GEFR-SP 168
CONF-791103--45
DATE October 19, 1979

TITLE: COPRECAL: Co-conversion of Pu, U Mixed Nitrate to Mixed Oxide

AUTHORS: C. B. Kincaid, E. A. Aitken, I. N. Taylor, D. C. Wadekamper, J. J. Zimmer

Prepared for presentation at:

ANS Winter Meeting
Conference

Held in: San Francisco, CA
City, State

on: November 15, 1979
Date

This paper contains material resulting from work performed for: Department of Energy

Under Contract No. DE-AT03-76SF71026

Under DA task 26

GENERAL ELECTRIC

ADVANCED REACTOR SYSTEMS DEPARTMENT

SUNNYVALE, CALIFORNIA

COPRECAL: Co-Conversion Of Pu, U Mixed Nitrate To Mixed Oxide

By

C. B. Kincaid
E. A. Aitken
I. N. Taylor
D. C. Wadekamper
J. J. Zimmer

General Electric Company
Vallecitos Nuclear Center
Pleasanton, California

1979 Winter American Nuclear Society Meeting
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COPRECAL: Co-Conversion of Pu, U Mixed Nitrate to Mixed Oxide

Every fuel cycle that uses aqueous processes to recover fuel requires a process step to convert the aqueous recovered fuel stream to an oxide powder prior to fabrication into new fuel elements. This paper describes DOE-sponsored research and development of a particular conversion process and equipment system in the Advanced Fuels Laboratory at General Electric's Vallecitos Nuclear Center in Pleasanton, California.

The process has been given the acroynm COPRECAL which stands for coprecipitation and calcination. The process involves the coprecipitation of a nitric acid solution of uranium and plutonium with ammonium hydroxide and subsequent calcination to the mixed oxide powder. While conversion can also be accomplished by precipitation with such agents as oxalic acid and hydrogen peroxide or by direct denitration, COPRECAL development has focused on co-conversion of uranium and plutonium with ammonium hydroxide because of its well-established behavior and the uniformity of its product.

The COPRECAL system currently in use is designed to produce 500 grams of mixed oxide per hour. It is shown schematically in Figure 1. Note that no filtration or centrifugation of the slurry takes place, but rather that the process entails direct slurry calcination. The mixed oxide and offgas from the calciner flow to a powder collector where the mixed oxide is de-entrained. This product mixed oxide is then batch-reduced, stabilized, and forwarded to a fuel fabrication line.

The main aspects of the COPRECAL process include:

1) controlled precipitation
2) slurry calcination
3) reduction/stabilization

Precipitation

The precipitation process is carried out in a continuous flow stirred tank reactor. The precipitation reactions are as follows:

1) $Pu(NO_3)_4 + 4NH_4OH \rightarrow Pu(OH)_4 + 4NH_4NO_3$
2) $3UO_2(NO_3)_2 + 7NH_4OH + H_2O \rightarrow (UO_3)_3 \cdot NH_3 \cdot 5H_2O + 6NH_4NO_3$
3) $HNO_3 + NH_4OH \rightarrow NH_4NO_3 + H_2O$

Precipitation is accomplished using the "reverse strike" method, wherein mixed nitrate solution is initially added to a pool of ammonium hydroxide. Both nitrate and hydroxide are then continuously added to assure that precipitation always takes place at high pH. Conventional co-precipitation is carried out within a specific narrow pH band to insure precipitate filterability and to prevent preferential precipitation (see Figure 2). The COPRECAL process eliminates need for this tight control in that co-precipitation is carried out at pH's above the filterability band, and eliminates the need for filtration since the precipitated slurry is pumped directly into a fluidized bed where it is calcined to the oxide. Further incentive exists for avoiding the conventional filterability pH band in that slurry of smaller precipitate crystals is more easily pumped than is a slurry of larger "filterable" crystals.

