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SLURRY CALCINATION PROCESS FOR CONVERSION OF AQUEOUS URANIUM AND PLUTONIUM TO A MIXED OXIDE POWDER*

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Abstract

Pilot plant studies indicate that a slurry calcination process for conversion of uranium and plutonium solutions to a mixed oxide powder can be operated at a plant scale.

* The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U. S. Department of Energy.

Introduction

Recent concerns about the more widespread availability of plutonium and its possible diversion for weapons material has led to the development of coprocessing recovery schemes. In coprocessing, the plutonium never exists as a separate process stream, but only as a mixture with uranium. One of the areas of technical uncertainty in coprocessing plant design is the finishing operation where the aqueous uranium and plutonium stream is converted to a mixed oxide powder.

The slurry calcination process, developed by General Electric, is a promising means of converting the mixed stream. In this process, ammonia coprecipitates the uranium and plutonium to form a slurry of ammonium diuranate and plutonium hydroxide mixed solid. A fluidized-bed reactor calcines the resulting slurry to produce the mixed-oxide powder. General Electric demonstrated the feasibility of the process in a laboratory-scale 3-inch-diameter calciner. On the laboratory scale, the process produces uranium and mixed uranium-plutonium oxide powders that are sinterable to at least 94% theoretical density. Mixed oxides containing up to 30% plutonium can be dissolved in nitric acid without fluoride assist.

The Savannah River Laboratory designed and built a finishing process development facility at its semiworks to assess the operability of large-scale slurry calcination equipment with depleted uranium and to develop a technical basis for a plant-configured design suitable for use in a full reprocessing complex including spent fuel receipt and storage, fabrication of mixed-oxide (MOX) fuels, and waste immobilization (Slide 1).

Two reprocessing plants were designed. In one plant, uranium and plutonium streams were separate (the conventional design). The other was a coprocessing plant where the plutonium is always diluted with uranium. These designs were presented to the technical community in 1978 and 1979.

Test Program

As an outgrowth of these designs, we identified areas of technology which we felt needed additional research and development to enable a firm design of a reprocessing plant. These areas included off-gas treatment, tritium removal, MOX fuel fabrication, and product conversion (Slide 2).

For our ongoing program on product conversion, we selected a design reference process, which I will discuss in more detail later, and implemented a test program with two objectives (Slide 3):

- Demonstrate the production-scale feasibility of the process by operating large-scale equipment at design conditions and at throughputs reasonable for use in a reprocessing plant.
- Collect and document process technical data that can be used in plant design.

Before proceeding, let me summarize briefly our status. In FY-79, we designed, built, and started up a pilot plant conversion process. The process is intended to be used in the uranium-plutonium conversion step in the coprocessing plant. We tested scaleup in a cold facility with depleted uranium feedstock. We have demonstrated a goal process throughput of 100 kg U/day, and have recently completed equipment development.

Conversion Processes

Slide 4 shows how our conversion process fits into the coprocessing flowsheet. Modules downstream of solvent extraction are the conversion modules.

The uranyl nitrate stream from the dissolver is rather sizable and contains about 90% of the total heavy metal throughput of the plant. The uranium in this stream is converted to UF_6 gas and then shipped off-site for enrichment. This other stream contains a blended uranium and plutonium stream. The blended stream is converted to a mixed oxide powder. The powder is pressed into pellets, and the pellets are loaded into metal casings for use as reactor fuel. There is quite a bit of contrast in the technology of these two processes. The conversion process for uranyl nitrate solution to UF_6 is well established. On the other hand, there are few processes for converting the blended uranium-plutonium solution to oxide powder.

Slide 5 shows a partial list of conceptual processes: direct thermal denitration, precipitate filtration and calcination, and slurry calcination. Most of these processes have drawbacks for converting a mixed uranium-plutonium stream. Very few have been used for a mixed stream. Some, if used, would have obvious process or equipment difficulties. The processes that have been used on mixed uranium-plutonium feeds do not make oxides that can be compacted to high enough densities for use as nuclear fuels.

We selected the slurry calcination process (Slide 6) as the reference conversion process for the coprocessing plant. Bench-scale studies showed that the process makes a high quality product that is sinterable to over 94% theoretical density. However, the extrapolation from the bench scale to plant scale was a 100X scaleup. About the time of the design integration study, we knew that we had a process that made a good product, but we did not know whether or not production-scale equipment could be built. These design uncertainties were investigated with depleted uranium feedstock in a pilot plant facility.

