in a vessel no larger than this imposes an economic penalty on overall costs.

The technical merits of a glass-like material over the primary product of any process are uncertain. Unless they are totally non-leachable, glasses will require containment; therefore, benefits of low leachability are realizable only with breached storage vessels. On Figure 14 an attempt is made to show qualitatively the relative degree of safety associated with storage of the various forms of radioactive wastes, viz, as a liquid, calciner product, or as a glass-like material. Of course, ultimate safety in the disposition of waste activity will result only with solids completely non-leachable in water and placed in

RELATIVE VOLUMES OF WASTES, CALCINER PRODUCTS AND GLASSES

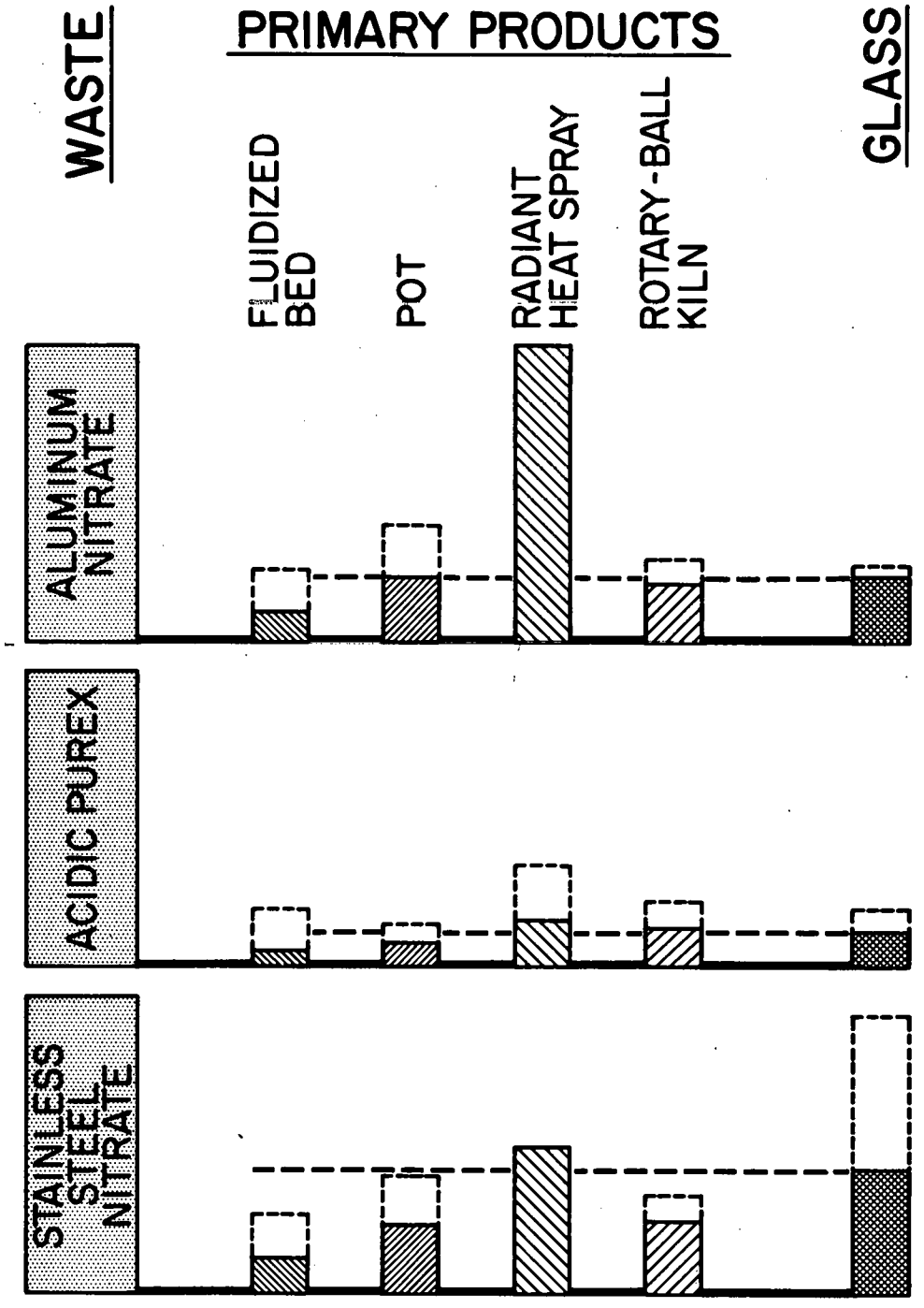

Fig. 13 Relative volumes of waste solutions compared with calciner products and glasslike materials that may result with the use of the various calcination processes.

