TECHNICAL DEVELOPMENT OF THE COPRECAL (COPRECIPITATION-CALCINATION) CO-CONVERSION PROCESS

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GENERAL ELECTRIC

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Technical Development of the COPRECAL (Coprecipitation-Calcination) Co-Conversion Process

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 the GE/DOE-sponsored research and development of a particular conversion process and equipment system at General Electric's Vallecitos Nuclear Center in Pleasanton, California. It will include both the initial development, using only uranium as the heavy metal, and the subsequent tests with a mixed feed of uranium and plutonium.

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 in this equipment system can also be accomplished by precipitation with such agents as oxalic acid and hydrogen peroxide or by direct denitration, COPRECAL development to date 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 under development 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 calcination of a concentrated but pumpable slurry in an elutritative fluid-bed. 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) $3UO_2(NO_3)_2 + 7NH_4OH + H_2O \rightarrow (UO_3)_3 \cdot NH_3 \cdot 5H_2O + 6NH_4NO_3$

or $2UO_2(NO_3)_2 + 5NH_4OH \rightarrow (UO_3)_2 \cdot NH_3 \cdot 3H_2O\ 4NH_4NO_3$

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 the specific narrow pH band which insures precipitate filterability, yet prevents 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.

Calcination

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

- High heat transfer rate
- 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

An in-bed jet grinder is utilized to aid in minimizing the buildup of mixed oxide in the bed. Pre-heated nitrogen is used as the fluidizing gas and motive medium for the jet grinder. 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.

In the calcination of slurry to the oxide, following generalized reactions predominate:

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

5) $(UO_3)_3 \cdot NH_3 \cdot 5H_2O \rightarrow 3UO_3 + NH_4OH + 4H_2O$

6) $2NH_4NO_3 \rightarrow 2N_2 + 4H_2O + O_2$

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

Note that Reactions 6 and 7 can be combined into a single thermal redox reaction:

8) $3NH_4NO_3 + 2NH_4OH \rightarrow 4N_2 + 11H_2O$

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 stoichiometrically effect the redox reaction (Reaction #8).

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 9 and 10 illustrate the reactions observed during this process.

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

10) $2UO_2 + xO_2 \rightarrow 2UO_{2+x}$

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.

Process Concept and Development with Uranium Only

Working with plutonium is tedious and time consuming because of the constraints of in-glove box operation. To defer this problem as long as possible, the mechanical/chemical feasibility of the concept was established and major problems were solved, in a development program in which the heavy metal used was uranium only. The final process model thus developed was then essentially duplicated and installed in the Advanced Fuels Laboratory glove boxes for final testing with a plutonium/uranium mixture. A photograph of the last (Mark 3) uranium only process system is shown in Figure 4. Some of the major concepts and problems encountered during this "uranium only" stage of development and the solutions arrived at are as follows:

Concept	Problem	Solution
Direct Denitration of Uranyl Nitrate, Acid	Poor powder quality low sintered density), NO_x Off-Gases	Pre-precipitation with ammonia
Slurry-bead Contact	Adherence to beads	Internal Jet Grinder
Inert bed-powder elutriation	Bead elutriation with product	Increased size, density difference between bead and product. Baffle, screens
Thermal demand	Inadequate through walls only, bed caking	Internal rod heaters High slurry concentration Exothermic chemical reaction
Mechanical problem	Nozzle plugging	High exit velocity, crucial bead/nozzle diameter ratio
Ammonia-air oxidation	Excess temperature excursions	Exclude air-use nitrogen as process gas

While a mechanically operable process was achieved with direct denitration, the powder quality was so poor that this approach was abandoned in favor of the precipitation technique in which the ultimate particle size (and hence sintered density) is established and retained through the subsequent calcination process. For example, the best results obtained with direct denitration in terms of sintered density was ca. 75% of theoretical; in contrast, under comparable test conditions, the precipitated product was in the desired 95% range. Photomicrographs of the respective UO_3 powders (Figure 5) at 10,000X indicate the reason for this very significant difference.

While techniques have been developed for adequate scrubbing of NO_x off gases emanating from a direct denitration process, the problem was essentially eliminated by taking advantage of the nitrate destruct reaction shown previously. The thermal oxidation-reduction reaction between ammoniacal nitrogen (-3 valence) and the nitrate nitrogen (+5) at proper stoichiometric ratios results in the formation of the more friendly molecular N_2 and water. The slight excess of ammonia can, if desired, be easily removed from the condensate by simple steam stripping for recycle. Additionally, the exothermic chemical reaction reduced the net heat demand on the calciner.

The buildup of calcined oxide on the inert bed Inconel beads was successfully controlled by the use of an internal jet grinder. The quality of the ground off powder was not adversely affected since the inherent surface area was fixed in the preceding precipitation process step. Sufficient powder remained adhering to the beads to prevent significant metal grinding.