Calcination

The fluidized bed calciner is an electrically-heated unit utilizing an elutriative inert bed of Inconel shot. Advantages of the inert bed include:

- No particle growth (uniform product)
- Low in-bed inventory
- Constant bed volume
- Readily drained for inventory
- Low scrap generation at enrichment or Pu/(Pu+U) change

A jet grinder is installed in the bed area to aid in minimizing the buildup of mixed oxide in the bed. Pre-heated nitrogen is used as feed for the jet grinder and also serves as the fluidizing gas. The calciner is heated internally and externally and will operate at bed temperatures up to 700°C. The calciner is shown schematically in Figure 3.

The calcination of slurry to the oxide is carried out per the following generalized reactions:

4) $Pu(OH)_4 \rightarrow PuO_2 + H_2O$

5) $(UO_3)_3 \cdot NH_3 \cdot 5H_2O \rightarrow 3UO_3 + NH_3 + 5H_2O$

6) $2NH_4NO_3 \rightarrow 2N_2 + 6H_2O + O_2$

7) $4NH_4OH + 3O_2 \rightarrow 2N_2 + 10H_2O$

Note that reaction 6 shows both N_2 and O_2 as products. To minimize the formation of nitrogen oxides, the calcination is carried out in an inert atmosphere with a sufficient excess of ammonium hydroxide in the slurry to consume the oxygen produced (reaction #7).

Reduction/Stabilization

The mixed oxide product from the calciner is processed in a reduction/stabilization step to produce ceramic-grade mixed oxide which will meet all pellet fuel fabrication requirements. This process reduces the UO_3 portion of the mixed oxide calciner product to UO_2. The UO_2 is then reoxidized slightly (stabilized). Typical reduction and stabilization temperatures range from 700 to 800°C. Equations 8 and 9 illustrate the reactions observed during this process.