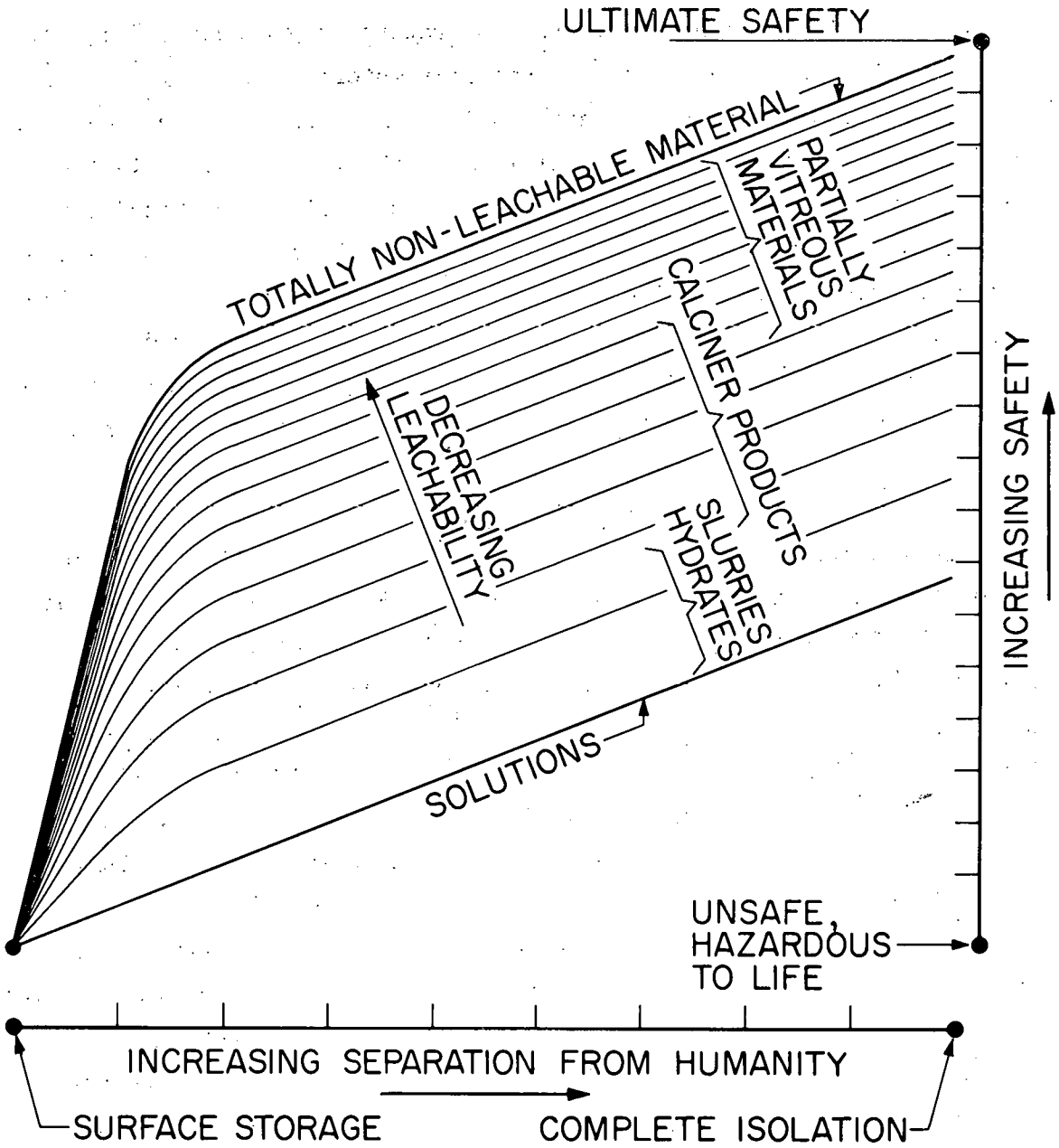

Fig. 14 A conception of relative safety that may result with storage of radioactive wastes as liquids, as calciner products, or as vitreous materials. There are at least two degrees of freedom for obtaining any level of safety, separation from humanity and degree of leachability. Even a totally nonleachable material--not yet obtainable--must be removed from the habitat of man; however, a modest separation results in the considerable improvement in safety as compared with that possible with solutions or highly leachable solid materials. Ultimate safety is represented by a totally nonleachable material stored in a completely isolated location, perhaps deep in the earth. Storage of solutions in this same location could result in a tolerable degree of safety. Between the extremes of solutions and totally non-leachable materials are various calciner products and vitreous materials with overlapping degrees of leachability. The assignment of values to the scales on this diagram is a challenge now facing the scientific community.

a totally remote location. A method to prepare such a material is not yet available; hence, even those glass-like materials that are technically feasible today must be placed inside containers for long term storage. At the other end of the scale, a minimum level of safety results from simple disposal of activity to the ground accessible to mankind. Between the two extremes are varying degrees of safety which depend on the type of storage container, its location, and the leachability of radioactive material. The threshold of minimum safety must be established for any given situation. For conditions above this threshold, economics should play a significant part in the selection of a waste disposal method.

WASTE ACTIVITY LEVEL

The activity level of a waste can have a considerable effect on waste disposal costs as shown on Figure 15. Since lowest storage costs are achieved by storing calciner products in the largest possible container, which is limited only by temperature considerations related to the radio-activity, it follows that remote handling considerations can prevent realization of lowest possible costs for many wastes. Figure 15 is based on an ORNL economic study[18,34] of a hypothetical nuclear power plant involving the use of a pot calciner, and on a parallel, Idaho Chemical Processing Plant study involving the use of a fluidized bed calciner[35]. However, the curves shown will apply equally well to any cellular material produced and stored in pots and to all granular materials stored in bins. The costs on the figure include expenses for storage containers, cooling facilities, vaults in which the storage containers are placed, and necessary transportation and surveillance costs for acidic wastes; calcination and processing costs have been excluded. The figure shows that costs diminish for granular materials with decreasing activities, but for cellular materials in pots, the costs become constant in spite of decreasing activity when the remote handling limitation on vessel size overrides the limitation imposed by maximum temperature in storage. The figure also shows that the cost of transportation and storage of radioactive materials in pots is several times that of bin type storage used in conjunction with pneumatic transport of granular calciner products.

