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PILOT PLANT PREPARATION OF  
THORIUM- AND THORIUM-URANIUM OXIDES

K. O. Johnsson  
R. H. Winget

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ORNL-2853

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

Pilot Plant Section

PILOT PLANT PREPARATION OF  
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DATE ISSUED

DEC 8 1959

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ABSTRACT

Thorium oxide and thorium-uranium oxides are being prepared by the Oak Ridge National Laboratory on a routine basis in 150-lb batches for experimental use. The thorium oxide is formed by the calcination of thorium oxalate precipitated under carefully controlled conditions. Material is produced with mean particle diameters of 1-5  $\mu$ . Some of the thorium oxide has had uranium added to it by decomposing uranyl carbonate on the thorium oxide followed by calcination. Most of the oxides prepared have been calcined to 1000°C or more and size classified to remove particles greater than 10  $\mu$ .

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O.O FOREWORD

The preparation of thorium oxide for use as a slurry extends back many years at the Oak Ridge National Laboratory. The early preparations were strictly on a laboratory scale and were made by J. P. McBride and others. When larger quantities were needed equipment was installed in the Pilot Plant Section of the Chemical Technology Division and operated by W. H. Carr in mid-1954.<sup>1</sup> Operating conditions were changed rather frequently, producing different types of material since at that time a clear picture of what constituted a good oxide was not available. In 1956 operation of the equipment was transferred to E. M. Shank and L. J. King.

Operations were taken over by C. V. Ellison in 1957 and later a regular operating group was established.<sup>2</sup> J. P. McBride and V. D. Allred and later R. L. Pearson in the Chemical Development Section provided most of the information which served as a basis for the operation of the process during this period. In the Unit Operations Section, E. O. Nurmi, W. M. Woods, and W. J. Clossey investigated alternative precipitation methods in their equipment. The Unit Operations Section continued to provide assistance on individual problems as needed and in 1958 assigned K. O. Johnsson to assist full time with the Pilot Plant Section.

After plans were completed for moving the operations to a new building in 1959, C. V. Ellison left the Laboratory and R. H. Winget assumed responsibility for the operation of the new facility.

Undoubtedly many names have been left out of this brief listing but perhaps it will serve to indicate that many individuals have been involved in the development of the process. Certainly, the over-all direction of D. E. Ferguson as Homogeneous Reactor Project problem leader for the Chemical Technology Division and the patience of the members of the Reactor Experimental Engineering Division in realizing that every batch of material produced will not be just what is wanted have both aided those directly engaged in preparing thorium oxide.

## 1.0 INTRODUCTION

This report describes the experimental facility at Oak Ridge National Laboratory for preparing thorium oxide and thorium-uranium oxide mixtures. Several reactors have been proposed utilizing a thorium oxide slurry, or a thorium oxide-uranium oxide mixture, as a blanket material or in a single-region reactor. In considering the use of these slurries the Reactor Experimental Engineering Division has made extensive engineering tests to determine what equipment is needed to handle a slurry and what the physical properties should be for ease of handling. The Pilot Plant Section of the Chemical Technology Division has prepared experimental batches of thorium and thorium-uranium oxides with various physical properties for test by the Reactor Experimental Engineering Division.

Oxides have been prepared in lots of from 100 to 2000 lb in size by an oxalate precipitation method followed by calcination. The average particle size of the product has ranged from a low of  $0.7 \mu$  diameter to as high as  $7.0 \mu$  diameter. The bulk of past production has been a pure thorium oxide; however, oxides have been prepared with a U/Th ratio as low as 0.005 and as high as 0.16. Current production is for the most part a thorium-uranium oxide with a U/Th atomic ratio of 0.03.