8) $UO_3 + H_2 \rightarrow UO_2 + H_2O$

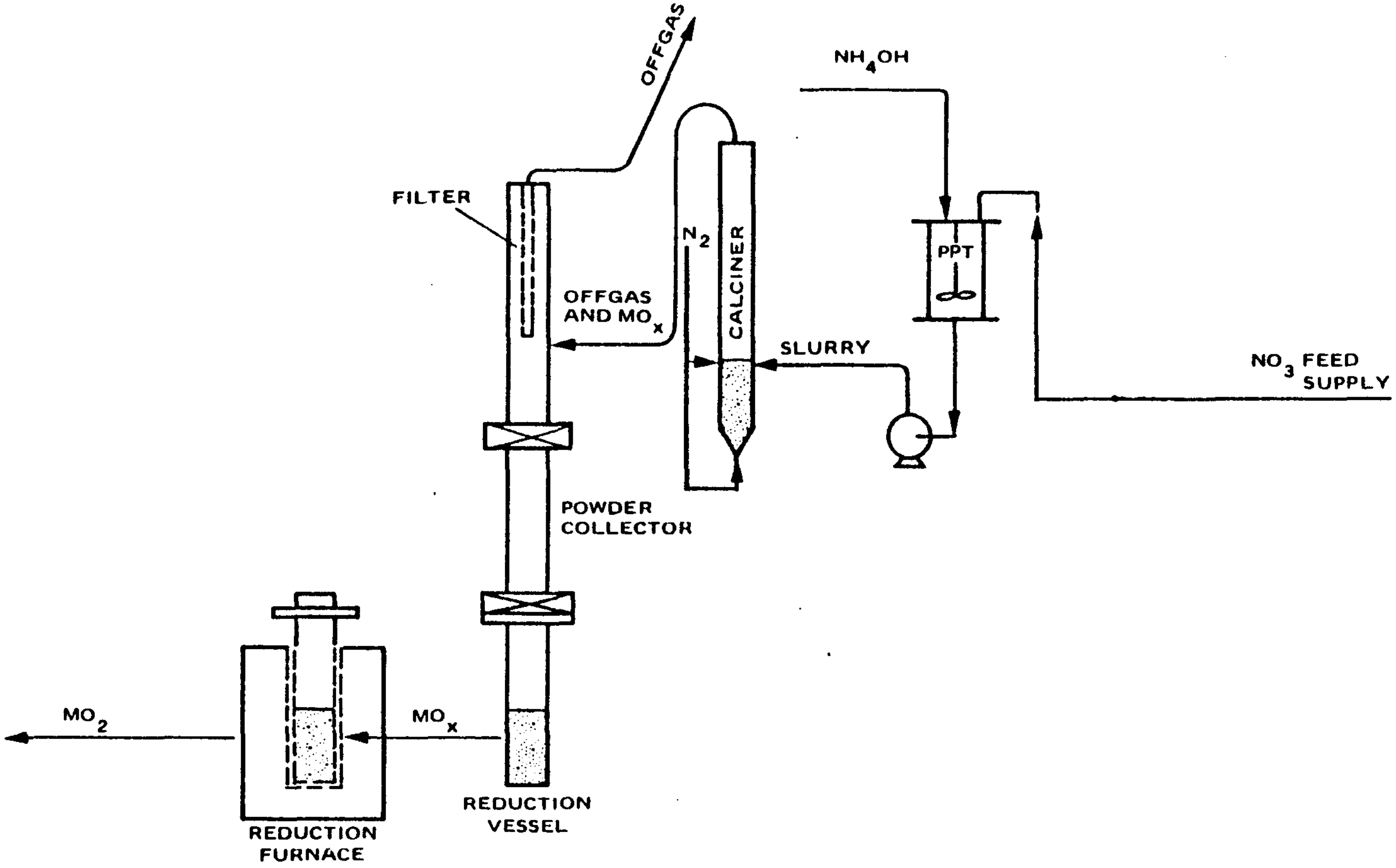
9) $2UO_2 + xO_2 \rightarrow 2UO_{2+x}$

Hydrogen is supplied for reduction in a non-explosive mixture of 6% H_2-94% inert gas. The stabilization portion of the process is accomplished by contacting the powder with CO_2 while the powder is still at the reduction temperature. The CO_2 thermally dissociates to a very slight extent, producing oxygen which is adsorbed by the UO_2 to produce UO_{2+x}. If this stabilization is not performed, the UO_2 may, upon exposure to air, rapidly oxidize to U_3O_8, rendering the mixed oxide unsuitable for fuel fabrication.

Accomplishments To Date

Approximately 35 Kg of COPRECAL mixed oxide have been produced. Of this total, 26 Kg contained 20% Pu based on total metal and 9 Kg contained 30% Pu. Testing has produced the following results:

- Sintered pellet density - >95% TD
- Sintered pellet integrity - excellent
- Plutonium homogeneity - > the FFTF figure of merit requirement of 0.96
- Nitric acid solubility - 100%



