27/11-4-77
25 cy. to NTIS

RFP-2601
October 14, 1977

MASTER

RFP-2601
October 14, 1977

SCREW CALCINER MECHANICAL DIRECT DENITRATION PROCESS FOR PLUTONIUM NITRATE TO OXIDE CONVERSION

Kenneth R. Souply

Walter E. Sperry

Chemistry Research and Development
PROCESS CHEMISTRY AND ENGINEERING GROUP

Work performed under 189 No. F-AL-10-001
for the
Savannah River Operations Office
U.S. Energy Research and Development Administration

Rockwell International

Atomics International Division
Rocky Flats Plant
P.O. Box 464
Golden, Colorado 80401

U.S. DEPARTMENT OF ENERGY
CONTRACT EY-76-C-04-3533

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Printed in the United States of America
Available from the
National Technical Information Service
U. S. Department of Commerce
Springfield, Virginia 22161
Price: Printed Copy $4.50 Microfiche $3.00
Price Is Subject to Change Without Notice

Printed
October 14, 1977

RFP-2601
UC-78 LIGHT WATER
REACTOR TECHNOLOGY
TID-4500-R66

SCREW CALCINER MECHANICAL DIRECT DENITRATION PROCESS FOR PLUTONIUM NITRATE TO OXIDE CONVERSION

Kenneth R. Souply

Walter E. Sperry

Chemistry Research and Development
PROCESS CHEMISTRY AND ENGINEERING GROUP

SUBJECT DESCRIPTORS
Plutonium Processing
Plutonium Nitrates
Plutonium Oxides

ROCKWELL INTERNATIONAL
ATOMICS INTERNATIONAL DIVISION
ROCKY FLATS PLANT
P. O. BOX 464
GOLDEN, COLORADO 80401

Prepared under Contract EY-76-C-04-3533
for the
Albuquerque Operations Office
U.S. Department of Energy

eB

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

CONTENTS

ACKNOWLEDGMENTS

Appreciation is expressed, for the preparation of this report, to the following members of the PNO Project Team: Rosamond M. Greinetz, George D. Lehmkuhl, and David H. Neal.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

SCREW CALCINER MECHANICAL DIRECT DENITRATION PROCESS FOR PLUTONIUM NITRATE TO OXIDE CONVERSION

ABSTRACT

This report describes a screw calciner direct-denitration process for converting plutonium nitrate to plutonium oxide. The information should be used when making comparisons of alternative plutonium nitrate-to-oxide conversion processes, or as a basis for further detailed studies. The report contains process flow sheets with a material balance; a process description; and a discussion of the process including history, advantages and disadvantages, and additional research required.

INTRODUCTION

Plutonium (Pu) recovered from spent nuclear fuel by the PUREX solvent-extraction process is in the form of plutonium nitrate [$Pu(NO_3)x$] solution, whereas, the starting material for fabrication of fuel rods containing Pu is solid plutonium oxide (PuO_2). It is, therefore, necessary to convert plutonium nitrate to PuO_2. In the event that fuel fabrication plants are separated geographically from reprocessing plants, shipping regulations require Pu to be in a solid form(1).[1] Therefore, PuO_2 is a logical product for a fuel reprocessing plant.

Many different processes exist for converting plutonium nitrate to oxide (PNO); seven are considered in the Rocky Flats PNO project. This report describes the screw calciner mechanical direct-denitration process. The others, described in separate reports, consist of the following: fluid bed direct-denitration, plutonium(IV) oxalate precipitation and calcination, plutonium(III) oxalate precipitation and calcination, batch direct-denitration, Sol Gel, and peroxide precipitation and calcination.

Each time an industrial or government organization considers building a PNO facility, various candidate processes are compared before making a final selection. The process selected depends on the information that organization has about the process and the criteria developed by that organization. This report (and the others in this series) will provide a body of information which may be used as a basis for comparison.

For comparison, all of the PNO processes are described for a fuel reprocessing plant with a maximum throughput of 100 kilograms (kg) of Pu per day. This is based on a 1500-metric ton per year fuel recycle facility, with feed containing 1 percent Pu, and an average operation of 300 days per year.

Feedstock to the PNO conversion unit is $Pu(NO_3)x$ from the PUREX process. Feedstock is expected to meet the ASTM C710-73, Standard Specification for Plutonium Nitrate Solutions, 1973. This should result in a product that will meet the PuO_2 impurity standards described in ASTM Standard C757-74a, listed in Table I.

At this time, product specifications have not been firmly defined. Some that have been used in fuel fabrication are listed in Table I, and include ASTM C757-74a, the Fast Flux Test Facility, the German Alkem, and the Barnwell Nuclear Fuel Plant. These can be compared with the expected specifications for feedstock from the PUREX process.

---

[1] Numbers in parenthesis refer to references at end of text.

A waste treatment plant is assumed to be on site. Liquid wastes below discharge limits will be transferred to the waste treatment plant. Discharge limits are defined as 1×10^{-3} grams of Pu per litre of solution. Liquid waste streams that exceed this limit will be recycled to the PUREX plant.

Solid recycle and waste streams will be processed in one of two ways. Recycle PuO_2 will be sent to the dissolution unit. (A special PuO_2 dissolution module may be necessary if halogens are to be kept out of the main process stream.) Line-generated solid wastes will be transferred to solid waste disposal.

Off-gas streams will be processed before release to the plant filter plenum. All required utilities are assumed to be provided. Resources which can be recovered (such as nitric acid) will be transferred by appropriate means to a utility system. Where needed for design calculations, standard plant values will be assumed for utilities (e.g., cooling water available at 27 °C returned at 37 °C).

Remote "hands off" operation and maintenance will be performed on those Pu streams which require protection from radiation hazards. The plant facility should be designed so as to limit the whole body dose to 1 rem per year.

DISCUSSION

History

Mechanical direct-denitration was first extensively investigated on a pilot-plant basis in 1953 at the Hanford site in Richland, Washington(2). The first experimental studies resulted in the development of an agitated-trough calciner(3). The performance of a paddle-agitated 4-inch diameter by 44-inch long reactor was sufficiently promising to warrant construction of a 16-inch diameter by 8-foot long semi-plant scale model.

The 8-foot long reactor was installed in January 1956, to increase the denitration capacity of UNH (uranyl nitrate hexahydrate) at Hanford by 450 tons per month(4). During the initial testing period, the reactor operated for approximately 310 hours, during which time about 19,000 pounds of uranium trioxide (UO_3) was produced. Production rates up to 150 pounds per hour of UO_3 were achieved over a short period of time.

The reactor was basically an enclosed trough which contained a paddle type agitator, as shown in Figure 1 at the end of the text. The agitator was driven by a 100-horsepower (hp) motor, capable of speed variations in the range of 20 to 50 revolutions per minute (rpm). During operation, the agitator was maintained 50 to 100 percent submerged in the UO_3 bed by an overflow weir at the discharge end of the reactor. Calcination of the UNH to UO_3 was done by introducing molten UNH (approximately 100 percent UNH solution) into the bed of hot UO_3 powder at four feed points through pipes terminating inside the UO_3 bed. The temperature at the feed points was maintained somewhere in the range between 250 and 350 °C, and the UO_3 was discharged at 350 to 450 °C.

During the early part of the operation, severe dusting caused frequent plugging of the off-gas system and difficulties were experienced in obtaining adequate shaft seals. As the UO_3 particle size increased, dusting was alleviated.

To achieve continuous and rapid removal of the reactor off-gas, the reactor pressure was maintained between three and five inches of water below atmospheric pressure. The off-gas leaving the reactor was filtered and sent to a conventional nitric acid (HNO_3) recovery system. The dust collected in the filters was returned to the reactor.

The UO_3 produced by the process was a dense, free-flowing powder composed of smooth surfaced, irregularly shaped particles. The median particle size was about 200 microns and only a small amount of dust was present. Metallic impurities were within product specifications.

On the basis of design criteria developed on the 16-inch diameter reactor, the decision was made to construct 26-inch diameter calciners to be used in the planned UO_3 expansion(5). The first of the 26-inch diameter calciners was operated as a prototype, and brought to light, important structural and design weaknesses peculiar to large massive equipment. These were subsequently corrected in the production calciners.

The production units were placed in operation in October 1956. By the end of April 1957, sufficient reliability was developed in the continuous system to permit a complete and permanent shutdown of the pot calciners, thereby, eliminating a costly and onerous mode of UNH operation.

Further progressive improvements made during the course of full-scale production operation of the agitated troughs included improved heat distribution and feed delivery, wet scrubbing of off-gas for fines removal, and automatic (programmed) start-up and shut-down. Besides providing a near complete technology, Hanford's agitated trough program had resulted in nearly a three-fold increase in designed capacity, operating efficiencies in the neighborhood of 90 percent, and one of the most reliable and trouble-free processing steps in the chemical processing department.