## 2.0 BUILDING AND EQUIPMENT

In 1958 it became evident that there would be a continuing need for the preparation of experimental types of thoria and thoria-urania in quantities ranging from 100 to several thousand pounds. The facilities and layout in Building 3019, where the material was being produced in 150-lb batches, were crowded and inefficient, and the physical space occupied was needed for expansion of the equipment for another program. Consequently, a separate building was constructed (Fig. 1) to house the process, Building 2528, and existing equipment was moved intact insofar as practicable so as to reduce the over-all expense. A few necessary equipment additions were made, and the layout (Fig. 2) was made to facilitate operation of the equipment. Tanks were constructed in front of the building for holdup and neutralization of process waste prior to discharge. The building is located immediately east of the X-10 steam plant and south of the Power Reactor Fuel Reprocessing building now under construction.

### 2.1 Ventilation

Since thorium is a long-lived alpha emitter it is particularly dangerous as a biological hazard. From early experiences with oxide production it was found necessary to take all possible precautions to prevent ingestion of thoria by operating personnel. Dry thorium oxide in the 1- to  $10\text{-}\mu$  size range is very dusty and consequently can very easily become air-borne. To reduce the possibility of the spread of contamination, closed tanks are used throughout the process and other pieces of equipment are covered with metal or plastic glove boxes.

As further insurance against air-borne contamination there are three off-gas systems and one filtered exhaust system for the building. The