-COPRECAL EQUIPMENT SYSTEM-

PRECIPITATION, CALCINATION, REDUCTION

Figure 1

URANIUM-PLUTONIUM COPRECIPITATION CURVES

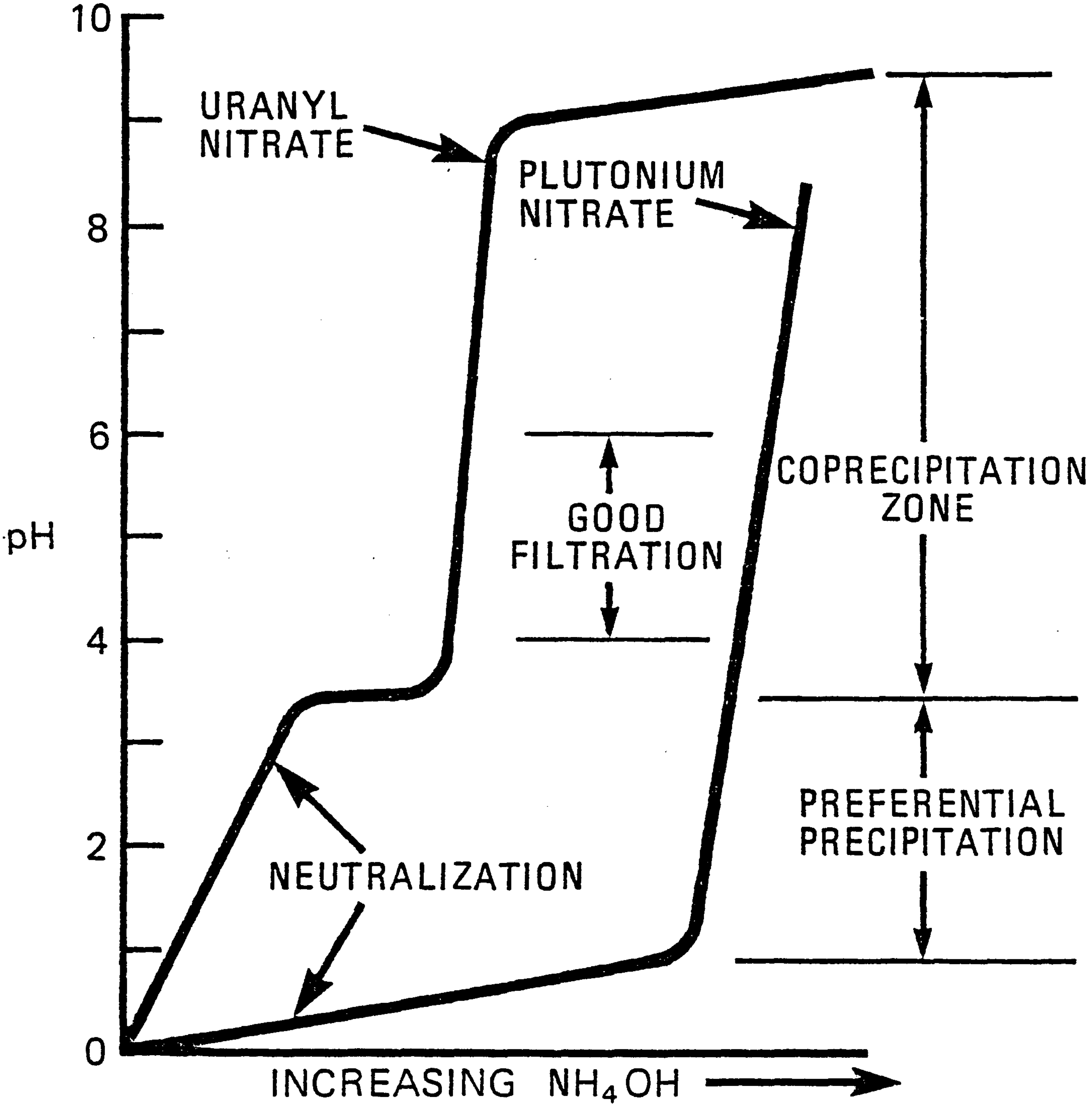
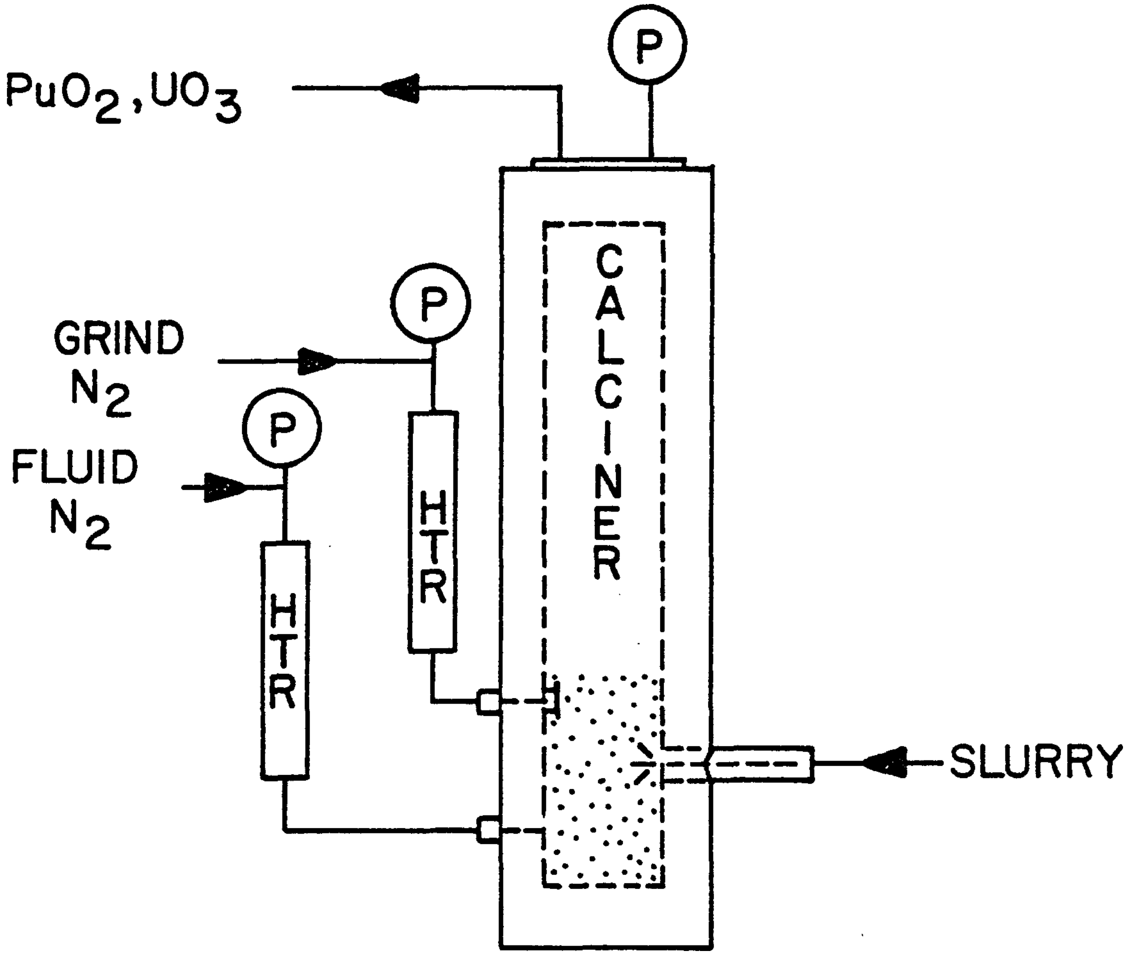