Bead elutriation with the powder product turned out to be one of the toughest to solve. It is a purely mechanical problem which was solved through a combination of bed particle size control (minimum size), internal baffles and final screening of the collected powder. An internal (to the calciner) non-plugging "Johnson screen" was obtained but not tested in the Advanced Reactor Laboratory system.

To ensure complete calcination and thus avoid bed caking, thermal demand must obviously not exceed heat availability. An adequate capacity rate of 0.5 kg/hr was attained and exceeded through the use of 4-1 kw electric heaters, mounted vertically from the bottom; heavy metal concentration in the slurry was ca 300 g/l.

As indicated in the slide, nozzle plugging was eliminated through the technique of keeping the exit velocity high (nitrogen injection upstream of the nozzle) which prevented precalcination in the nozzle, and bead backup by using a sufficiently low nozzle/bead diameter ratio.

The potential for a temperature excursion due to ammonia oxidation was eliminated through the substitution of nitrogen for air as the process gas.

Accomplishments To Date with Mixed Oxide System

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.

Two major differences between COPRECAL uranium and mixed oxides became apparent when uranium-plutonium testing began:

1) Mixed oxide is more active than uranium oxide

2) Unreduced mixed oxide is more screenable than UO_3

When the mixed metal COPRECAL system was installed, a pure uranium stream was processed to verify process repeatability. The UO_3 product was calcined at $\simeq$ 400°C and reduced to UO_2 at $\simeq$ 500-550°C. When 20% Pu was processed the calcination and reduction temperatures were raised as high as 700°C and 900°C, respectively to achieve successful powder stabilization after reduction.

Screening of UO_3 before reduction to UO_2 proved impractical - it would not flow through the screen. Unreduced mixed oxide, on the other hand, flowed quite readily through a 150-mesh screen.

Mixed oxide testing has produced the following results:

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

The sintered pellet density is reported as "> 95% TD" rather than as an average value because each batch of mixed oxide powder was made under different parametric conditions. No parametric optimization has been attempted to date; rather, the testing conducted with Pu, U mixed nitrate feed has been designed specifically to only identify those parameters having the greatest effect on sintered pellet quality. In general, the sintered pellet densities encountered ranged from ≃ 92% to ≃ 95% TD.

The integrity of the sintered pellets was very good. No end capping, chipping, flaking, or cracking was observed.

Examination of the alpha autoradiographs (dark areas represent high plutonium concentrations) prepared from four different lots of COPRECAL powder revealed that the material contained a very uniform distribution of plutonium, see Figure 6 for a typical example. Comparison of these alpha autoradiographs with the FFTF figure of merit (FM) standards referenced in RDT Standard F11-5T, Determination of Fuel Pellet Homogeneity by Alpha Autoradiography, indicated the COPRECAL pellets exhibited an FM value in excess of the most homogeneous standard (FM = 0.999), see Figure 7. Since the minimum acceptable FM value for the FFTF reactor is 0.96 (see Figure 8 for a standard in which the FM = 0.963), the COPRECAL material very easily surpassed the current homogeneity criteria for a breeder reactor.

A major advantage of the COPRECAL process is that the mixed oxide product, both sintered and unsintered, is completely soluble in nitric acid. No fluorides are required. Figures 9 and 10 are plots of dissolution time vs nitric acid concentration for 20% Pu and 30% Pu COPRECAL powder. Note that the material in all cases proved to be soluble within 8 hours (240 minutes) in strong nitric acid.