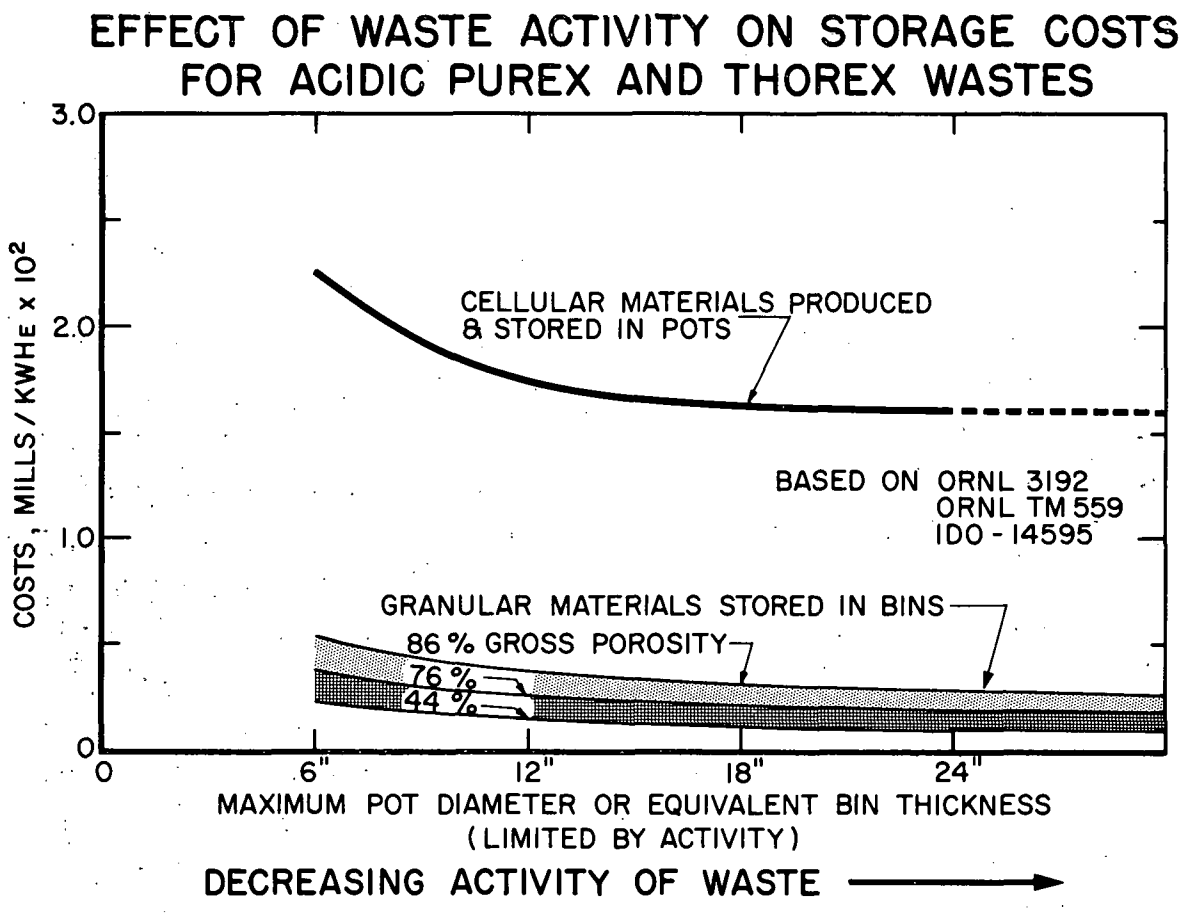

Fig. 15 Relative storage costs for cellular and granular materials produced from acidic Purex and Thorex type wastes. Costs shown exclude all expenses associated with processing per se; only the cost of storage container, cooling facilities, vaults in which the storage containers are placed, and necessary transportation and surveillance costs are included. The broad range of granular materials covers products from the fluidized bed, rotary-ball kiln, and radiant-heat spray calcination processes. By employing a principle of interim storage, overall storage costs for granular products would be still lower. For wastes less active than indicated on the figure, significantly lower costs for granular products are indicated, but no appreciable reduction in the costs of storage of cellular materials is possible because of the size limitation on pots imposed by remote handling requirements.

WASTE COMPOSITION

The composition of a waste will affect product properties and may also affect the selection of operating conditions, feed additives, and perhaps certain processing equipment. On Figure 16, the types of waste which can be processed in each one of the calciners are shown. Aluminum nitrate and stainless steel nitrate wastes can be calcined in any of the calcination processes without difficulty. Purex-type wastes containing sulfate will require an additive, such as calcium, during processing in the pot calciner[2] to prevent equipment corrosion at the high processing temperatures. Purex-type neutralized wastes can be processed in the fluidized bed, the radiant-heat spray, and the rotary-ball kiln calciners by using an organic material to destroy sodium nitrate, a procedure experimentally demonstrated with the radiant-heat spray