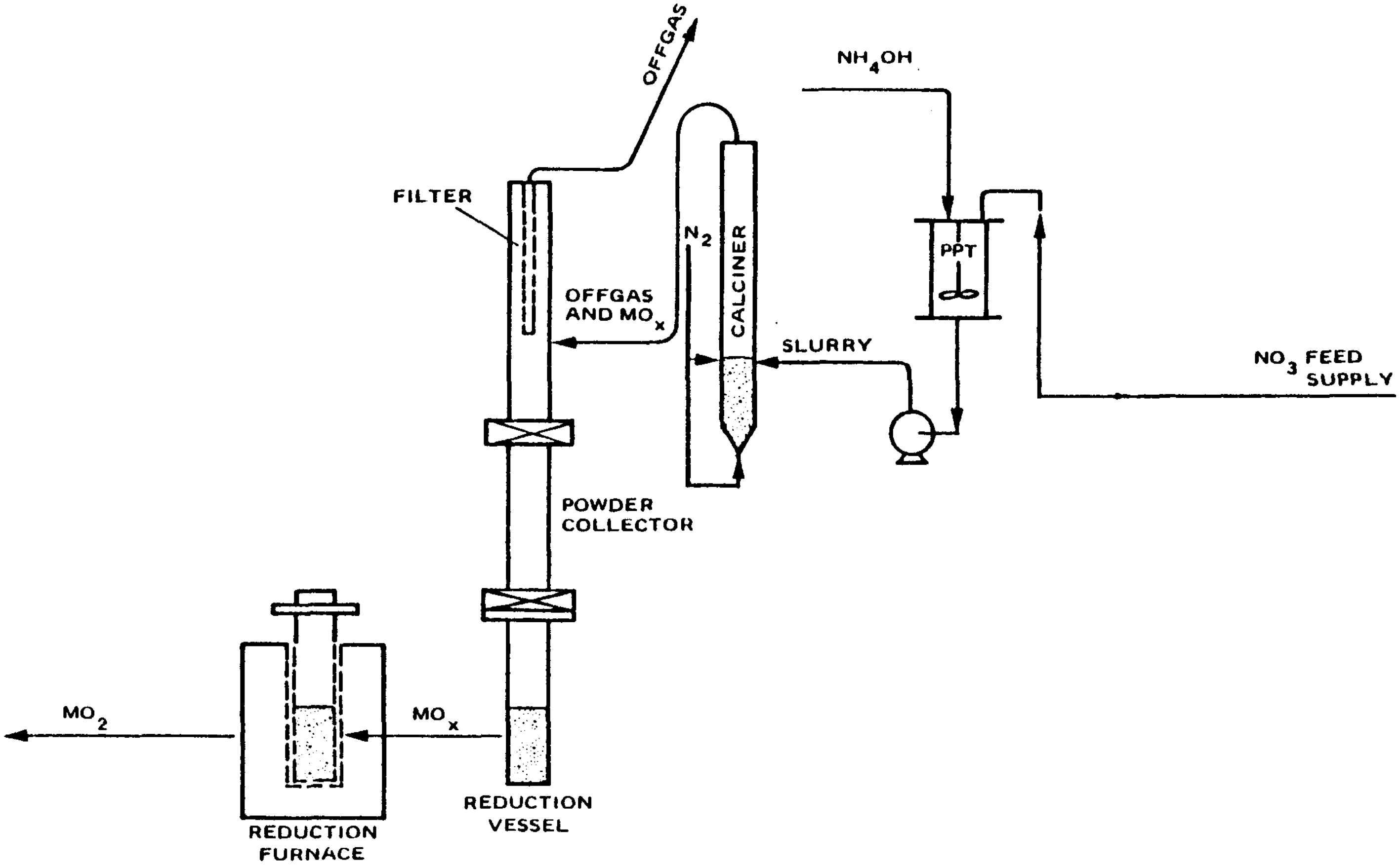
Figure 2



-COPRECAL CALCINER-

Figure 3

Slide #1



-COPRECAL EQUIPMENT SYSTEM-

PRECIPITATION, CALCINATION, REDUCTION

COPRECAL PROCESS

- CONTROLLED PRECIPITATION
- SLURRY CALCINATION
- REDUCTION/STABILIZATION