A study was made to compare the agitated trough to the fluidized bed for use in calcining UNH at Hanford. This study included both technological and economical comparisons. At that time, it was concluded that the agitated trough offered the most reliable and effective method of UNH calcination suitable for use in the Hanford program. The agitated trough had the advantage of technology that had matured by years of production and experience, and assured a minimum of risk and investment.

The agitated trough process is presently being used for UNH calcination at Oak Ridge, Tennessee.

In the early 1960's, direct calcination was investigated as a potential replacement for the oxalate precipitation process which was being used at the Hanford site to convert plutonium nitrate to plutonium oxide(6). The reasons for considering the replacement were:

1. Simplification of the process with an attendant reduction in the amount of process equipment and process instrumentation.
2. Improved nuclear safety through the use of closed, geometrically safe process vessels.
3. Improved operation and housekeeping, resulting in lower radiation exposure to operating personnel.
4. Elimination of precipitation filtrates and associated filtrate processing.

The main disadvantage was the loss of purification afforded by the precipitation step, but it was believed that this disadvantage could be overcome by suitable processing of the feed solution or by subsequent pyrochemical refining of the product.

The first attempts to calcine $Pu(NO_3)x$ continuously on a 100-gram scale were made in a four-inch diameter trough calciner similar to those used in UNH calcination(7). A serious reactivity problem was recognized, which required additives to overcome. (Reactivity is the rate and extent of halogenation of the PuO_2 during the subsequent production of plutonium metal.) In addition, it was found that shaft seals rapidly wore out when they were submerged in powder — even those employing lantern rings. Also a great deal of oxide was entrained in the off-gas. A vertical calciner appeared to be the solution to these mechanical problems, as well as alleviating the reactivity problem(8).

Before the continuous vertical calciner was built, a less sophisticated mockup was made and tested. This was done both to check on the mechanical feasibility of the proposed design and to assure that reactive powder would be produced. The mockup was a large, stainless steel beaker containing an inverted smaller beaker, and was heated with a heating mantle. Plutonium oxide was prepared on a batch basis by dropping nitrate solution onto a stirred bed of oxide powder at 250 °C. The duration of each run was two hours with a feed rate of approximately 300 millilitres (ml) per hour. Large, spherical agglomerate-type particles were produced with a density of 3.0 g per cubic centimetre (cm^3). The chemical reactivity of the oxide was reported to be satisfactory.

The vertical calciner, shown in Figure 2, was actually a combination calciner and off-gas filter. The solution was calcined in the lower-unit, and the vapors were filtered in the upper unit.

Essentially, the calcination unit consisted of an 8-inch length of 5-inch diameter stainless steel pipe, a capped piece of 3-inch diameter stainless steel pipe 6 inches long, and three flange plates. The 3-inch pipe was inserted into the 5-inch pipe to form a concentric annulus, in which calcination occurred. Product powder was discharged through a slot in the 3-inch pipe, down an overflow tube, and into a receiver. The product receiver had to either be heated or vented to prevent vapor condensation. The height of the adjustable overflow tube determined the bed volume. Thermocouples and feed lines were located in the annulus and entered the bottom of the calciner through drilled-out tube fittings. Feed solution was pumped into the calciner by an adjustable pump at 0.046 to 0.068 gallons per hour.

The bed was stirred by a U-shaped agitator fitted over the capped-pipe insert, and which was driven by a 1/4-hp gearmotor at speeds up to 155 rpm. Heat was supplied by three 1000-watt strip heaters wrapped around a 5-inch pipe, and a 1000-watt tubular heater, which was coiled and inserted into the 3-inch pipe.

The denitrator functioned by calcining solution on a stirred bed of powder at 300 °C. The powder produced overflowed the adjustable weir in the hollow center of the denitrator and was collected in a receiver. Ceramic filter elements for the off-gas were blown back alternately and periodically. Capacity for the calciner was one litre per hour.

The operating temperature of the calciner was maintained in the range of 250 to 480 °C. Plutonium nitrate was not completely decomposed at temperatures below 250 °C and the reactivity of the oxide decreased at temperatures above 480 °C.

The ratio of heat transfer to bed volume was about 30 percent larger for the vertical calciner than a comparable trough calciner. Because plutonium processing equipment is limited in size due to criticality considerations; a larger area to volume ratio meant that the vertical calciner had a greater throughput capacity than the trough calciner.

The characteristics of the vertical calciner which differed from calciners previously designed were:

1. The agitator shaft seal was not submerged in powder — an overhead seal minimized both powder leakage and maintenance.

2. The Pu was contained in a thin, cylindrical annulus, which was a favorable configuration from a criticality view point.

3. The ratio of heated surface to bed volume was relatively large.
4. The off-gas filters permitted entrained fines to be periodically returned to the bed.
5. Particle size classification occurred in the bed with fine particles settling on the bottom, and large particles overflowing.

During the construction phase of the vertical calciner, development work was well advanced on the horizontal screw calciner, and tests showed it to be superior to the vertical calciner. These tests showed that the vertical calciner had a lower throughput and an oxide product not as reactive as that from a screw calciner(9).

The development work that had been done on the agitated trough calciner and the vertical calciner firmly established the necessary design criteria for the design of the horizontal screw calciner. These criteria were conveniently categorized as plutonium processing requirements and equipment design requirements. The proper balance between criteria was established after two unsuccessful designs of the horizontal screw calciner were tested.

The horizontal screw calciner differed from the stirred bed calciners in that the liquid phase was continuous throughout the major working portion of the calciner. Figure 3 shows a flow diagram for a horizontal screw calciner. Since wall-to-liquid heat transfer coefficients are much greater than wall-to-powder heat transfer coefficients, the screw calciner was inherently more efficient than the stirred-bed calciners. Thus, calciner wall temperatures could be lower and the inventories in the calciner could be smaller with, consequently, shorter residence times.

The disadvantages of the liquid-phase continuous calcination relative to powder-phase continuous calcination were the possibility of sticking, plugging, etc., and increased corrosion. In the case of plutonium nitrate and in contrast to UNH, the oxide is insoluble in the liquid phase, and therefore, the liquid-to-solid transition was smooth, and no extensive caking, scaling, or sticking to the screw was observed. Corrosion was minimized by the proper choice of materials of construction.

The body of the horizontal screw calciner was a 38-7/8-inch long U-shaped trough, 2-inches in diameter. The trough height was 3-inches with a wall thickness of 3/16 inch. End plates and leg assemblies supported each end of the calciner trough. Graphite bearings, centered in each end plate, supported the screw.

The screw can best be described as a single flight screw conveyor having a 2-inch diameter, a pitch of 2 inches, and a flight thickness of 3/32 inch. A chopper disk, welded to the screw, meshed with a comparable stationary disk bolted to the calciner body. This was intended to grind any large lumps of oxide in order to get a more uniform product.

The conveying screw was rotated in a clockwise direction to move the calcined oxide toward the outlet port at the end of the calciner. A 1/8-hp DC gear-head motor with a speed range of 0 to 72 rpm was used to turn the screw. This drive mechanism was located outside of the calciner hood, and was connected to the calciner through a shaft seal. The screw speed was regulated by a DC control unit to give an operating speed range of 0 to 40 rpm.

The calciner trough was enclosed by a rectangular top plate containing the exit port for the off-gas filter and the feed inlets. The bottom half of the calciner was heated by two tube furnaces having rated capacities of 825 and 1287 watts. The top plate was heated by two 500-watt heating elements.

The calciner body, screw, and top plate were all fabricated from type ASTM B-348 titanium. Titanium had been demonstrated as a safe material for all nitric acid-water systems. Corrosion of titanium by boiling HNO_3 was found to be undetectable; and to insure that titanium corrosion products (which could be pyrophoric) were not accumulating, the PuO_2 was constantly analyzed for titanium. The additional effects of calcination additives such as ammonium sulfate were also considered.

An off-gas filter was mounted on the top plate at the feed end of the calciner. The filter consisted of a porous ceramic thimble-cartridge and was mounted in a glass filter housing.

The adequacy of the horizontal screw calciner was verified during 200 hours of operation in which 67.5 kg of PuO_2 were produced. Operating parameters and capacities were established at:

1. Feed rate, 0 to 500 g Pu per hour.
2. Temperature, 400 to 500 °C.
3. Screw speed, 10 to 20 rpm.
4. Calcination additive, 0.25 moles per mole Pu.

A satisfactory oxide could be produced by direct calcination in the screw calciner, and the oxide product showed little impurity pickup across the calciner(10). By using an activating agent, the oxide could be halogenated to better than 95 percent under optimum operating conditions. The optimum direct calcined oxide was found to be equal in reactivity with the oxide produced from the oxalate precipitation process.