Future Plans for Development and Application

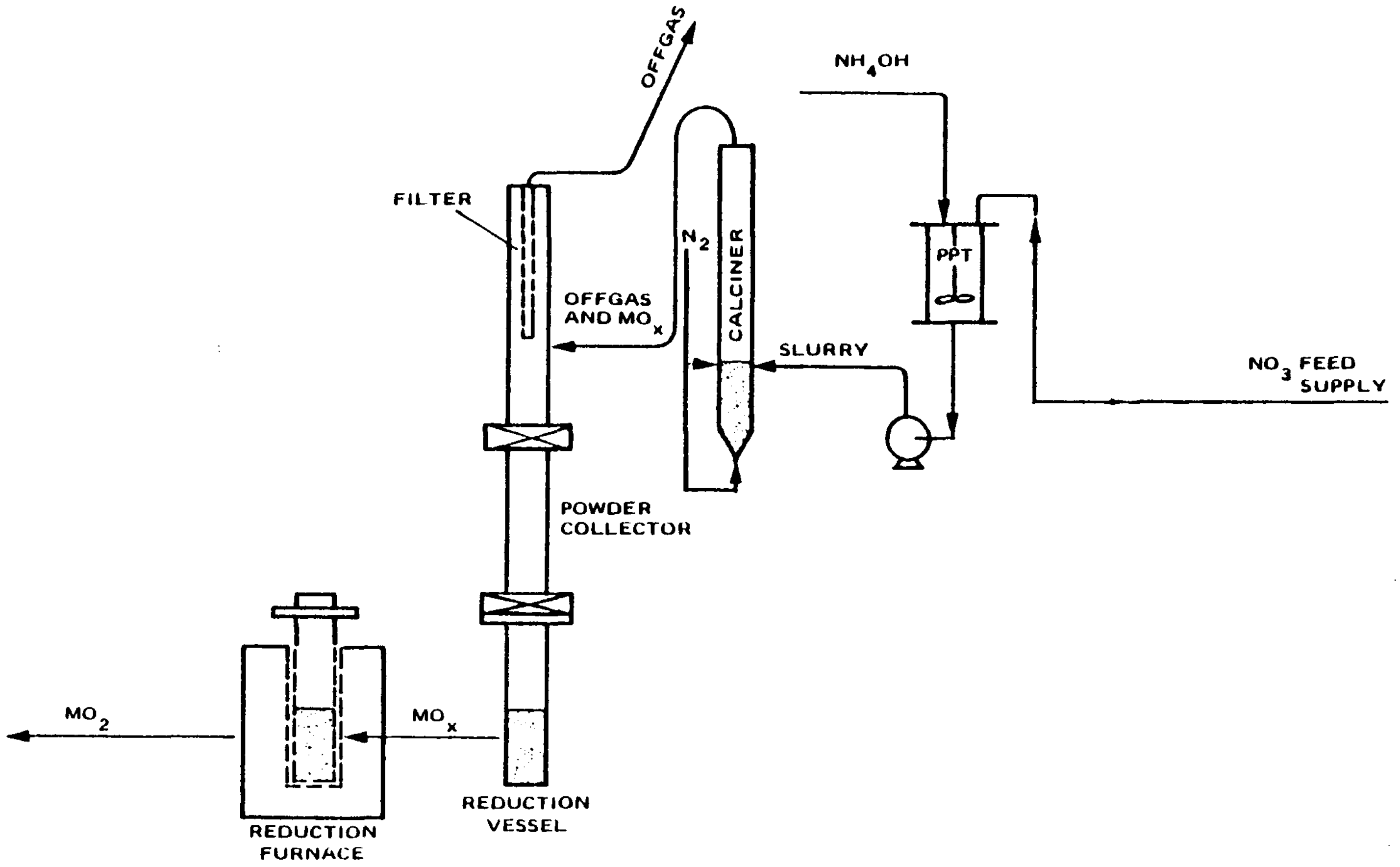
The foregoing has presented a summary description of the COPRECAL process, a brief history of the development and the present state-of-the-art. What of the future?

Another advantage of the process, not addressed previously, is its ameniability to measures which enhance potential resistance to the diversion of plutonium. These potential security techniques, which range from simple dilution of the fissile plutonium with uranium, to high gamma spiking, were addressed by Buckham at the San Francisco meeting in November 1979. It seems logical that in the present energy and political climate, the potential advantages should be pursued.

General Electric has evaluated and recommended further technical development options and plans for scale-up. Based on technical information provided by us, scale-up experiments are successfully under way at the Savannah River laboratories. COPRECAL has also been identified as the reference process for implementation into the HEDL scrap recovery facility.

The most fruitful technical process improvements appear to be (a) the development of a continuous reduction process step to replace the current batch-wise operation, (b) testing of an on-line "Johnson screen" for bead retention in the calciner, and (c) further development of calciner heating to increase throughput.

COPRECAL also appears to be a very feasible method for processing of ammonium nitrate-containing wastes such as those generated by the Sol-Gel process. General Electric has recently received serious inquiries from the Swiss, Italians, Belgians, and Japanese as to possible assistance for both mixed oxide production and nitrate waste destruction.