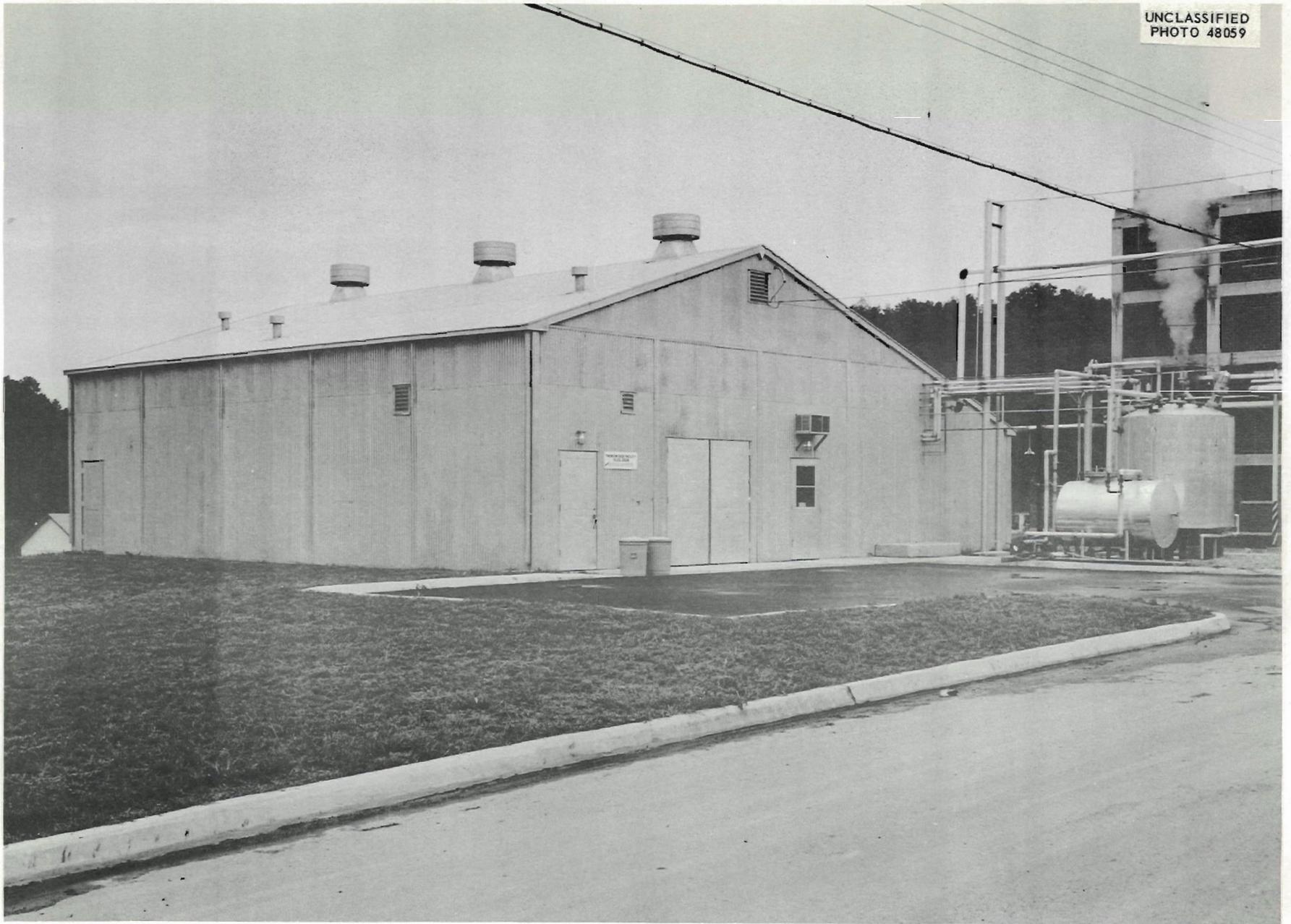


Fig. 1. Thorium Oxide Facility, Building 2528.