In recent years, interest has been shown in the screw calciner for use in the reprocessing of spent reactor fuel. Exxon Nuclear Company, Incorporated, submitted a Preliminary Safety Analysis Report (PSAR) to Nuclear Regulatory Commission, Washington, D.C., for approval of a reprocessing facility to be built in Oak Ridge, Tennessee(11). In this facility, they propose to use the screw calciner for the direct-denitration of plutonium nitrate. Exxon indicated in the PSAR that development work is planned to confirm the reliability of the unit before a decision will be made to use it. The plutonium(IV) oxalate precipitation and calcination process will be the backup process if the screw calciner proves to be unreliable in the pilot tests.

Process Description

The screw calciner mechanical direct-denitration process is designed to convert $Pu(NO_3)x$ solution directly to a PuO_2 solid suitable for blending with UO_2 and fabrication into fuel pellets for Light Water Reactor (LWR) fuel.

The main process stream and the waste streams are shown in Figure 4. The main stream starts with a storage of the feed solution. It is then evaporated, with the bottoms stream from the evaporator being sent to storage tanks. The more concentrated solution is then fed to the calciner where it emerges as the PuO_2 solid. This is then screened and packaged as the finished product.

A more detailed description is given below. A description of the equipment and a material balance are shown on the equipment flow sheet, Figure 6 (consisting of three sheets). The process lines and items of equipment are identified numerically, with the process lines being referenced by number in the material balance.

Detailed Process Description

1. Plutonium nitrate from the PUREX process is piped into storage at a plutonium concentration of 250 g

per l and a molarity of 3M in nitric acid, at a flow of 400 l per day(12) with a decay heat of 60 BTU per hr per kg of Pu.

2. The feed solution is then evaporated to a nitric acid concentration of 4.7M, with a plutonium concentration of 373 g per l. The distillate is 0.6M in nitric acid, with a flow of 132 l per day. The bottoms stream flow is 269 l per day.

3. The evaporator bottoms stream is fed to the electrically heated screw calciner where the water and nitric acid are evaporated. The reaction is:

$$Pu(NO_3)_4 \xrightarrow{\Delta} PuO_2 + 3.4NO_2 + 0.6\ NO + 1.3O_2 (13)$$

   The reactor has a 6-inch inside diameter and a 38-inch length (scaled-up from the pilot unit as reported by R. E. Felt)(9).

4. The product plutonium dioxide is discharged from the calciner, cooled, and screened. The screened product is packaged and sent to storage or transferred to the fuel fabricator. The screen overs are processed in a ball mill and recycled to the screen.

5. The overhead product from the calciner is condensed. The condensate is sent to an evaporator where it is concentrated. The evaporator bottoms stream is discharged to contaminated waste disposal. The noncondensables from the evaporator, including some water vapor, are scrubbed in a venturi type scrubber. The bottoms stream from the scrubber joins the condenser condensate for evaporation. The scrubber off-gas discharges to the filter plenum.

6. The distillate from feed evaporation and waste evaporation are sampled for plutonium and, if below discard limits, are transferred to Waste Treatment. If the distillates are above discard limits, they are recycled, with the feed evaporation distillate being sent to feed storage, and the waste evaporation distillate being sent to the condenser bottoms storage.

Advantages and Disadvantages

The following advantages and disadvantages were obtained from literature research and conversation with individuals who have had operating experience with the screw calciner process. A separate report will be published at a later date which will compare the seven denitration processes relative to the advantages and disadvantages as they exist in present technology.

Advantages

1. No feed preparation is required in the process. No valence adjustment is needed as in some other denitration processes. Although an evaporation step is shown on the flow sheets, it is an optional step and could be bypassed.

2. The screw calciner is simple and reliable to run because it has only two operating parameters; screw speed and temperature, which are both easy to control.

3. No hazardous chemicals are used in the process other than the HNO_3 and the Pu being processed.

4. There are no precipitation filtrates and associated filtrate processing.

5. Because the throughput per unit is high, only two process trains are needed in a 100 kg per day plant.

6. Because of fewer process trains, less equipment and process instrumentation will be needed. This should mean that fewer maintenance

problems should be encountered in the process operation.

7. Inventory of the Pu should be simple because of the fewer process trains and lesser equipment needs.

8. Pilot plant experience for the screw calciner using Pu has demonstrated reliability of the equipment for a hands-on operation.

9. The process generates small volumes of liquid waste, and off-gases consist mainly of the oxides of nitrogen.

Disadvantages

1. The process does not purify the product. A feed solution of sufficient purity will be needed to obtain an oxide that will meet specifications.

2. There could be considerable difficulty in detecting the controlling process upset conditions because of the lag time between the introduction of the feed and the emergence of the calcined oxide. If the oxide emerged not completely calcined, then the calciner would probably be full of the faulty product, which would then present a significant recycle problem.

Research and Development

Before a denitration facility is built, some development work will have to be done. In the case of the screw calciner direct-denitration process, the need for this work was defined as a result of a literature search and discussions with individuals who have studied and/or have had experience with the process. The suggested development work for the screw calciner is as follows:

1. It should be determined that acceptable LWR fuel can be manufactured using PuO_2 from this process. The equipment design should be studied to determine what the optimum equipment characteristics should be to produce the desired oxide. This would include determination of the optimum length of the calciner to achieve complete calcination. Also, a method should be developed for detecting and controlling the percent moisture, nitrate, etc. This should be a feedback control for continuous operation.

2. Work should be done on verifying process parameters such as feed rates, screw speed, and temperature. Although operating parameters have been reported for the denitration of Pu(9), a pilot facility is needed to confirm the proper operating conditions and point out potential problems.

3. A remotely operated denitration facility will introduce unique equipment and operational problems. A better understanding of these problems are needed before a production size plant can be built.

SUMMARY

This report described a screw calciner mechanical direct-denitration process for the conversion of plutonium nitrate to plutonium oxide. A history of the process was given to provide background information for the process and to provide a perspective as to it's stage of development. The process description provided a guide for better understanding of the block flow diagram and equipment flow sheets. The advantages and disadvantages were listed to provide an insight as to the various assets of the process and problems that will be encountered. Some suggestions for development work were listed, and should be implemented before any plant scale unit is constructed.

No conclusions are reached at this time as to how this process compares with other denitration processes. The comparison of the processes will be made in a separate report which will be issued later.

REFERENCES

1. The Generic Environmental Statement on the Use of Recycle Plutonium In Mixed Oxide Fuel in LWR's - GESMO - Volumes 1, 2, 3, and 4. Atomic Energy Commission - Directorate of Licensing. Washington, D.C. August 1974.

2. J. Belle. Uranium Dioxide, Properties and Nuclear Applications. USAEC. pp. 33-44. 1961.

3. M. J. Szulinski. Continuous Denitration, Status of Development. HW-34470. Hanford Atomic Products Operation. Richland, Washington. January 12, 1955.

4. M. J. Szulinski and R. G. Geier. Hanford Atomic Products Operation. Richland, Washington. Private Communication. January 4, 1955.

5. B. F. Campbell. Comparative Evaluation of the Agitated Trough and Fluidized Bed Denitration Processes for Application to the Hanford NPF Program. HW-61594. Hanford Atomic Products Operation. Richland, Washington. June 1, 1959.

6. F. D. Fisher. Reactivity of Plutonium Dioxide Prepared by Direct Calcination of Nitrate Solutions. HW-77846. Hanford Atomic Products Operation. Richland, Washington. October 15, 1963.

7. M. J. Rasmussen, G. L. Stiffler, and H. H. Hopkins, Jr. Parameters in the Conversion of Plutonium Nitrate to Plutonium Trichloride by a Direct Calcination - Fluid Bed Chlorination Process. HW-69738. Hanford Atomic Products Operation. Richland, Washington. May 31, 1961.

8. A Vertical Calciner for Converting Plutonium Nitrate Solution to Plutonium Dioxide Powder. HW-73765 Hanford Atomic Products Operation. Richland, Washington. June 1, 1962.

9. R. E. Felt. Equipment for the Direct Calcination of Plutonium Nitrate. RL SEP-674. Hanford Atomic Products Operation. Richland, Washington. December 1965.

10. H. T. Fullam and T. S. Soine. Chlorination Reactivity of Plutonium Oxide Prepared in a Screw Calciner. RL-SEP-673. Hanford Atomic Products Operation. Richland, Washington. December 1965.

11. Nuclear Fuel Recovery and Recycling Center. PSAR. Volume 4. Exxon Nuclear Company, Incorporated. June 16, 1976.

12. PNO Conversion Project Process Selection Assumptions and Criteria. Revision 0. Rockwell International, Golden, Colorado. August 4, 1976.