-COPRECAL EQUIPMENT SYSTEM-

PRECIPITATION, CALCINATION, REDUCTION

Fig. 1

URANIUM-PLUTONIUM COPRECIPITATION CURVES

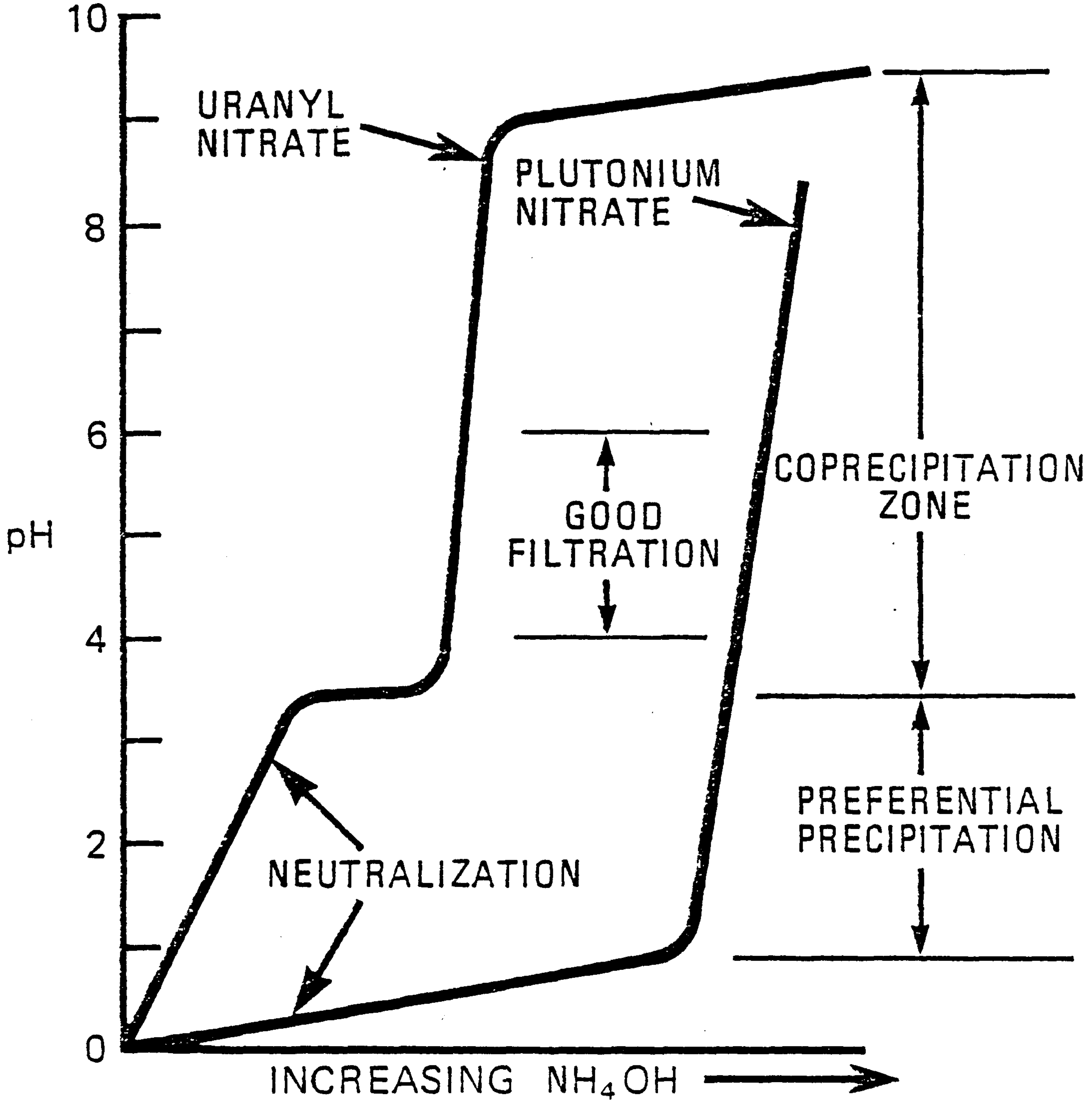
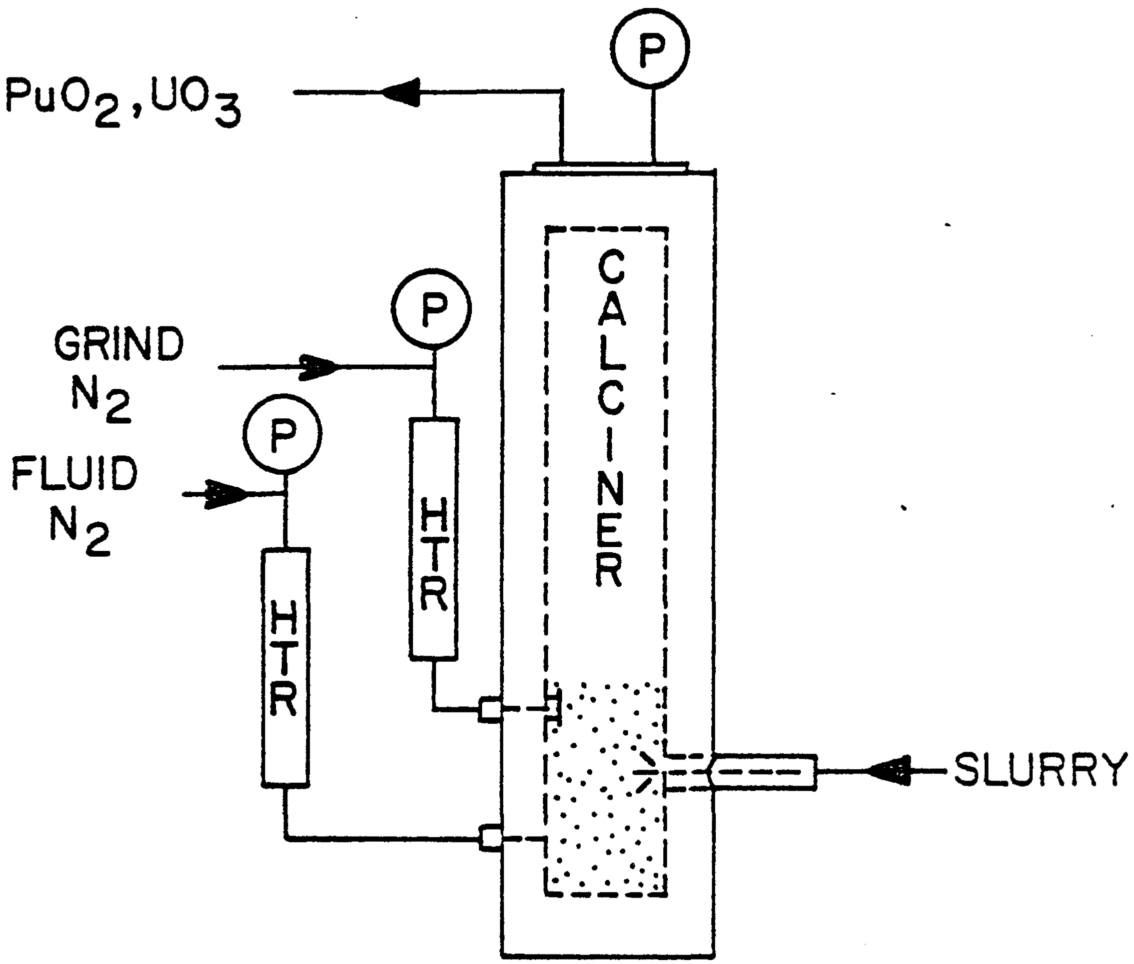