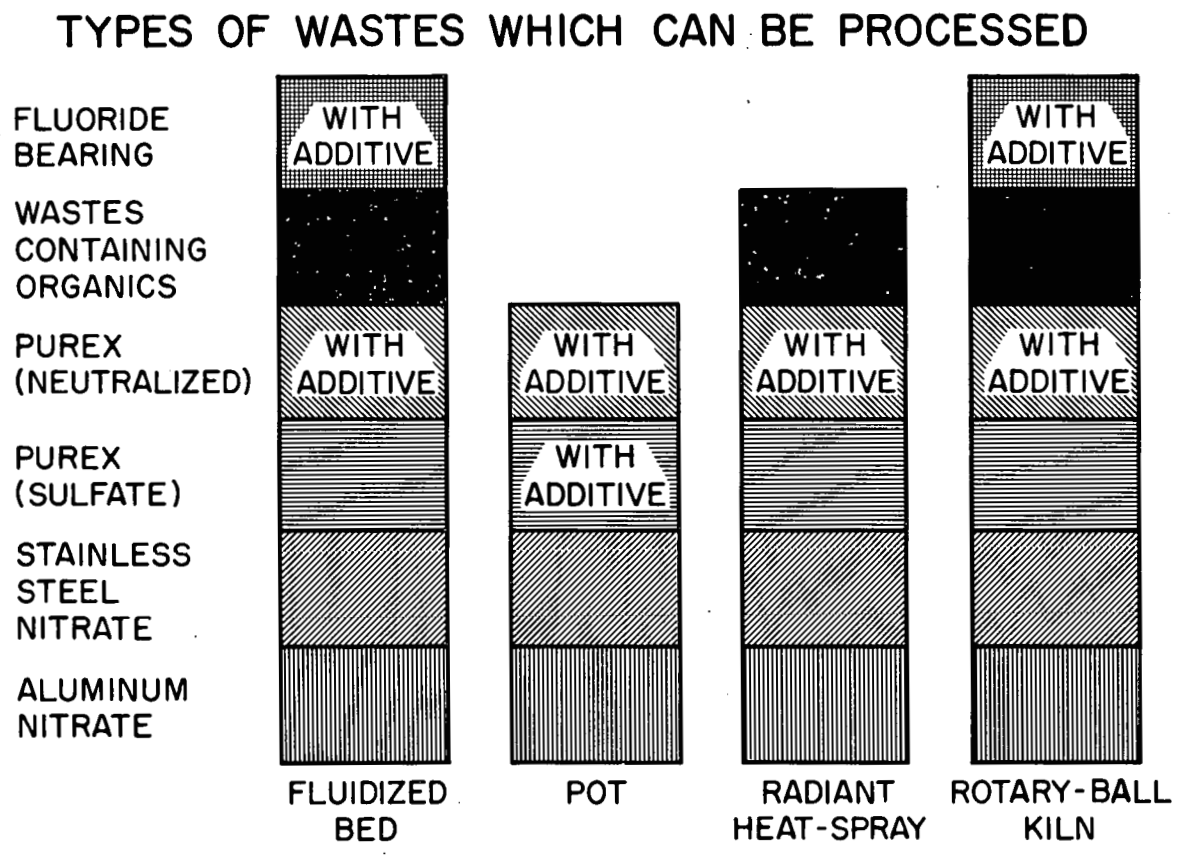

Fig. 16 Types of wastes which can be processed in the various calcination processes.

calciner.[19] Such a procedure is not feasible with the pot calciner since stringent precautions must be taken to keep even small concentrations of organic compounds out of waste as some organic materials could react violently with nitric acid in the vessel at the high temperature;[2] neutralized wastes must be reacidified for processing in a pot calciner[18]. Experimental work has shown that waste solutions containing organic materials can be calcined safely in the other calcination processes[13,19].