Slide 7 shows a flowsheet of the pilot plant slurry calcination process. The precipitation and slurry calcination steps of the process are at our semiworks. At the process headend, ammonia precipitates the uranium out of solution to make a slurry of ammonium diuranate (ADU) solids. The slurry is pumped to a fluidized-bed calciner where the slurry water vaporizes, and the ADU calcines to uranium oxide. The oxide particles formed in the calciner are small enough to be entrained in the calciner off-gas, and the UO_x is pneumatically conveyed to the off-gas scrubber. The scrubber condenses water vapor in the off-gas and knocks out virtually all of the uranium oxide dust. Our experimental facility has provisions for collecting small quantities of product. An actual production facility would have extensive solid-gas separation equipment to collect the product.

Pilot Plant Facility Arrangement and Operation

I know when I say "pilot plant" facility, it creates a variety of impressions.

Slide 8 is a photograph of the facility showing most of the process equipment. Material flows from the near side of the photograph to the far side. This facility is the first pilot-plant demonstration of the slurry calcination process.

The pilot plant equipment consists of process feed tanks, a continuously operated precipitator, a 6-inch-diameter fluidized bed calciner, a venturi off-gas scrubber, HEPA filters, a process control center, and chemical transfer stations outside the building.

The test process is designed for rapid turnaround of uranium to minimize the inventory of uranium. Feed tanks receive uranyl nitrate and aqueous ammonia solutions at the head-end of the process. Ammonia precipitates the uranium as ammonium diuranate, and the slurry is calcined to make uranium oxide.

The calciner produces oxide powder, which is swept out in the off-gas. The product-laden off-gas passes through a venturi scrubber that condenses the water vapor and recovers the uranium solid. The oxide and its condensate are routinely transferred to an auxiliary feed preparation area, where fresh uranyl nitrate feed is made.

The throughput goal of the pilot plant process was 100 kg of heavy metal/day. Equipment was sized in the pilot facility to be critically safe for the conceptual plant feedstock containing 10% plutonium, although only depleted uranium would be used. The design throughput and criticality criteria could be met with a 6-inch-diameter calciner.

An actual production facility would include solids handling steps. Product collection equipment would separate the oxide powder from the calciner off-gas prior to venturi scrubbing. Additional equipment would reduce the uranium oxide to UO_2 and then slightly reoxidize the powder to the more stable $UO_{2.07}$.

Equipment

Feed Receipt and Storage

The head-end of the process has feed tanks and pumps. The tanks receive (1) a 400 g U/L solution that is 1 molar in free nitric acid and (2) a 29% aqueous ammonia solution.

Positive displacement pumps transfer the uranium and ammonia solutions from the tanks to the precipitator. The pumping rates are manually adjusted to give a specified volumetric ratio of throughputs.

Uranium Precipitation

The uranyl nitrate and ammonia reagents mix just before entering a 6-inch-diameter precipitator.

The slurry is pumped out of the precipitator through a discharge line at the bottom of the vessel. Slurry from the vessel goes either to the calciner through a slurry feed line or returns to the precipitator through a recirculation line. An automatic valve in the slurry feed line to the calciner opens or closes, as required, to keep a constant liquid level in the precipitator or maintain a constant feed rate to the calciner, depending on the control mode selected.

The key operating consideration in the calciner is the alkalinity of the slurry. An excess of ammonia reagent assures that all of the uranium is precipitated into a slurry of finely divided solids.

Calcination

Slurry passing through the control valve goes to the calciner which is a heated vessel containing a fluidized bed of 1000-micron Inconel® (Huntington Alloys) beads. As many as four nozzles atomize the slurry with nitrogen gas and spray the slurry into the bed where the water vaporizes and the slurry calcines to UO_3/U_3O_8. Fluidizing gas, atomizing gas, vaporized slurry water, and the uranium oxide powder leave the calciner through an overhead process line. The calciner is operated at conditions that yield a uranium product and off-gas temperature of 550°C.