Fig. 2



-COPRECAL CALCINER-

Fig. 3

"URANIUM PROCESS SYSTEM"

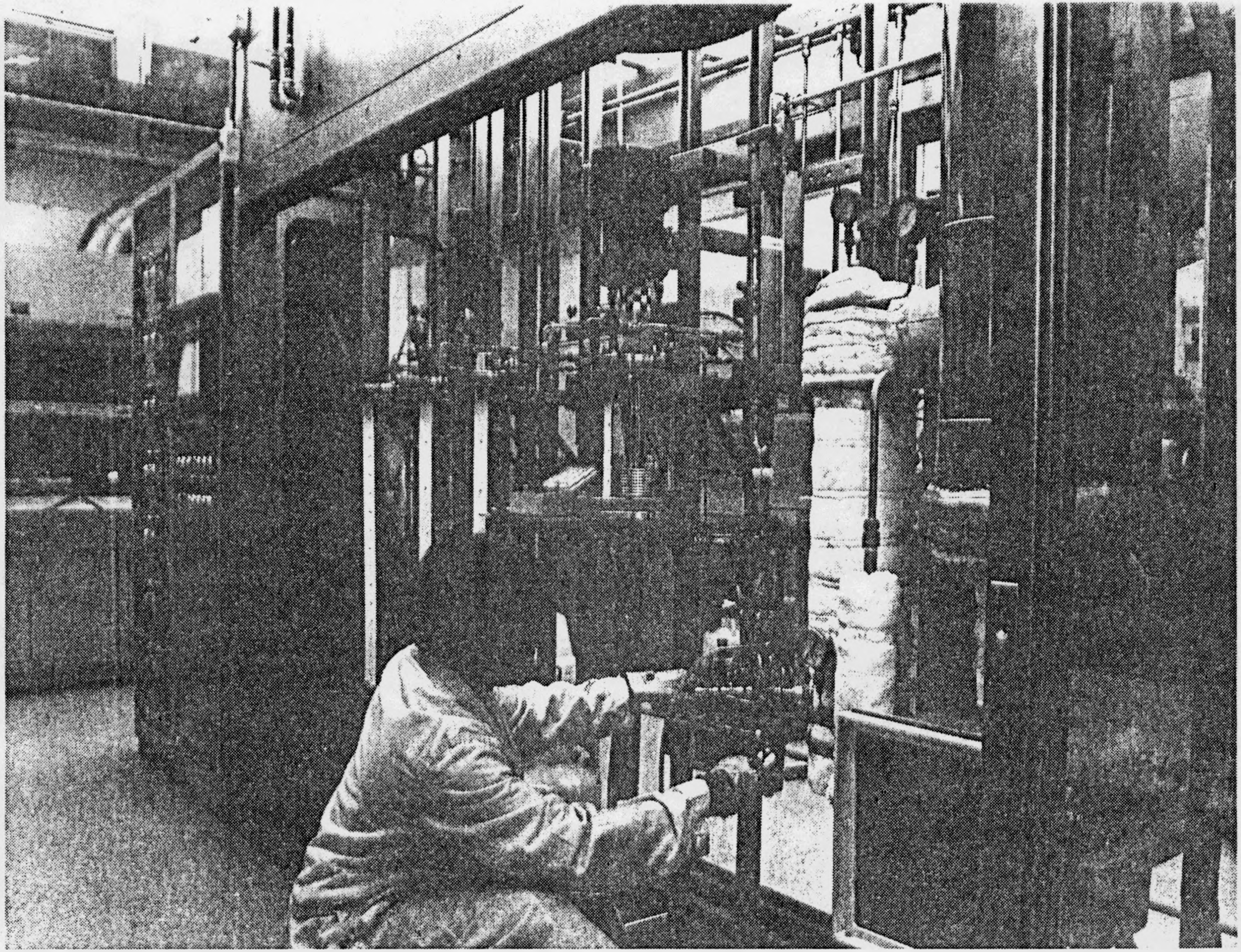
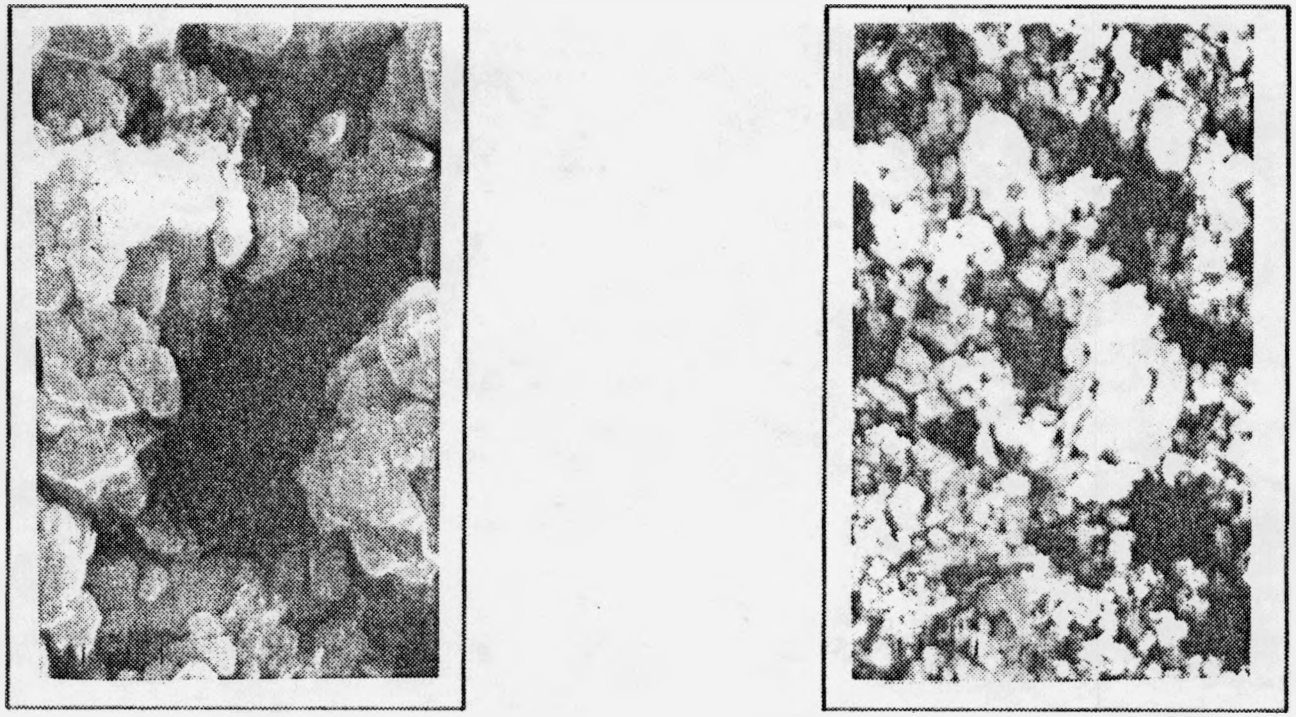