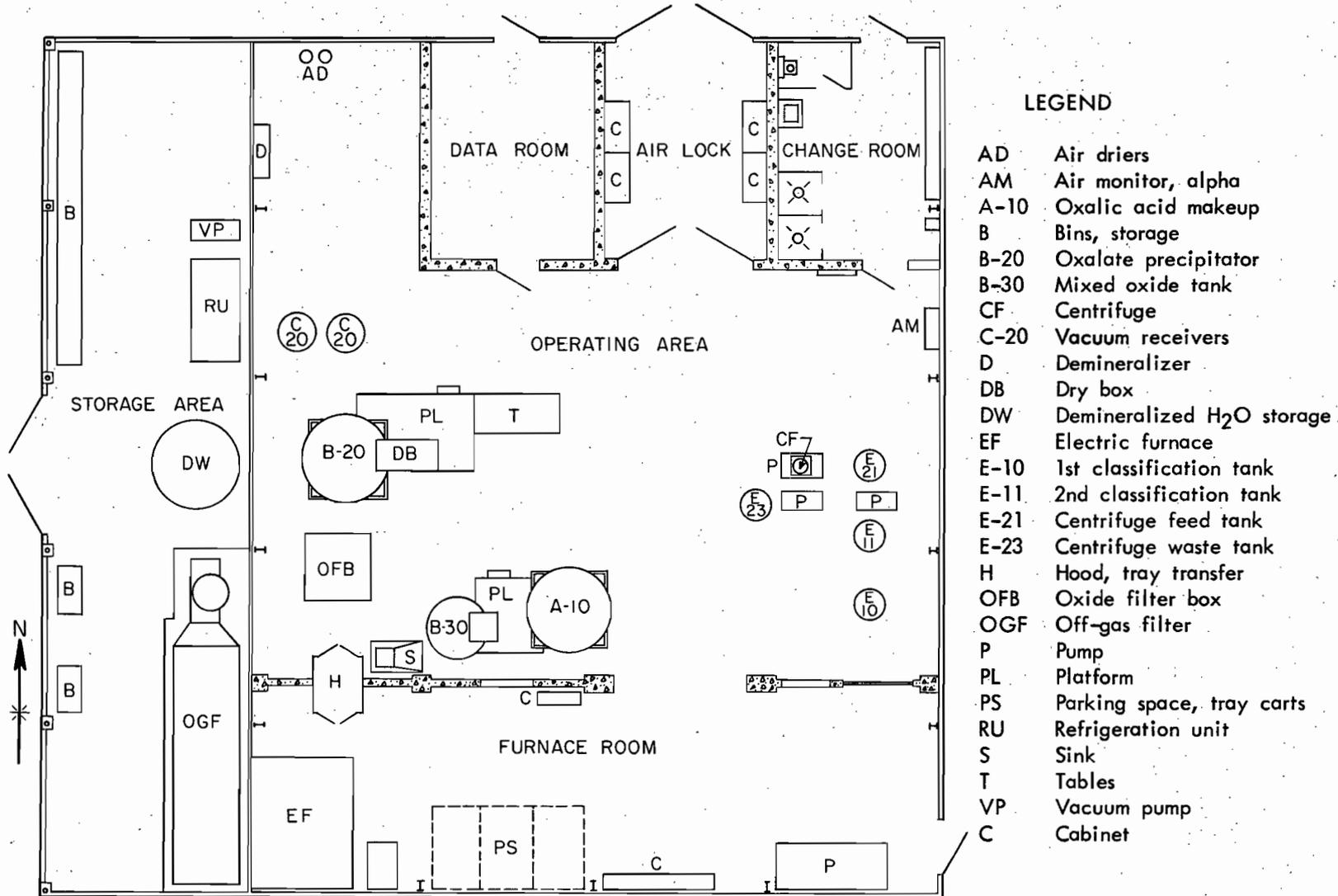


Fig. 2. Thorium oxide equipment layout.

building ventilation is a once-through system with a flow of 37,000 cfm of air. The air enters through a set of coils used for winter heating and is exhausted through a stack above the building. The exhaust blower is preceded by a bank of roughing filters and a bank of absolute air filters to prevent any thoria in the exhaust from being spread outside the building. One off-gas system is connected to a Nash Hytor (water sealed) vacuum pump. This system is used to provide vacuum for the filtration step and pump off-gas from the process tanks. A packed demister column is ahead of the pump to avoid any spray reaching the pump. The exhaust from the pump is connected to the building exhaust system. The second off-gas system is from the various glove boxes and hood over the process equipment and is connected to a small blower which exhausts to the building filter system. The third off-gas system is an air jet providing a slight negative pressure in the electric furnace. This also exhausts to the building filter system.

## 2.2 High-temperature Calcination Equipment

The high-temperature calcination furnaces were not moved and are still located just north of Building 3019. This necessitates transporting the thoria and thoria-urania to that location for calcinations at temperatures from 1000 to 1600°C.

## 2.3 Facility Capacity

During the period from July 1, 1958 until March 31, 1959, when operations ceased for moving equipment to Building 2528, a total of 7700 lb of oxide was prepared on a seven days per week schedule. During this time several types of oxide, differing in uranium content and calcination temperature, were prepared. Changing from one type of oxide to another requires a total of an extra day of processing time for cleaning out the various pieces of equipment to prevent cross-contamination.

## 3.0 PROCESS DESCRIPTION

The process flowsheet for the preparation of both thorium oxide and the thorium-uranium oxide is shown in Fig. 3. In general, materials in solution or slurry are pumped from one piece of equipment to another while solids and pastes must be transferred by hand. The batch size for current operation has been chosen to utilize two full drums of thorium nitrate tetrahydrate totaling 400 lb. This results in the formation of approximately 186 lb of dry thorium oxide. With normal process losses and removal of oversize particles from the product oxide, the final product weight will be approximately 175 lb.

### 3.1 Solution Makeup

A 0.7 M solution of thorium nitrate is made by dissolving 400 lb of thorium nitrate tetrahydrate in water to make 117 gal of solution in a 400-gal stainless steel tank. The transfer from the drums is made by hand in a glove box, located on top of the tank, so as to prevent the spread of dust. The oxalic acid precipitant is made up from 180 lb of

\*The engineering flowsheet is ORNL Dwg. E-33872.