13. R. E. Felt. Fluorination Reactivity of Plutonium Dioxide Prepared by Direct Calcination of Plutonium Nitrate in a Screw Calciner. RL-SEP-675. Hanford Atomic Products Operation. Richland, Washington December 1965.

14. Harrington and Ruehle. Uranium Production Technology. pp. 181-187. 1959.

15. Plutonium Handbook, Volume II. p. 562. March 1967.

TABLE I. Plutonium Oxide Powder Specifications

	Specification			
Element/Property	ASTM[a]	FFTF[b]	ALKEM[c]	BARNWELL[d]
U; ppm[e]	5,000	2,000	<2,600	5,000
Th; ppm	30	--	--	--
Am; wt %	See ASTM	See FFTF	0.25, 6 months	0.28
Pu; wt %, dry	87.5	87.5	87.6	87.2
O/Pu ratio	1.95 to 2.0	1.96 to 2	2	--
C	200	200	150	500
N	200	200	50	200
Cl+F	125	75	75	125
S	300	300	--	300
Fe + Cr + N	1,000	850	600	1,000
Zr + Nb; µCi/g Pu	5	-	-	5
Gamma emitting; µCi/g Pu	40	-	<8	40
Moisture; wt %	0.5	-	-	0.3
Total of below; ppm Al, Be, C, Ca, Cd, Cl, Co, Cr, Cu, F, Fe, Li, Mg, Mn, Mo, N, Ni, P, S, Si, Sn, Ta, Ti, W	5,000	5,000	2,500	5,000
Particle Size; max, avg, micrometers	90, 10	90, 10	40, --	76, --
Surface Area; m^2/g	--	>2.5	>5 m^2/g	--
Bulk Density; g/cm^3	>1	-	2 ±0.3	>1

TABLE I. Plutonium Oxide Powder Specifications (Cont.)

	Specification			
Element/Property	ASTM[a]	FFTF[b]	ALKEM[c]	BARNWELL[d]
Sinterability Test:				
Cold Pressure, KPSI	See ASTM	30 to 50	mechanically	--
Soak Temp & Time	1550 °C, 1 hr	1550 °C, 1 hr	blendable, UO_2	--
Sintered density; % theoretical	90	90	--	--

---

a. ASTM Standard C 757-74a, 1974. The $Pu(NO_3)x$ from the PUREX Process is expected to have less impurities than those listed in this ASTM specification.

b. Fast Flux Test Facility Ceramic Grade Plutonium Dioxide, Reactor Development Technology Standard, RDT E13-1T, June 1971.

c. Standard Specification of PuO_2 for Fabrication of Mixed Oxide Rods, Alkem GmbH, Grassauheim be: Hanau, West Germany, 1972.

d. Barnwell Nuclear Fuel Plant, License Application, PSAR, Allied-General Nuclear Services, Barnwell, S.C. Docket-50332-38, July 1974.

e. ppm refers to parts per million parts by weight of plutonium element.

ILLUSTRATIONS ⟶

Figures 1 through 6

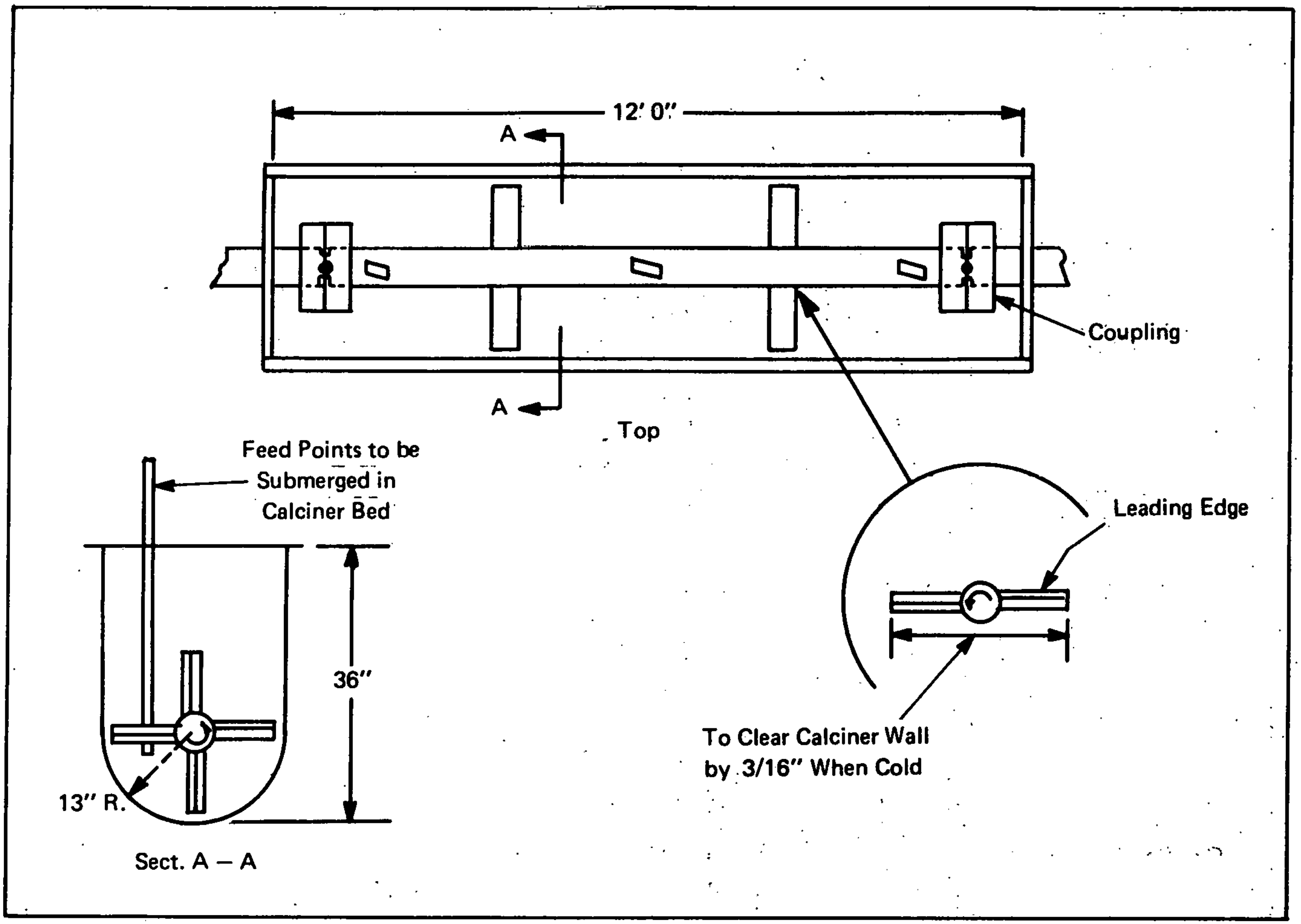


FIGURE 1. Trough-Type Reactor for Continuous Calcination of Uranyl Nitrate Hexahydrate (UNH).