Fig. 4

UO_3 PHOTOMICROGRAPHS

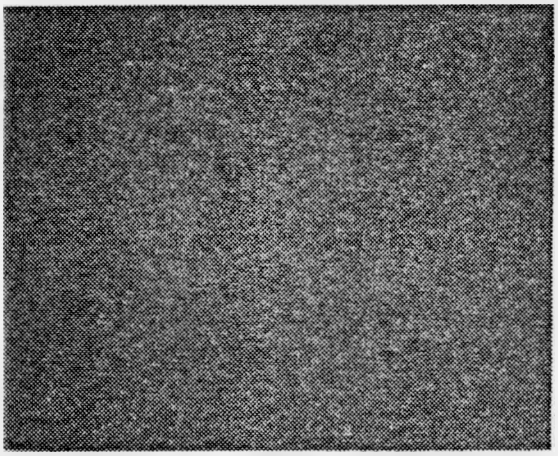


UO_3 CALCINED
FROM UNH
MAG. 10,000X

UO_3 CALCINED
FROM ADU
MAG. 10,000X

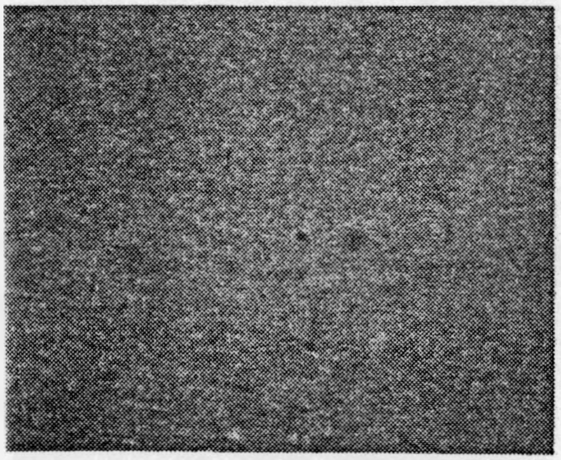
Fig. 5

COPRECAL MIXED OXIDE HOMOGENEITY EVALUATION



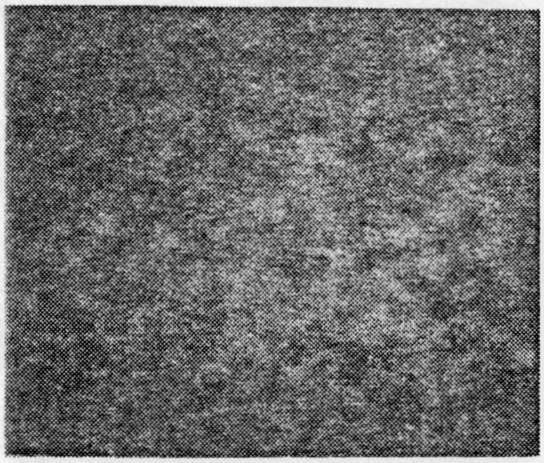
COPRECAL Powder Lot B0719 (100X)

Fig. 6



FM = 0.999

Fig. 7



FM = 0.963

Fig. 8

FFTF STANDARDS (100X)