An adequate heat supply and good bed fluidization assure process operation at the goal throughput. The calciner bed operates between 600 and 650°C; most of the heat is supplied by eight 2-KW cartridge heaters that extend into the bed through the calciner bottom cone. The fluidizing gas rate is twice the rate theoretically needed to initiate bed fluidization. The outside of the calciner is heated to reduce heat losses through the calciner wall. Fluidizing gas is heated to 700°C before entering the calciner.

Process Gas Scrubbing

The main process gas line leaving the calciner routes calciner off-gas to a scrubbing and filtration system which traps the uranium powder and condenses the process water. The first step of the calciner off-gas treatment is a venturi scrubber selected specifically for its efficiency in removing particulates from gas streams. The venturi removes most of the uranium dust and condenses water in the off-gas stream. A catch tank below the scrubber collects scrub solution, and cooling coils in the tank remove heat recovered from the off-gas. Scrubbing solution is rerouted to the venturi through a recirculation line between the tank and the scrubber. Condensate and the suspended uranium oxide are drained into portable containers as required and moved to a feed preparation area.

Gases from the venturi pass through a heated pipe to HEPA filters for final cleanup before being discharged into the building exhaust.

Scale of Equipment

One question that people ask is, "Is it full scale?"

Actually, no. The conversion area of a reprocessing plant would be much larger. However, crucial pieces of equipment is this facility are production scale. We are limited in equipment size in the actual plant due to nuclear safety considerations. For 10% plutonium feedstock, which we anticipate for an actual production facility, a 6-inch-diameter cylinder is critically safe. The calciner and precipitator vessels are 6 inches in diameter, so they are full scale. In an actual production facility, the throughput requirements would be met by making parallel lines. About 12 parallel lines similar to the one in this photo would be required in a 10-MTHM/day coprocessing plant. (Slide 8)

Key Process Considerations

Slide 9 lists three important things to consider in the operation of the process.

The precipitation step is critical for making the high quality product. Without this step, the process becomes a direct denitration process, and the product may not be usable as MOX fuel. Precipitation should be in an excess of ammonia so that the plutonium and uranium come out of solution as an intimate mixture. Apparently, the crystal structure established in the precipitation step is maintained in the oxide form and leads to the product's favorable properties.

The calcination step is important because it is the throughput-limiting step of the process. The process vaporizes large amounts of water and heats the resulting vapor to 500-600°C. Good heat transfer from the heat sources to the product stream is necessary for good process operation. I'll discuss calciner design on the next slide.

Ammonium nitrate is formed as a byproduct of the acid neutralization and ADU precipitation steps of the process. The ammonium nitrate decomposes as it enters the calciner. However, ammonium nitrate can be reformed in calciner off-gas lines during process upsets or by ammonia reactions with NO_x.

Slide 10 shows a glass replica of the process calciner. The design of the calciner is rather novel in that fluidized bed is not the material being calcined but rather a bed of inert metal shot. The bed is heated by cartridge heaters that protrude from the base cone of the vessel. The bed is fluidized by nitrogen gas entering through these 5 feed lines. The slurry sprays into the bed through feed nozzles around the perimeter. The ADU particles in the slurry are 1 to 5 microns in diameter and are entrained in

the fluidizing gas and water vapor. The bed shot diameter is about 1000 microns; the process is operated so that the product exits the calciner, but the bed shot remains in the vessel.