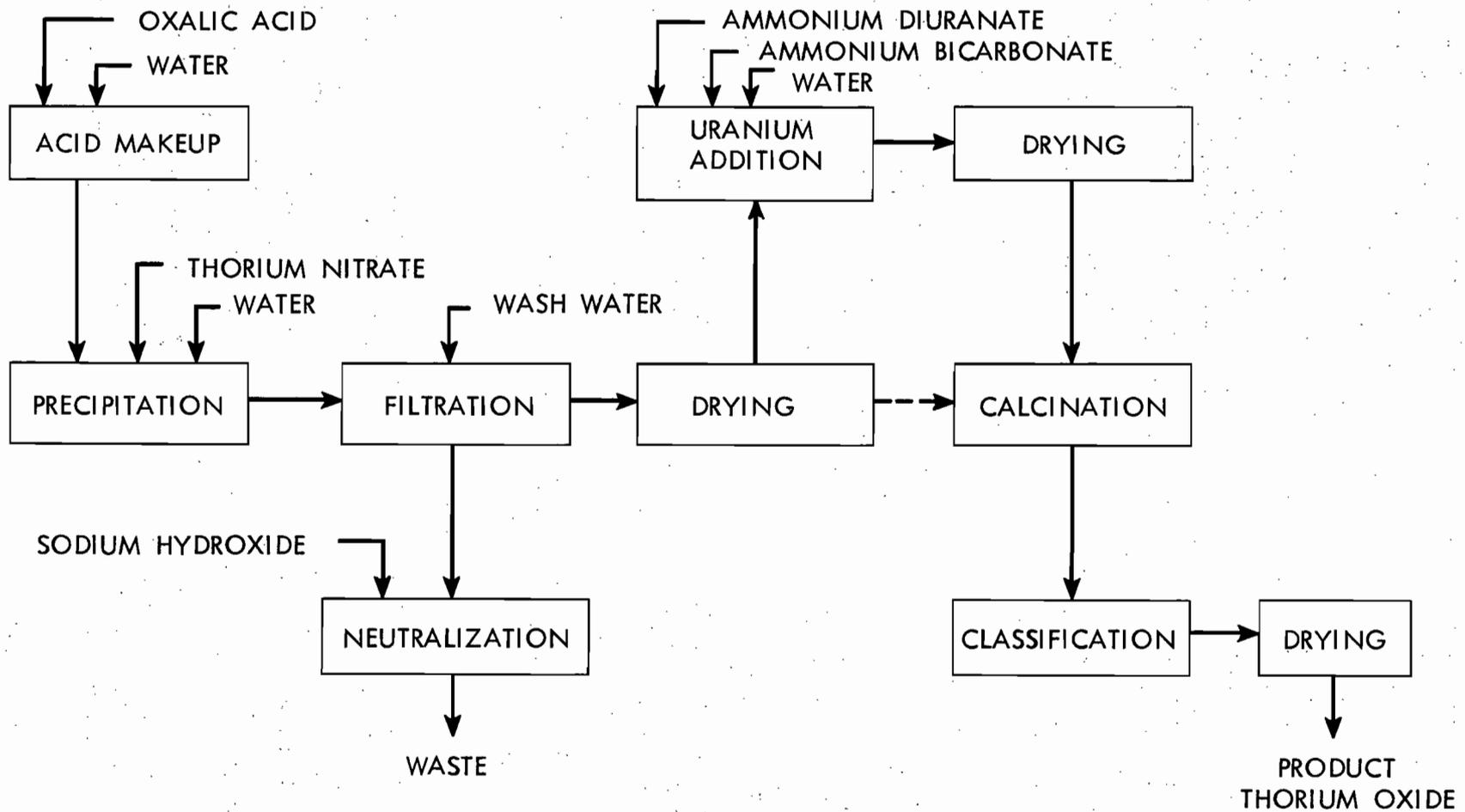


Fig. 3. Flowsheet for preparation of thorium oxide.

reagent-grade oxalic acid in water to form 257 gal of 0.7 M solution in a 600-gal stainless steel tank. This quantity of acid provides the stoichiometric amount of oxalate ion for the precipitation plus 10% excess.