20% Pu - MO_2 DISSOLUTION

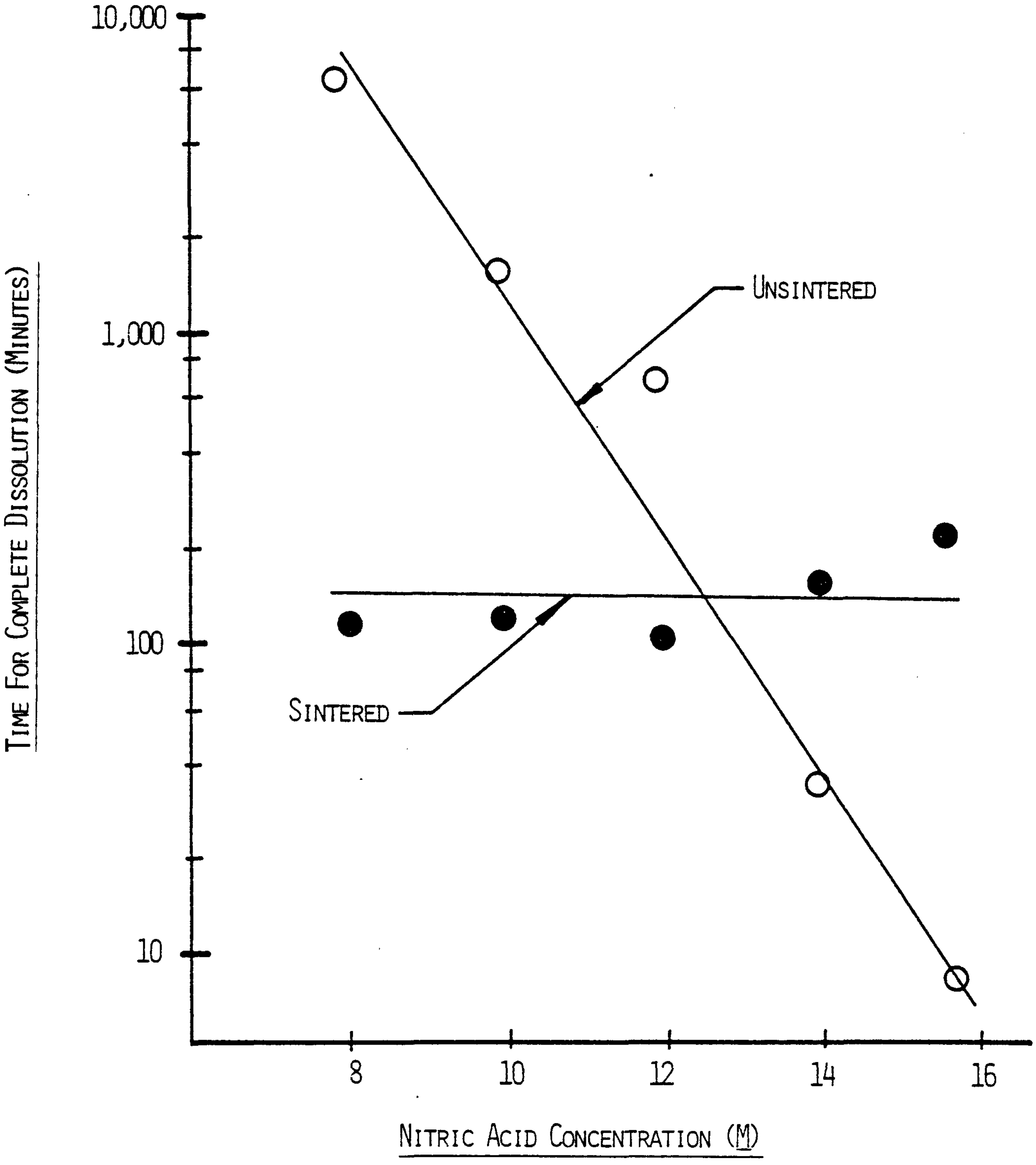


Fig. 9