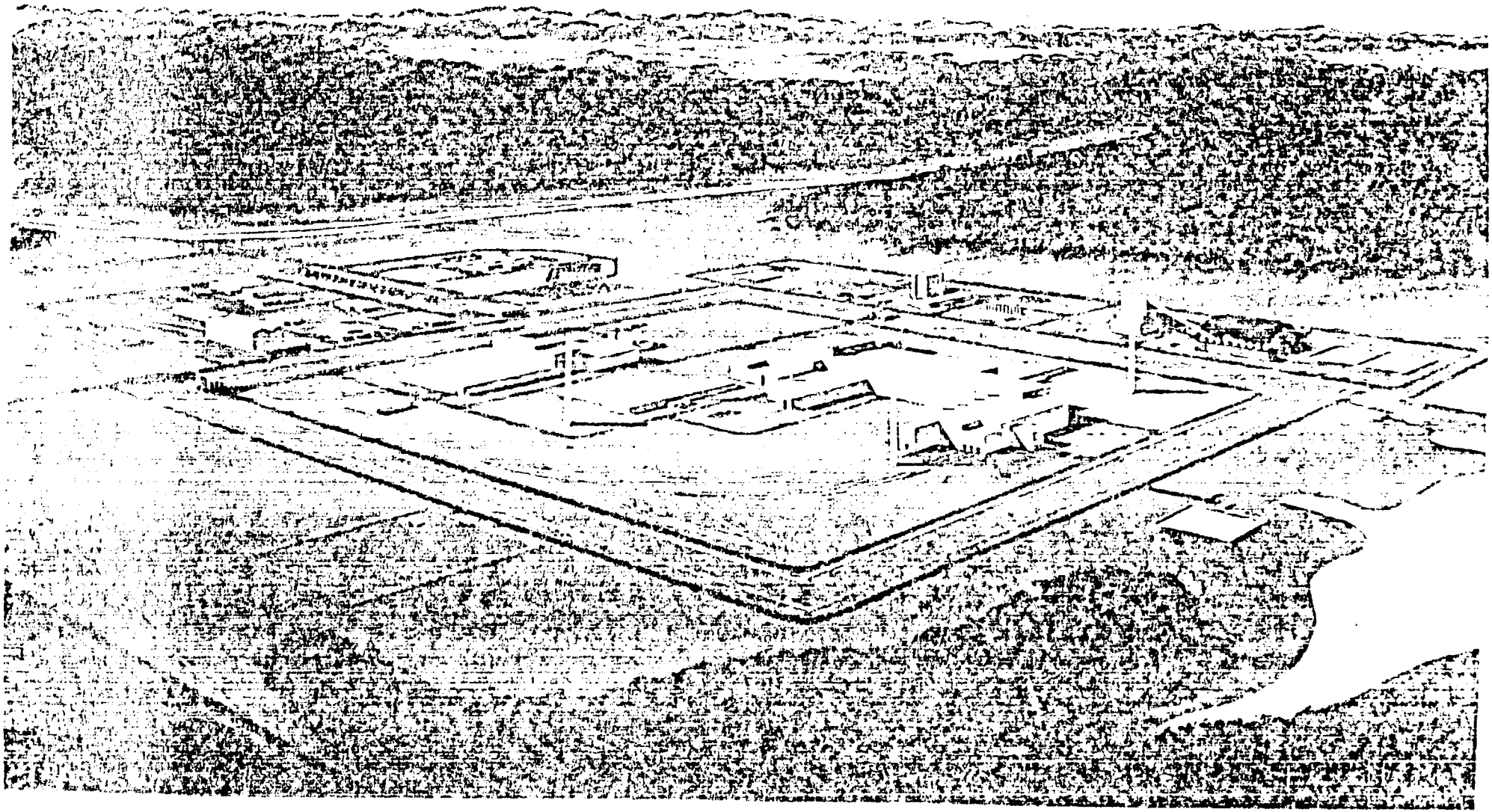
Results of the Test Program

Slide 11 summarizes accomplishments of the recently completed pilot-plant test program. We demonstrated production-scale throughput of single pieces of equipment and in doing so showed the production-scale feasibility of the process. Work with plutonium may be the next logical step for the process study. Of course, our facility does not have plutonium capabilities.

We did process and equipment development work, and that work is grouped into these three headings. Pumping slurry was difficult, as you might expect, but these problems were resolved, and I see no problems in handling slurry in the process. The fluidized-bed calciner operates at goal throughput, so heat transfer is adequate. The design engineer will be able to identify areas for improvement from the technical data that we have collected. Product collection is an area requiring some additional investigation but was not within the scope or budget of our study.

References

Slide 12 lists references that give details that could not be included in a twenty-minute discussion. DP-CFP-79-121 is the Design Integration Study description of the entire fuel reprocessing plant. DP-1571 documents design of the slurry calcination pilot plant facility that I discussed today. A report is being prepared that provides design technical data for the slurry calcination process.