Fluoride-bearing wastes probably can be calcined in the fluidized bed and rotary-ball kiln processes because of the relatively low operating temperatures involved. Fluoride-bearing wastes from reprocessing of zirconium-uranium alloy fuel elements appear to present the greatest problem in calcination. Of the two possible approaches to calcining this waste, it appears that the most practical is addition of calcium oxide to the waste followed by calcination at a suitably low temperature, less than 500°C. Such a procedure has been demonstrated satisfactorily in laboratory-scale equipment with no detectable amount of fluoride being volatilized[36]; however, further development work in pilot plant-scale equipment is necessary. In theory, a second approach for calcining these wastes is possible by employing special corrosion-resistant equipment. Suitable construction materials for a calcination vessel have been demonstrated for this at temperatures less than 700°C; however, the problem of finding suitable materials for off-gas processing equipment has not been solved. Economically practical materials for equipment in which to decontaminate a highly corrosive mixture of contaminated nitric and hydrofluoric acids by evaporation or distillation techniques are unknown.

SAFETY CONSIDERATIONS

An intensive hazards evaluation of the many facets of calcination has been made in the case of the fluidized bed process[37] but not for the other processes. Although such an all-inclusive analysis is desirable, it is beyond the scope of this paper. Some of the more obvious factors, however, are as follows:

(a) Organic materials of sufficient quantity in waste solutions may form explosive mixtures with nitric acid at temperatures exceeding 150°C, as evidenced by experimental work[38]. Wastes may contain small but significant quantities of organic material due to mal-operation of solvent extraction equipment or inadvertent discharge of certain decontaminating solutions to waste storage tanks. Only in the case of the pot calciner are organic materials in waste solutions expected to cause any problem, because the other processes have virtually no liquid holdup in the calcination vessel.

(b) Equipment corrosion can be hazardous; usually, it can be minimized by employing a combination of suitable construction materials, relatively low operating temperatures, and suitable complexing agents. In the case of the fluidized bed calciner, at the relatively low temperature employed, corrosion should be low; with the other calciners, corrosion is expected to be a much greater problem. The pot calciner operating at a temperature level of 900°C can develop undetectable localized hot spots as experienced in pilot plant operation[39] resulting in serious corrosion. With the radiant-heat spray calciner, high rates of corrosion may be experienced at the 800°C temperature level normally employed. Hot spots due to wall deposits observed during development work[3,27] may accelerate corrosion. It appears therefore, that special corrosion resistant material for the calcination vessel of the radiant-heat spray unit is highly desirable. With the rotary-ball kiln calciner, corrosion and erosion of the rotating kiln may be relatively high because of the high wall temperatures coupled with moving balls.

(c) Product overheating must be prevented to avoid volatilization of fission products or corrosive compounds. No problems are expected

with the fluidized bed calciner. In the case of the pot calciner, residual heat requirements near the end of the run can be exceeded by heat release from activity; at this time, heat must be removed from the pot by employing a suitable furnace. Wall deposits in the radiant-heat spray calciner may result in product overheating as observed during development work[40].

(d) Pressurization of pot calciners, due to line plugging, as observed during some pilot plant runs[41] could rupture a pot of highly radioactive material and result in a difficult situation.

FACILITY AND PERSONNEL REQUIREMENTS

Facility and personnel requirements of a waste disposal plant will be affected to a greater extent by the number of calciners in simultaneous operation and by the type of product than by the size of the calcination equipment involved. For the pot calcination process, Perona et al[18], estimate that between 41 and 84 people would be required for operating two to sixteen pot calciners simultaneously to process waste, from a 15000 MW nuclear economy using 1500 metric tons of uranium converter fuel and 270 metric tons of thorium converter fuel annually. Extrapolation of cost figures given by Perona to other situations is difficult. More broadly based cost figures are expected to be generated from the operation of the full-scale demonstration pot calciner at Hanford in 1965. In a preliminary study for the same hypothetical situation, based on actual cost for the ICPP Waste Calcining Facility,WCF, Stevens[35] estimated that 25 people would be required to process the waste in a single fluidized bed calciner with the operating cost being independent of the processing rate. A similar study has not been made for either the radiant-heat spray or the rotary-ball kiln calciners. In general, it is expected that the cell area and labor requirements, and hence, the operating cost for the fluidized bed and rotary-ball kiln calcination processes will be almost independent of throughput capacity because a single unit can be employed for most applications. Also conducive to a small facility and labor force, at least in the case of the fluidized bed calciner, is the absence of significant amounts of remote handling equipment, a minimum amount of equipment with moving parts in radioactive areas, and a lack of a clear need to melt the calciner product. With the pot calcination process, which requires a large facility and a large highly trained operating crew because of the necessary remote handling involving specialized equipment and cells, overall costs are expected to be high. Similar high costs would be expected for the radiant-heat spray calciner if operated in conjunction with a series of batch product collection and melt pots.