Slide #2

Slide #3

COPRECAL PRECIPITATION REACTIONS

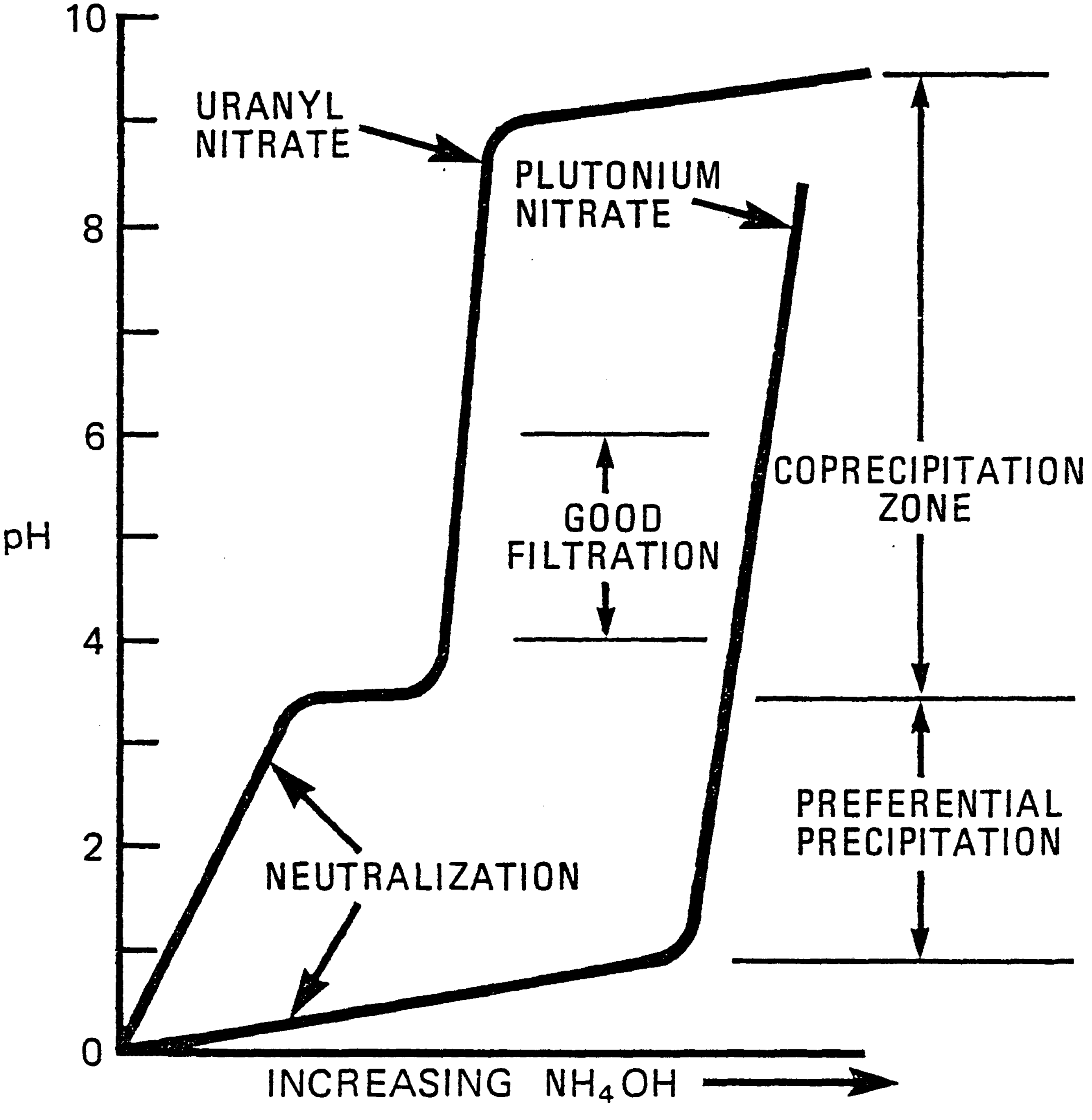
1) $Pu(NO_3)_4 + 4NH_4OH \rightarrow Pu(OH)_4 + 4NH_4NO_3$

2) $3UO_2(NO_3)_2 + 7NH_4OH + H_2O \rightarrow (UO_3)_3 \cdot NH_3 \cdot 5H_2O + 6NH_4NO_3$