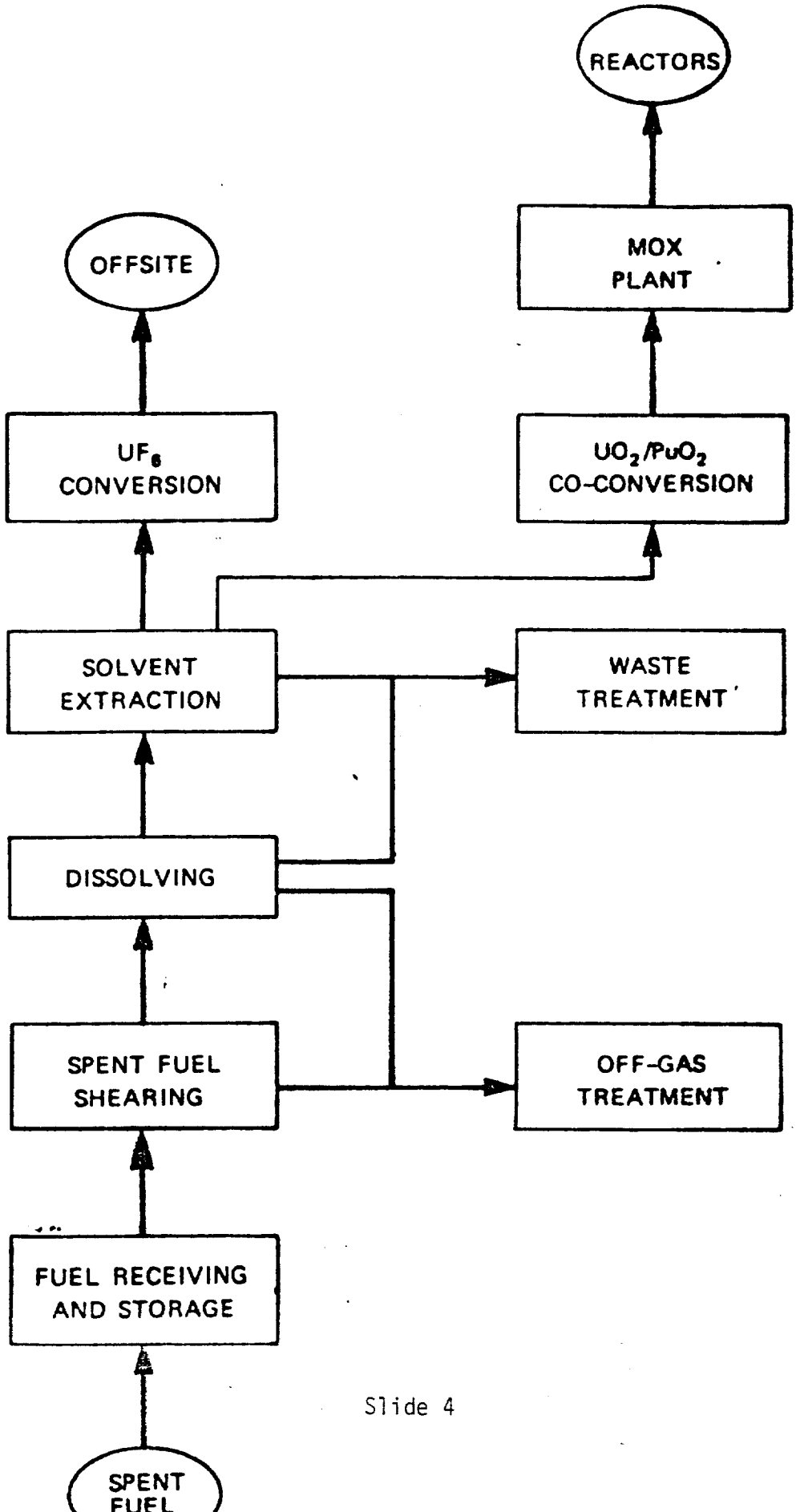
AREAS OF TECHNICAL UNCERTAINTY:

- OFF-GAS TREATMENT
- VOLOXIDATION/TRITIUM REMOVAL
- MOX FUEL FABRICATION
- PRODUCT CONVERSION

OBJECTIVES

- DEMONSTRATE FULL-SCALE EQUIPMENT OPERABILITY AND THROUGHPUT
- DEVELOP DESIGN TECHNICAL DATA

COPROCESSING FLOWSHEET



Slide 4

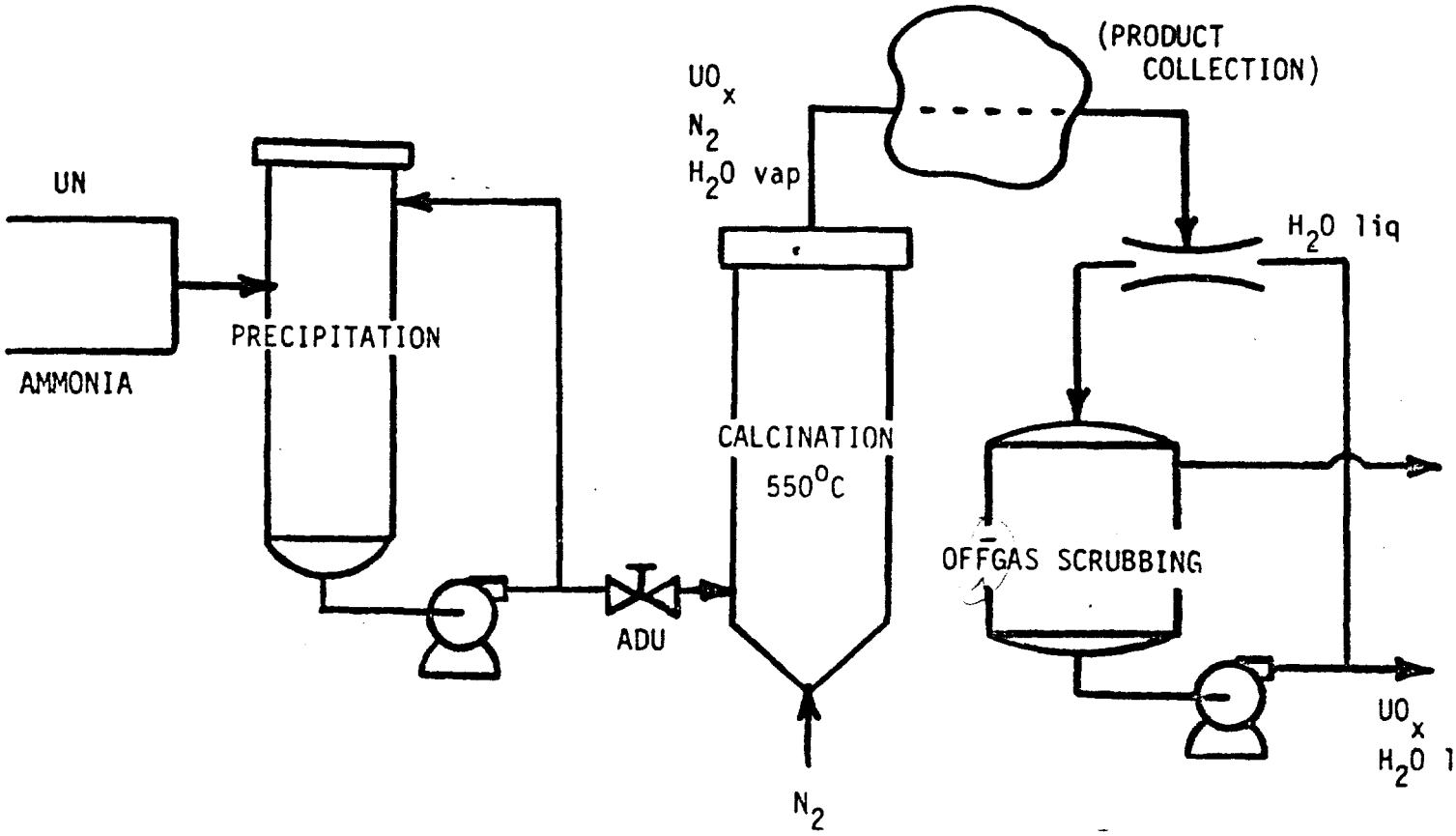
CONVERSION PROCESSES