30% Pu - MO$_2$ DISSOLUTION

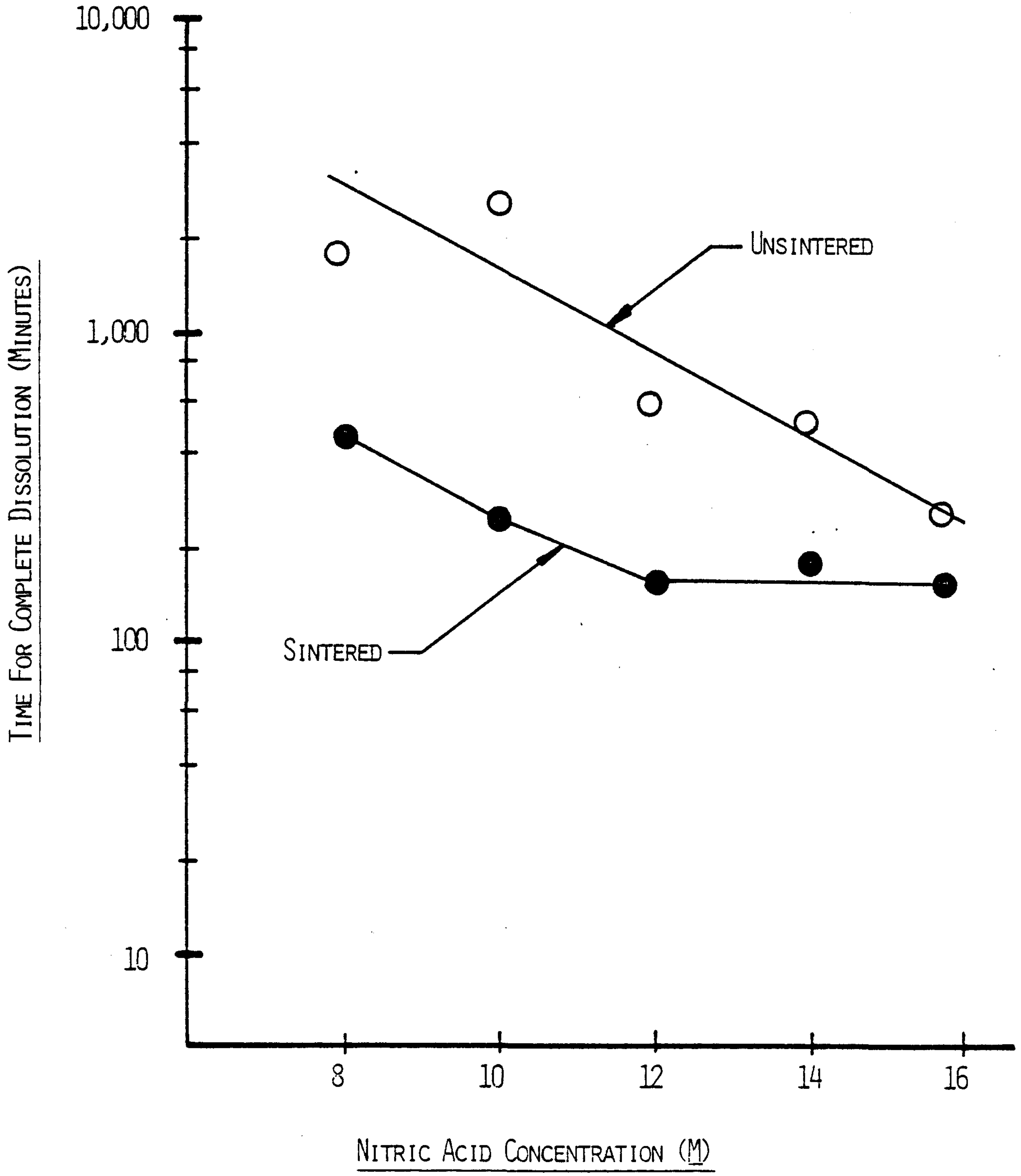


Fig. 10