3) $HNO_3 + NH_4OH \rightarrow NH_4NO_3 + H_2O$

Slide #4

URANIUM-PLUTONIUM COPRECIPITATION CURVES

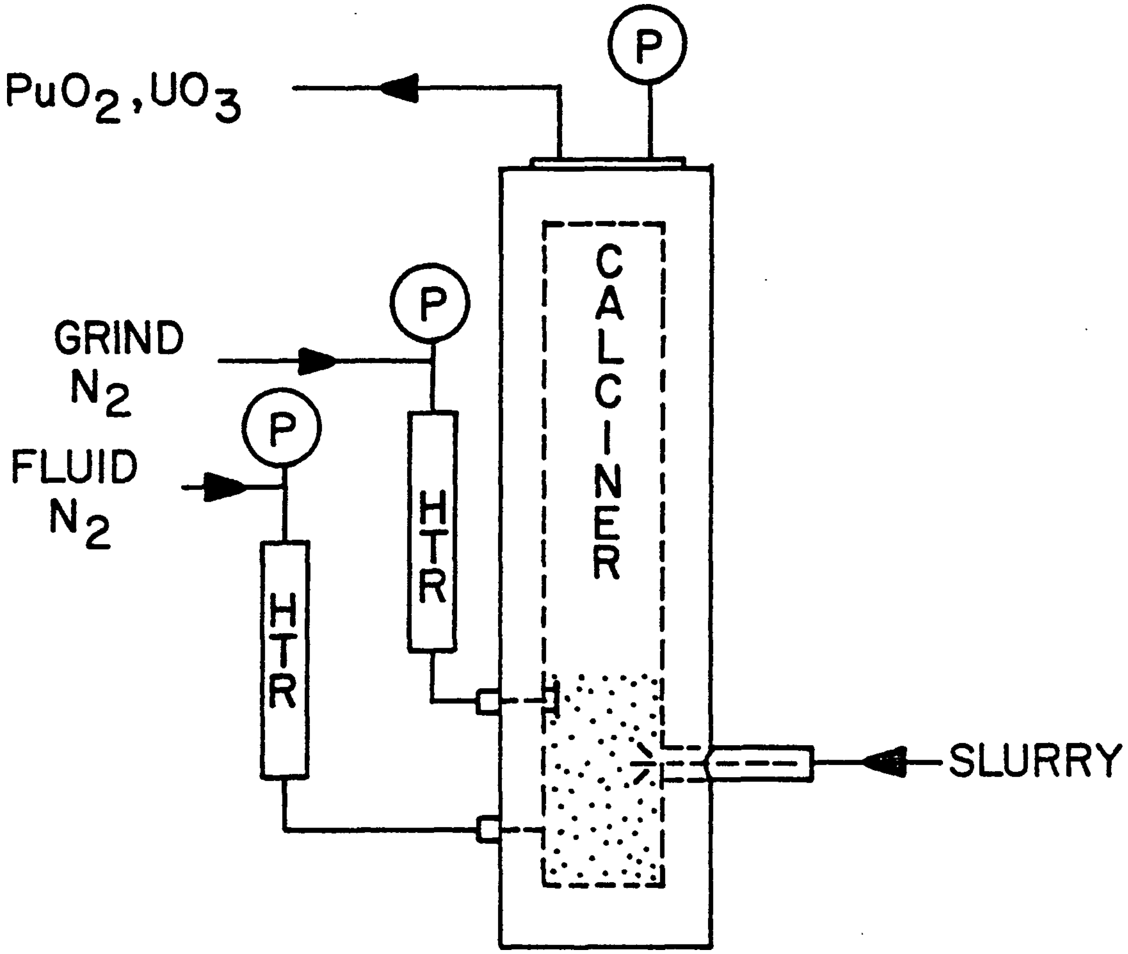


Slide #5

ADVANTAGES OF COPRECAL INERT BED

- NO PARTICLE GROWTH (UNIFORM PRODUCT)
- LOW IN-BED INVENTORY
- CONSTANT BED VOLUME
- READILY DRAINED FOR INVENTORY
- LOW SCRAP GENERATION AT ENRICHMENT OR Pu/(Pu+U) CHANGE

Slide #6



-COPRECAL CALCINER-

Slide #7

COPRECAL CALCINATION REACTIONS

1) $Pu(OH)_4 \rightarrow PuO_2 + H_2O$

2) $(UO_3)_3 \cdot NH_3 \cdot 5H_2O \rightarrow 3UO_3 + NH_3 + 5H_2O$

3) $2NH_4NO_3 \rightarrow 2N_2 + 6H_2O + O_2$

4) $4NH_4OH + 3O_2 \rightarrow 2N_2 + 10H_2O$

Slide #8

COPRECAL REDUCTION REACTIONS

1) $UO_3 + H_2 \rightarrow UO_2 + H_2O$

2) $2UO_2 + xO_2 \rightarrow 2UO_{2+x}$

COPRECAL TEST RESULTS

- SINTERED PELLET DENSITY —> 95% TD
- SINTERED PELLET INTEGRITY — EXCELLENT
- PLUTONIUM HOMOGENEITY > FFTF FIGURE OF MERIT REQUIREMENT OF 0.96
- NITRIC ACID SOLUBILITY — 100%