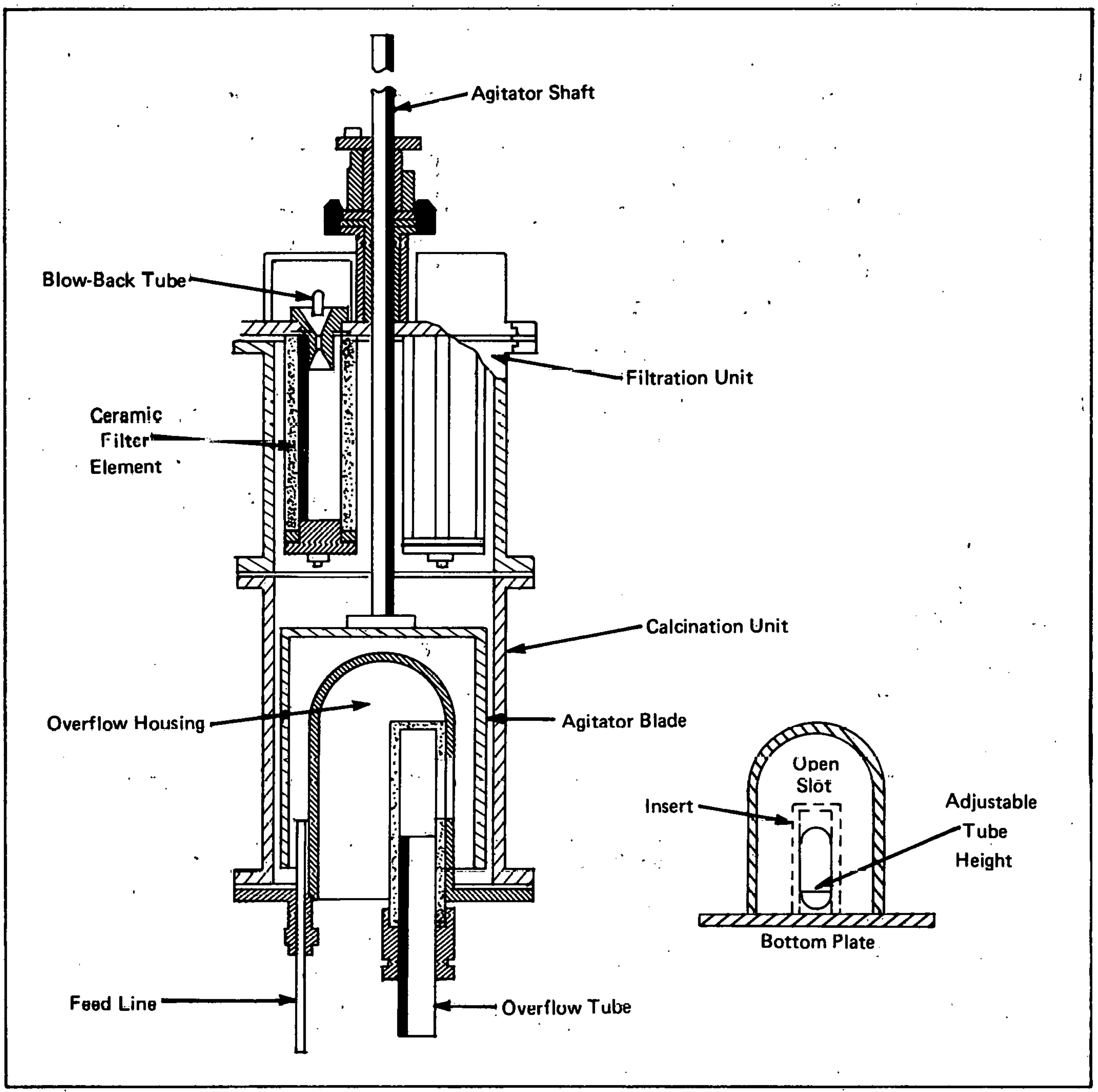


FIGURE 2. Vertical Calciner.

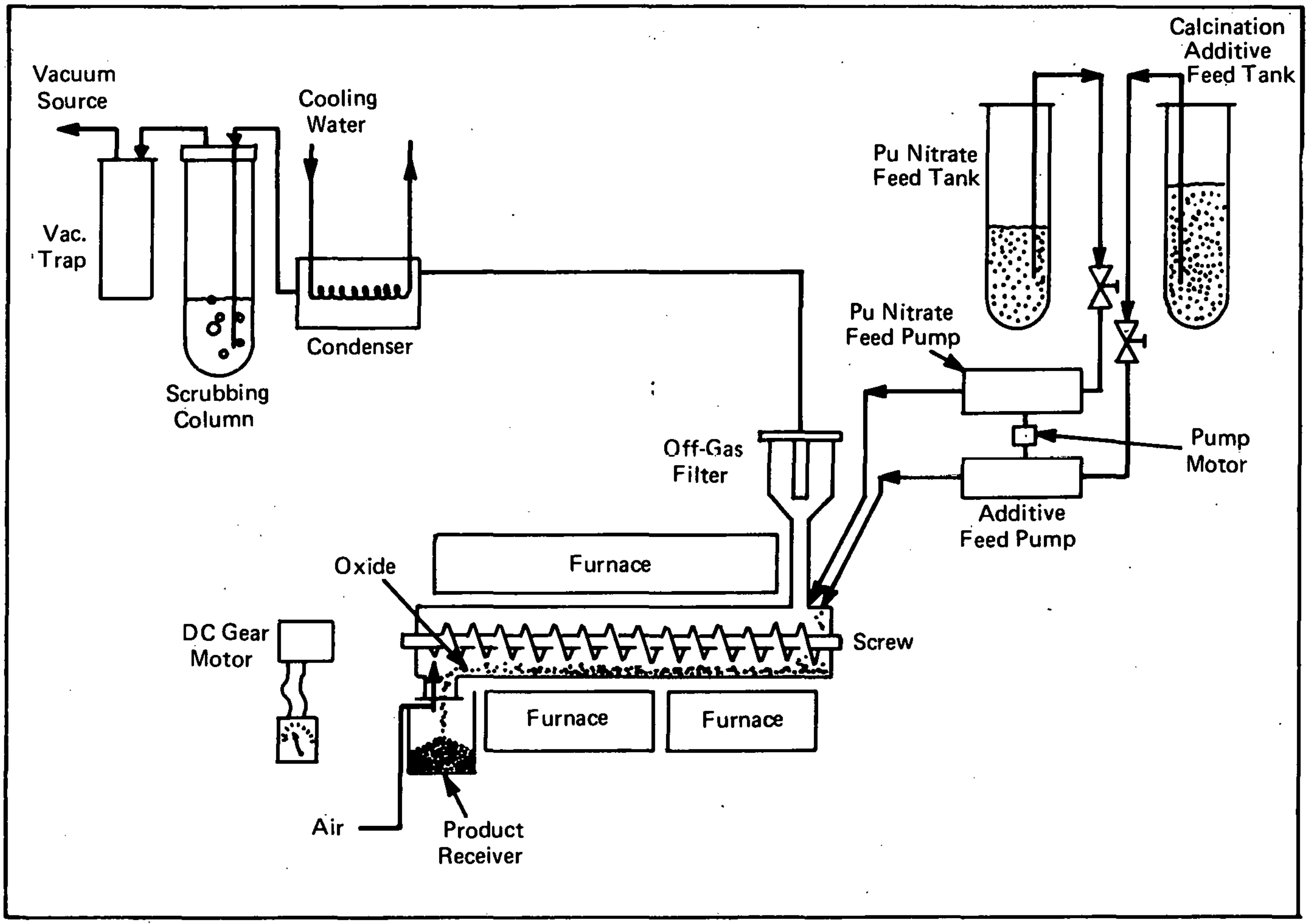


FIGURE 3. Flow Diagram for Horizontal Screw Calciner.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

DIRECT DENITRATION (SCREW CALCINER)

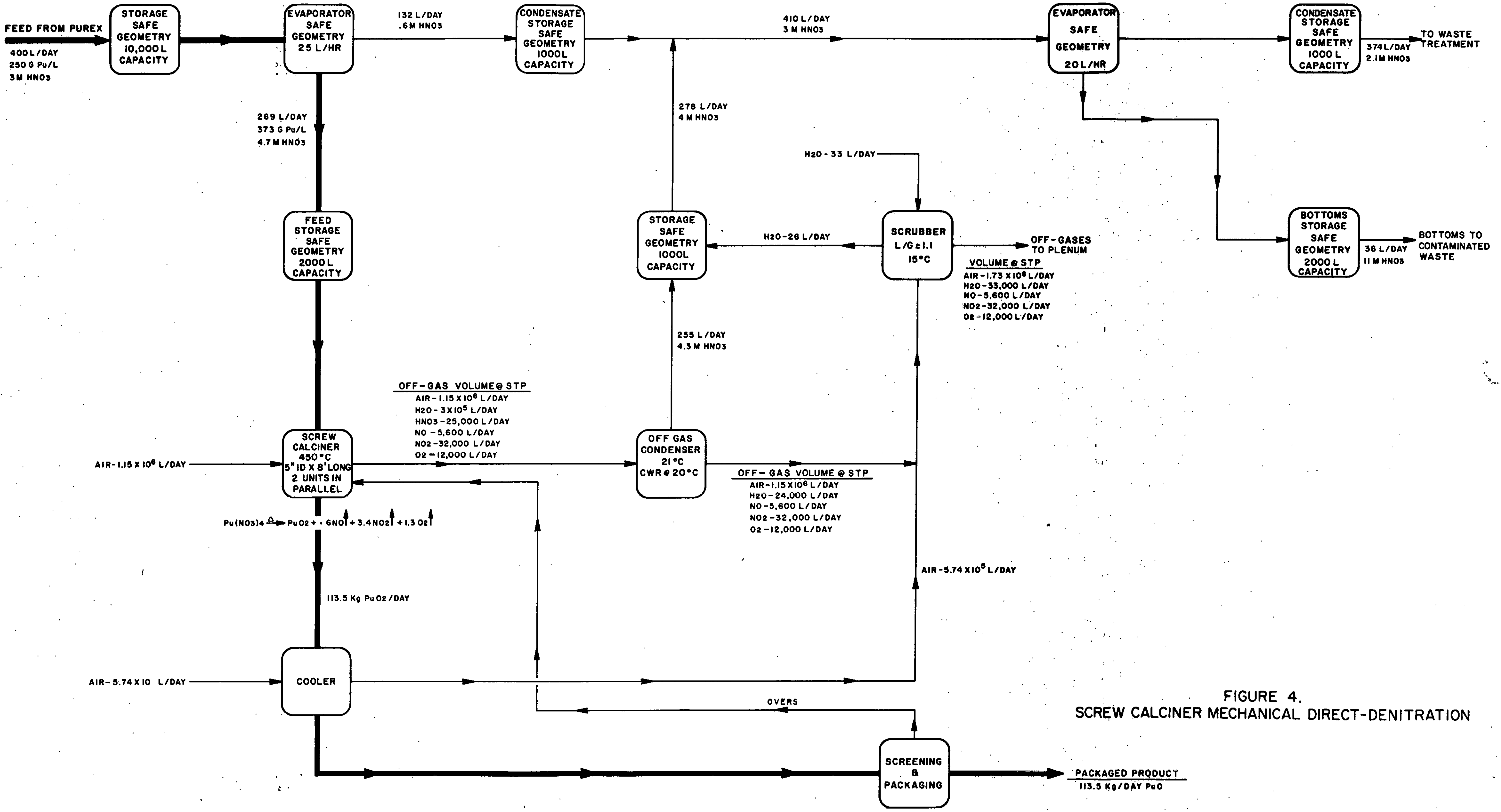
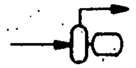
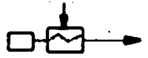
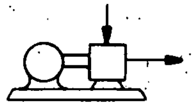
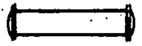
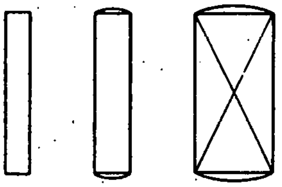
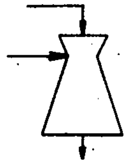