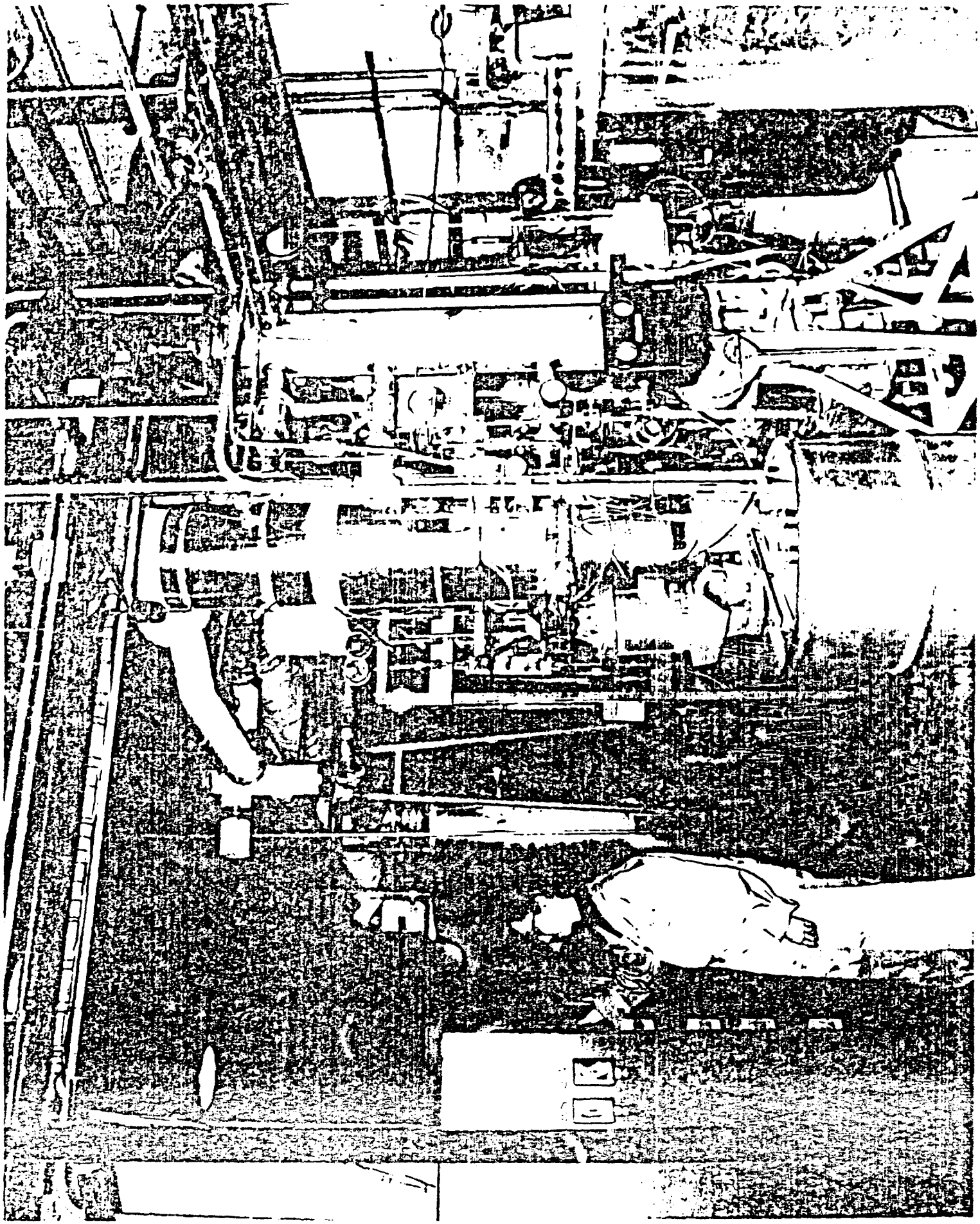
- DIRECT DENITRATION
- PRECIPITATE CALCINATION
  - OXALATE
  - HYDROXIDE
  - PEROXIDE
- SLURRY CALCINATION (COPRECAL)

SLURRY CALCINATION SELECTED FOR FRP DESIGN

- BENCH SCALE DEVELOPMENT
- MAKES USEABLE MOX PRODUCT
- SCALEUP UNCERTAINTIES COULD BE ADDRESSED IN COLD PILOT PLANT FACILITY