POTENTIAL PROBLEMS

(a) With the fluidized bed calciner, potential problems exist with a few pieces of necessary mechanical equipment, namely, off-gas blowers and scrubbing-solution pumps. These units are installed in duplicate in the WCF; however, erosion and wear may necessitate their occasional replacement.

(b) With the pot calciner, considerable maintenance is envisioned for the remote handling equipment necessary for this process. Other possible problems involve solution foaming during calcination, fouled or plugged equipment from volatilized mercury, pot failure due to hot spots occurring from thermocouple failure, product bridging in a pot, and satisfactory programming of heat input and removal for very high activity wastes.

(c) With the radiant-heat spray calciner, remote handling equipment subject to wear may be required to manipulate pots for collecting and melting product. Product deposition on vessel walls must be prevented to avoid reduced throughput and vessel corrosion. The remote use of vibrators and automatic hammers as have been employed in development work[14,20] is far from ideal, and may be troublesome in plant-scale operation. Other potential problems involve a remotely operated product valve to seal the outlet of the calciner while product pots are changed. Inherently poor flow characteristics of the product, the possibility of loosening scale from calciner walls through vibration, and excessive wear of valves may all prove troublesome.

(d) With the rotary-ball kiln calciner, there are many moving parts, all of which may require frequent replacement. Entirely satisfactory rotary seals have not yet been demonstrated. At best these seals and the balls in the kiln must be periodically replaced. Perhaps even the kiln, itself, will have to be replaced occasionally. A satisfactory means of dispersing feed over the entire heated length of kiln remains to be demonstrated. The feed nozzle inside the 500-700°C kiln may require cooling to prevent product caking and plugging. The design of a satisfactory two-fluid nozzle, together with its connection through a rotary seal to the sources of the solution, could present many problems.

DEVELOPMENT STATUS

Based on the length of time each of the calciners has been under development and the scale and intensity of the development effort, it is believed that the four calcination processes stand in the following decreasing order of advancement; fluidized bed, pot, radiant-heat spray, and rotary-ball kiln calcination.

(a) For the fluidized bed calciner, radioactive waste solution was successfully calcined in the pilot plant unit at Argonne National Laboratory in 1958;[13] although diluted 8:1 with a nonactive synthetic solution, the problems of activity containment, and off-gac dccontamination and personnel protection were not appreciably different from those which will be encountered with any radioactive waste. The calcination of high activity wastes in the WCF at about 60 gph late in 1963 will record the first plant-scale operation of any waste processing facility in the free world.

(b) With the pot calciner, calcination of high activity waste in a laboratory-scale unit was started at Hanford late in 1962.[42] The first full-scale pot calciner is scheduled for pilot plant operation at Hanford with radioactive waste--possibly by 1965.[12]

(c) With the radiant-heat spray calciner, high activity wastes have been processed in a laboratory-scale unit since late in 1962.[42] Reported feed rates, thus far, have been in the range 0.5 to 0.7 gph. A pilot plant-scale radiant-heat spray calciner is scheduled for operation with radioactive waste late in 1965.[12]

(d) With the rotary-ball kiln calciner, most of the development effort has been devoted to rotary seal and feed introduction problems, hence, there are few process data available for detailed evaluation. High activity wastes have not been processed in this calciner in the United States. No plans for additional development work have been announced.

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