FIGURE 4.
SCREW CALCINER MECHANICAL DIRECT-DENITRATION

PART		DESCRIPTION	MATERIAL

LEGEND SHEET FOR "PNO" FLOW SHEETS

EQUIP. SYMBOL	LETTER SYMBOL	DESCRIPTION
	—	LINE IDENTIFICATION
	P	CENTRIFUAL PUMP
	P	GEAR PUMP
	P	DIAPHRAGM PUMP
	B	BLOWER
	C	COMPRESSOR
	E	HEAT EXCHANGER
	D, R	VESSEL, REACTOR
	J	JET, EDUCTOR

MISCELLANEOUS

—	A	AGITATOR
—	CV	CONVEYOR
—	CY	CYCLONE
—	F	FURANCE
—	FL	FILTER
—	H	HOPPER
—	ME	MISCELLANEOUS MECHANICAL EQUIP
—	W	DRYER
—	Z	VIBRATOR
—	STM	STEAM
—	COND	CONDENSATE
—	PW	PROCESS WATER
—	CWS	COOLING WATER SUPPLY
—	CWR	COOLING WATER RETURN
—	CHWS	CHILLED WATER SUPPLY
—	CHWR	CHILLED WATER RETURN

FIGURE 5.
PNO. FLOW SHEET LEGEND

A	ORIGINAL ISSUE	2-3-77				
		DATE	A1	ERDA	CLASS	JOB NO.

	BY	DATE
DESIGNED	D. NEAL	1-25-77
DRAWN	S. HATCH	2-3-77
CHECKED		
APPROVED		
SUBMITTED		
APPROVED A1		
APPROVED ERDA		

U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
ROCKY FLATS AREA OFFICE GOLDEN, COLORADO

SIZE	DRAWING NUMBER	ISSUE	SHEET
D		A	1 of 1

D-1 THRU 5
FEED STORAGE TANK
SST
GEOMETRICALLY SAFE "SLAB TANKS"
10,000 LITER CAPACITY TOTAL
(30 TANKS REQ.)

P-1
PUMP
SST.
CANNED PUMP
1 GPM

D-6
EVAPORATOR
SST
GEOMETRICALLY SAFE
25 L/H CAPACITY

E-2
REBOILER
SST SHELL & TUBE
DUTY: 25,000 BTU/HR

P-3
CONDENSATE TRANSFER PUMP
SST
CANNED PUMP
0.1 GPM

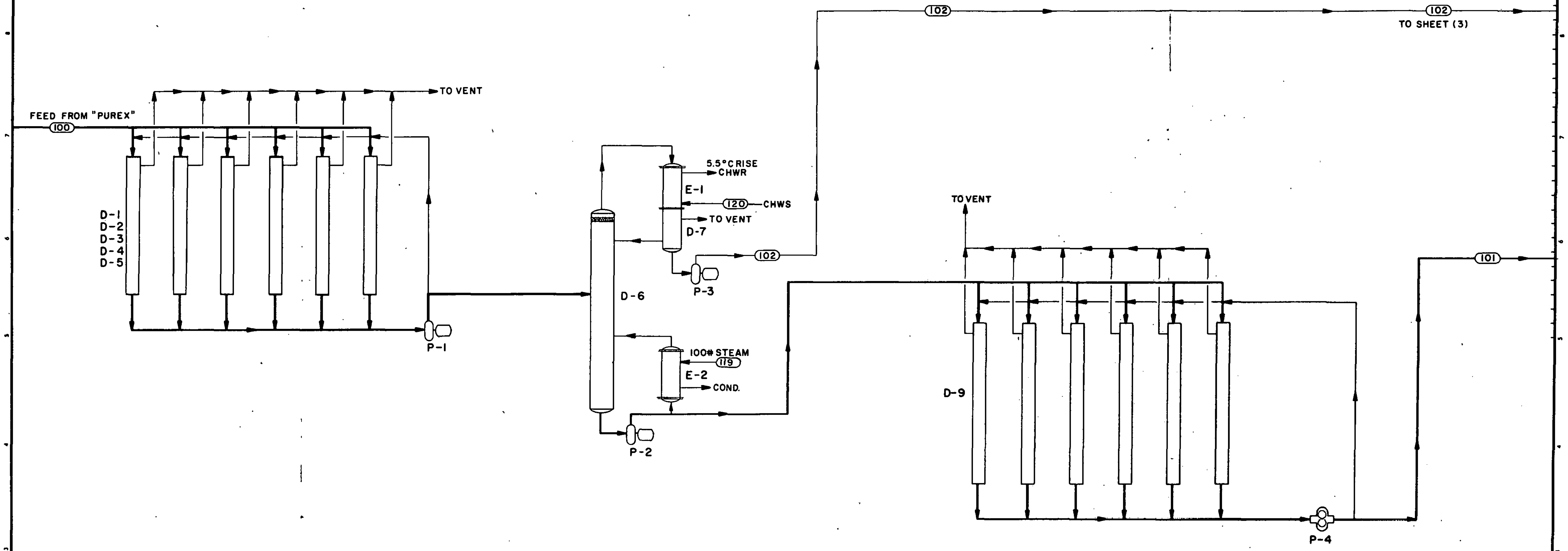
P-4
CALCINER FEED PUMP
SST
.1 GPM METERING PUMP

E-1
CONDENSER
SST SHELL & TUBE
DUTY: 25,000 BTU/HR.

D-7
CONDENSER SUMP TANK
SST
GEOMETRICALLY SAFE
10 LITER CAPACITY

P-2
BOTTOMS PUMP
SST CANNED PUMP
0.5 GPM

D-9
CALCINER FEED STORAGE TANKS
SST
GEOMETRICALLY SAFE SLAB TANK
2000 LITER CAPACITY



STREAM GMS/HR COMPONENT	100	101	102	119	120 CHWS							
$Pu(NO_3)_4$	8,489	8,489										
H_2O	15,214	10,000	5,214		1,400#/HR							
HNO_3	3,156	2,950	206									
URANIUM	42	42										
SULFUR	4.	4.										
HALIDES (F & Cl)	.6	.6										
METAL IONS	42	42										
NO												
NO_2												
O_2												
PuO_2												
ROOM AIR												
STEAM				20#/HR								
TOTAL GMS/HR	26,947	21,527	5,420	20#/HR	1,400#/HR							
Pu, GMS/L	250	372.75										
FLOW, L/HR	16.7	11.2	5.5		2.8 GPM							
PRESS, PSIA	SYSTEM	SYSTEM	SYSTEM	100	SYSTEM							
TEMP. °C	AMB	109	AMB		15							
MOLARITY	3 HNO_3	4.7 HNO_3	.6 HNO_3									
PHASE	LIQUID	LIQUID	LIQUID	VAPOR	LIQUID							

NOTES:

1. STREAM FLOW RATES GIVEN ARE FOR THE TOTAL PLANT THROUGHPUT. THROUGHPUT FOR EQUIPMENT SPECIFIED IN PARALLEL IS EQUAL TO THE TOTAL PLANT THROUGHPUT DIVIDED BY THE NUMBER OF UNITS IN PARALLEL.