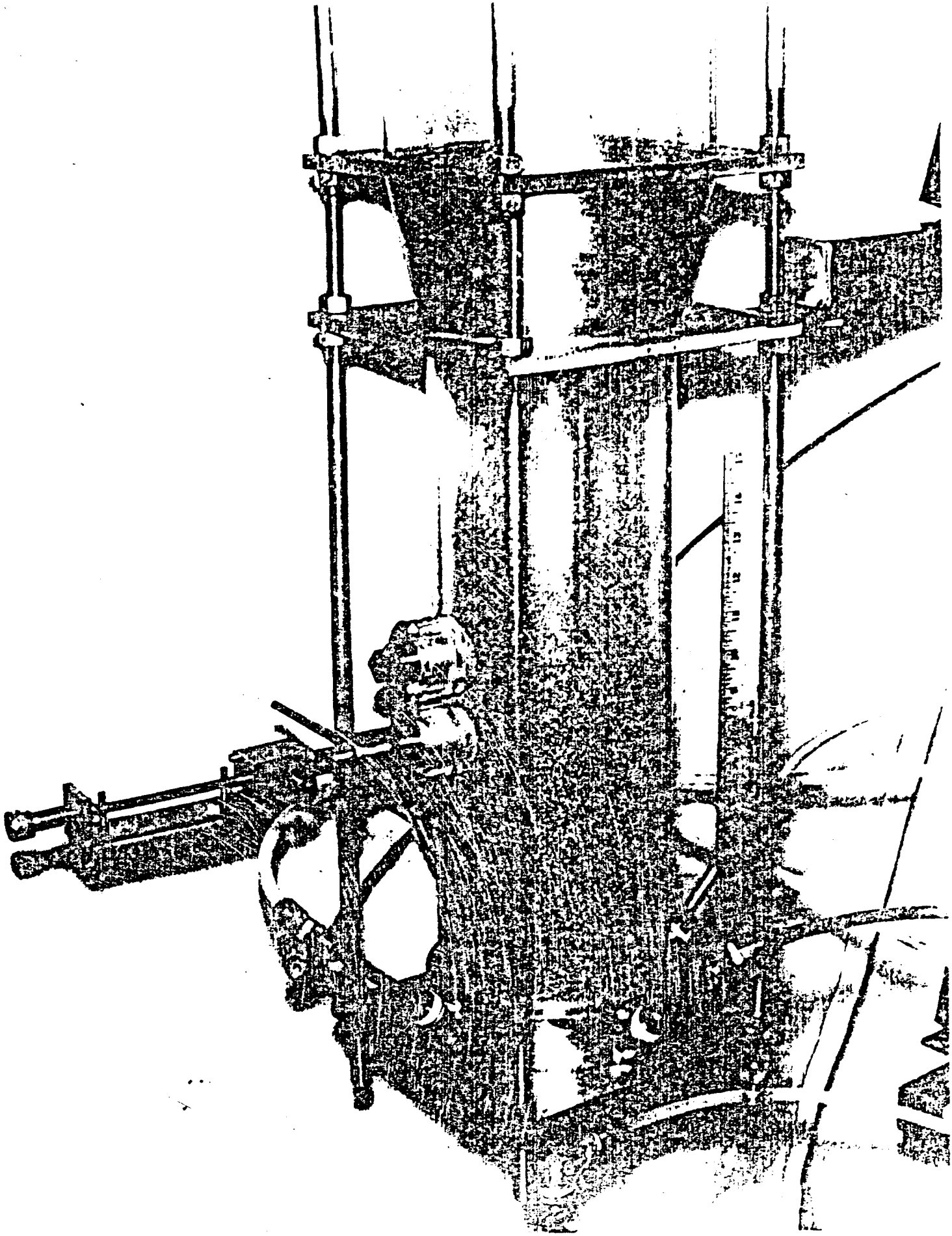
PROCESS FLOWSHEET





KEY PROCESS CONSIDERATIONS:

- HIGH pH PRECIPITATION
- HEAT TRANSFER IN CALCINER
- AMMONIUM NITRATE DISPOSAL



Slide 10

ACCOMPLISHMENTS

PRODUCTION SCALE THROUGHPUT OF 100 KG U/DAY/LINE WAS ATTAINED

URANIUM OXIDE SAMPLES WERE COLLECTED FOR ANALYSIS

AREAS FOR PROCESS IMPROVEMENT HAVE BEEN IDENTIFIED:

- SLURRY PUMPING
- HEAT TRANSFER
- PRODUCT COLLECTION

REFERENCES

DP-CFP-79-121	COPROCESSING PLANT DESIGN
DP-1571 (IN PRINT)	PILOT PLANT DESCRIPTION