2. UNLESS OTHERWISE SPECIFIED GEOMETRICALLY SAFE SLAB TANKS INSIDE WIDTH & HEIGHT SHALL BE STANDARDIZED TO 4" X 48" RESPECTIVELY, WITH TANK LENGTH LEFT AS A VARIABLE TO MEET VOLUME REQUIREMENTS. OTHER GEOMETRICALLY SAFE TANKS, REACTORS, & HEAT EXCHANGERS SHALL BE 5" ID CYLINDRICAL VESSELS OF VARIABLE LENGTH.

3. GAS VOLUME FLOW RATES ARE GIVEN AT S.T.P.

4. WHERE NOTED RASCHIG RING (BORON GLASS) PACKED TANKS OF EQUAL NET VOLUME MAY BE SUBSTITUTED FOR TANKS SPECIFIED GEOMETRICALLY SAFE.

5. ALL ROOM AIR DRAWN THROUGH HOOD & SIZING SCREEN (ME-6) IS FILTERED BY FL-2.

FIGURE 6.

A ORIGINAL ISSUE 1-20-77
DESCRIPTION DATE AI ERDA CLASS JOB NO.
DESIGNED W. SPERRY 1-13-77
DRAWN S. HATCH 1-20-77
CHECKED
APPROVED
SUBMITTED
APPROVED AI
APPROVED ERDA
NEXT ASSEMBLY
SCALE

U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
ROCKY FLATS AREA OFFICE GOLDEN, COLORADO
ROCKWELL INTERNATIONAL
ATOMICS INTERNATIONAL DIVISION
ERDA CONTRACT E (29-2)-3533
ROCKY FLATS PLANT GOLDEN, COLORADO 80401

FLOW SHEET & MATERIAL BALANCE
SCREW CALCINER
CONVERSION OF $Pu(NO_3)_4$ TO PuO_2

SIZE D DRAWING NUMBER ISSUE A SHEET 1 OF 3

ME-6
SIZING SCREEN
SST
VIBRATING SCREEN
5kg/HR. CAPACITY
2 REQ. IN PARALLEL

ME-8
CONVEYOR
2 REQ. IN PARALLEL

ME-10
BALANCE
2 REQ. IN PARALLEL

E-4
CONDENSER
SST SHELL & TUBE
DUTY: 26,000 BTU/HR

D-11
STORAGE TANKS
SST
GEOMETRICALLY SAFE "SLAB TANKS"
1000 LITER CAPACITY

P-5
FEED & CIRCULATION PUMP
SST CANNED PUMP
1GPM

FL-1
FULL-FLOW FILTER
SST CASE
SINTERED METAL OR
CERAMIC CARTRIDGE
FILTER

P-6
CIRCULATION PUMP
SST-CANNED PUMP
1GPM

D-10
CONDENSER SUMP TANK
SST
GEOMETRICALLY SAFE
10 LITER CAPACITY

ME-7
MANIPULATOR
SST
REMOTE TRANSFER MECHANISM
25# CAPACITY

ME-9
CANNER
2 REQ. IN PARALLEL

ME-1
SCREW CALCINER
TITANIUM TROUGH 5" ID.
THERMAL REQUIREMENTS
ZONE 1-22,000 BTU/HR
ZONE 2-33,000 BTU/HR
SCREW WITH B_4C INSERTS
SPEED 20 RPM
5kg/HR CAPACITY
2 REQ. IN PARALLEL

ME-2
CONVEYOR
GRAVITY-(VIBRATOR ASSIST)
5Kg/HR CAPACITY
2 REQ. IN PARALLEL

ME-3
DRAG-CHAIN CONVEYOR
SST
5Kg/HR
2 REQ. IN PARALLEL

ME-4
CONVEYOR
GRAVITY-(VIBRATOR ASSIST)
5 Kg/HR CAPACITY
2 REQ. IN PARALLEL

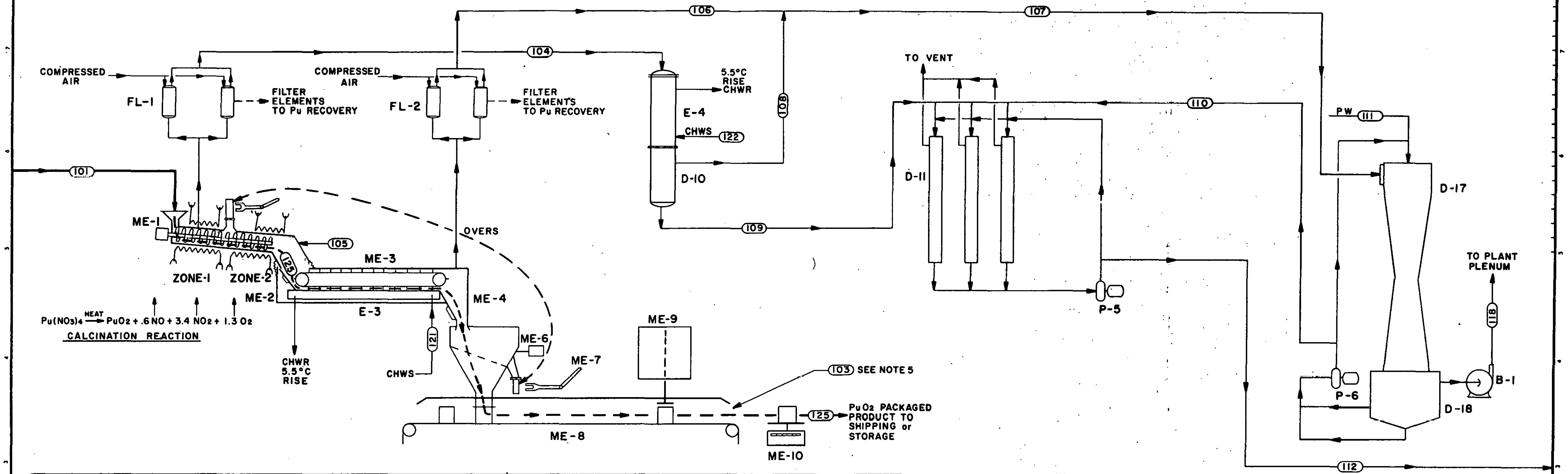
E-3
COOLING TABLE
SST-
DUTY: 1000 BTU/HR
5Kg/HR CAPACITY
2 REQ. IN PARALLEL

FL-2
(SEE FL-1)

D-17
VENTURI SCRUBBER
SST-GEOMETRICALLY SAFE
L/G = 1.1
125scfm CAPACITY

D-18
SCRUBBER SUMP & GAS-LIQUID SEPARATOR
SST-GEOMETRICALLY SAFE
20 LITER CAPACITY

B-1
BLOWER
SST
125 scfm CAPACITY



STREAM GMS/HR COMPONENT	107	108	109	110	111	112	118	101	103	104	105	106	121 CHWS	122 CHWS	125								
$Pu(NO_3)_4$								8,489															
H_2O	819	819	9,181	1,073	1,362	10,254	1,108	10,000		10,000			60#/HR	2,600#/HR									
HNO_3		TRACE	2,950	TRACE		2,950	TRACE	2,950		2,950													
URANIUM								42							42								
SULFUR								4							4								
HALIDES (F&Cl)								.6							.6								
METAL IONS								42							42								
NO	313	313					313			313													
NO_2	2,720	2,720					2,720			2,720													
O_2	724	724					724			724													
PuO_2	TRACE	TRACE	TRACE	TRACE		TRACE				TRACE					4,731								
ROOM AIR	92,499	61,666					92,499		30,033	61,666	61,666	30,833											
STEAM																							
TOTAL GMS/HR	97,075	66,242	12,131	1,073	1,362	13,204	97,364	21,527	30,833	78,373	61,666	30,833	60#/HR	2,600#/HR	4,820								
Pu, GMS/L								372.75															
FLOW, L/HR	75,060	51,220	10.6	1.07	1.36	11.6	75,283	11.2	23,840	60,600	47,680	23,840	.12 GPM	5.2 GPM									
PRESS, PSIA	SYSTEM	SYSTEM	SYSTEM	SYSTEM	SYSTEM	SYSTEM	SYSTEM	SYSTEM	SYSTEM	SYSTEM	SYSTEM	SYSTEM	SYSTEM	SYSTEM									
TEMP. °C	AMB	21	21	AMB	AMB	AMB	15	AMB	AMB	350	AMB	AMB	15	15	AMB								
MOLARITY			4.3 HNO_3			4. HNO_3		4. HNO_3															
PHASE	GAS	GAS	LIQUID	LIQUID	LIQUID	LIQUID	GAS	LIQUID	GAS	VAPOR	GAS	GAS	LIQUID	LIQUID	SOLID								
	NOTE 3	NOTE 3					NOTE 3		NOTE 3		NOTE 3	NOTE 3											

SEE NOTES SHEET (1)

FIGURE 6.
(Continued)

ISSUE	DESCRIPTION	DATE	AI	ERDA	CLASS	JOB NO.
A	ORIGINAL ISSUE	1-21-77				

	BY	DATE
DESIGNED	W.SPERRY	1-13-77
DRAWN	S.HATCH	1-21-77
CHECKED		
APPROVED		
SUBMITTED		
APPROVED AI		
APPROVED ERDA		

TOLERANCES
FRACT. ±
ANGLE ±
DEC. ±
UNLESS NOTED OTHERWISE

REMOVE BURRS AND SHARP EDGES

NEXT ASSEMBLY

SCALE

U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
ROCKY FLATS AREA OFFICE GOLDEN, COLORADO

ROCKWELL INTERNATIONAL
ATOMICS INTERNATIONAL DIVISION
ERDA CONTRACT E (29-2)-3533
ROCKY FLATS PLANT GOLDEN, COLORADO 80401

FLOW SHEET & MATERIAL BALANCE
SCREW CALCINER
CONVERSION OF $Pu(NO_3)_4$ TO PuO_2

SIZE	DRAWING NUMBER	ISSUE	SHEET
D		A	2 of 3

P-7
TRANSFER & CIRCULATION PUMP
SST-CANNED PUMP
1 GPM

P-9
TRANSFER PUMP
SST-CANNED PUMP
5 GPM

P-8
TRANSFER & CIRCULATION PUMP
SST-CANNED PUMP
1 GPM

D-12
EVAPORATOR
SST
GEOMETRICALLY
20 L/HR CAPACITY

E-5
CONDENSER
SST-SHELL & TUBE
DUTY: 42,500 BTU/HR.

E-6
REBOILER
SST-SHELL & TUBE
DUTY: 42,500 BTU/HR

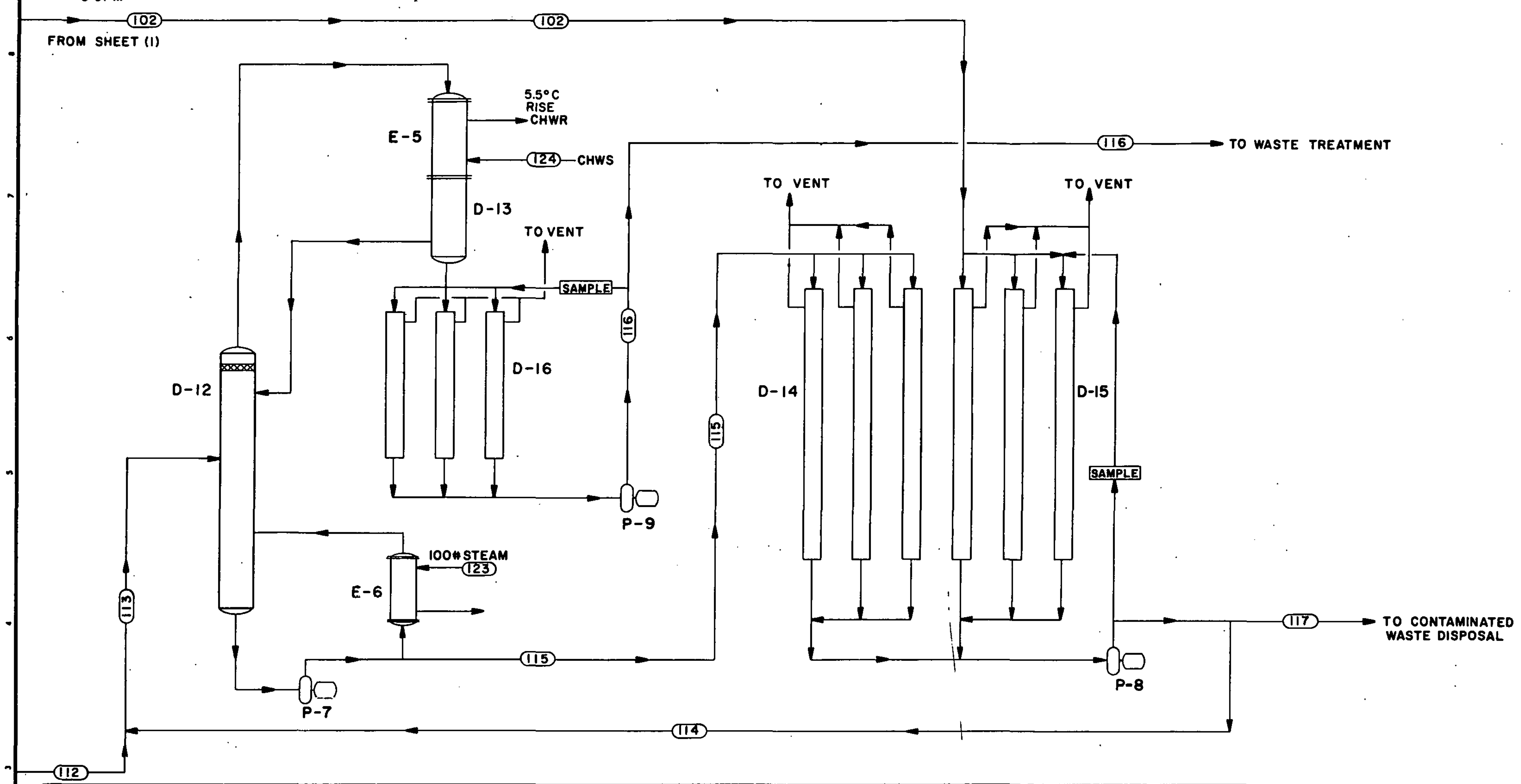
D-13
CONDENSER SUMP
SST
GEOMETRICALLY SAFE
15 LITER CAPACITY

D-14
WASTE STORAGE TANK
SST
GEOMETRICALLY SAFE "SLAB TANKS"
1,000 LITER CAPACITY

D-15
RECYCLE STORAGE TANKS
SST
GEOMETRICALLY SAFE "SLAB TANKS"
1,000 LITER CAPACITY
(SEE NOTE 4)

D-16
CONDENSATE STORAGE TANK
SST
GEOMETRICALLY SAFE "SLAB TANKS"
1,000 LITER CAPACITY
(SEE NOTE 4)

PART	CODE	DESCRIPTION	MATERIAL



STREAM / GMS/HR COMPONENT	102	112	113	114	115	116	117	123	124 CHWS														
$Pu(NO_3)_4$																							
H_2O	5,214	10,254	15,468	5,214	1,040	14,428	1,070		3,800#/HR														
HNO_3	206	2,950	3,156	206	1,028	2,128	1,028																
URANIUM																							
SULFUR																							
HALIDES (F & Cl)																							
METAL IONS																							
NO																							
NO_2																							
O_2																							
PuO_2		TRACE	TRACE		TRACE		TRACE																
ROOM AIR																							
STEAM								45#/HR															
TOTAL GMS/HR	5,420	13,204	18,597	5,420	2,068	16,556	2,068	45#/HR	3,800#/HR														
Pu, GMS/L																							
FLOW, L/HR	5.5	11.6	17	5.5	1.5	15.5	1.5		7.6 GPM														
PRESS, PSIA	SYSTEM	SYSTEM	SYSTEM	SYSTEM	SYSTEM	SYSTEM	SYSTEM	100	SYSTEM														
TEMP. °C	AMB	AMB	AMB	AMB	100	AMB	AMB		15														
MOLARITY	.6 HNO_3	4 HNO_3	3 HNO_3	.6 HNO_3	11 HNO_3	2.1 HNO_3	11 HNO_3																
PHASE	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	VAPOR	LIQUID														

SEE NOTES SHEET (1)

FIGURE 6.
(Continued)

ISSUE	DESCRIPTION	DATE	AI	ERDA	CLASS	JOB NO.
A	ORIGINAL ISSUE	1-24-77				

TOLERANCES
FRACT. ±
ANGLE ±
DEC. ±
UNLESS NOTED OTHERWISE
REMOVE BURRS AND SHARP EDGES
NEXT ASSEMBLY
SCALE

	BY	DATE
DESIGNED	W.SPERRY	1-13-77
DRAWN	S.HATCH	1-24-77
CHECKED		
APPROVED		
SUBMITTED		
APPROVED AI		
APPROVED ERDA		

U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
ROCKY FLATS AREA OFFICE GOLDEN, COLORADO
ROCKWELL INTERNATIONAL
ATOMICS INTERNATIONAL DIVISION
ERDA CONTRACT E (29-2)-3533
ROCKY FLATS PLANT GOLDEN, COLORADO 80401

FLOW SHEET & MATERIAL BALANCE
SCREW CALINER
WASTE STREAMS

SIZE	DRAWING NUMBER	ISSUE	SHEET
D		A	3 of 3