### 3.2 Precipitation

The precipitation takes place in the tank in which the thorium nitrate solution was made up, the oxalic acid being pumped to this tank. The acid is added at a controlled rate through a pipe which discharges the acid just above the agitator in the precipitation tank. Agitation is provided by an 8-in.-dia modified turbine impeller located in a draft tube, the turbine blades having been modified by being given a slight pitch. Temperature is controlled by one set of coils in the tank for steam or cooling water and a second set connected to a 5-hp refrigeration unit. After the precipitation the slurry is digested at 95°C for 6 hr to improve the particle-size distribution.

### 3.3 Filtration

After digestion the slurry is cooled to room temperature and filtered on a 4-by 4-ft open-bed filter. The filter medium currently used is a close-weave Dacron cloth. The mother liquor is discarded and the cake washed several times with warm water. The cake is then loaded by hand into fused silica trays for calcination.

### 3.4 Calcination

The first calcination takes place in an electrically heated furnace approximately 2 by 3 by 4 ft deep. The silica trays containing the thorium oxalate cake are supported by a metal race in the furnace. Since this calcination consists both in drying the cake and decomposing the oxalate to the oxide, the heating is done stepwise. The temperature is first brought up to 180°C and remains there for several hours. It is then raised to 380°C for several hours and finally to 650°C for 4 hr. The furnace is then allowed to cool and the oxide removed.

### 3.5 Uranium Addition

Uranium is added to the 650°C calcined thoria by depositing basic uranyl carbonate on the thoria in a slurry. Ammonium diuranate prepared by the Y-12 Plant is used as the source of uranium for this preparation. A quantity of the ammonium diuranate sufficient to provide the desired uranium/thorium mole ratio for a batch is dissolved in excess ammonium bicarbonate to form an ammonium uranyl carbonate solution. To this solution, made up to 200 gal in a 300-gal stainless steel tank, is added the thorium oxide. The resultant slurry is heated to boiling and maintained close to 100°C until the uranyl carbonate has deposited on the thoria and the excess ammonium bicarbonate decomposed. When there is no longer any uranium in solution, the slurry is cooled and filtered. The filter cake is washed and calcined just as for the first filtration and calcination.

### 3.6 High-temperature Calcination

Particles of thoria and thoria-urania calcined at 650°C do not have sufficient strength to resist particle size degradation when pumped as a slurry such as would be done in a reactor. Consequently, it has been found necessary to calcine the oxide at higher temperatures to improve its rheological properties. Calcination of plain thoria at 1600°C ensures desirable characteristics, and studies now being made by the Reactor Experimental Engineering Division indicate that final calcination temperatures of 1400 or even 1250°C may be sufficient. Calcination of thoria-urania has been limited to a maximum of approximately 1050°C since there is apparently a sintering of the mixed oxide at higher temperatures, resulting in an excessively large portion of the product being much larger than the desired particle size range of 1 to 5  $\mu$  dia.

The high-temperature calcination is currently being done in a small gas-fired furnace located adjacent to Building 3019 (the old thorium oxide facility location). The 650°C calcined oxide is transferred from the silica trays used in the electric furnace to alundum crucibles for the high-temperature calcination. The furnace holds eight crucibles 6 in. dia and 8 in. high, which will permit a total of about 60 lb of oxide to be handled per firing. The furnace is heated slowly, maintained at the desired temperature for 4 hr, and then allowed to cool. A complete cycle requires approximately 24 hr so that a single batch (180 lb) requires three days.

### 3.7 Classification

Although it has been possible to produce oxides with an average particle size reasonably close to 2 or 3  $\mu$  and with a "flat" particle size distribution curve, there usually is about 2% of the material below 1.0  $\mu$  dia and 1 to 2% above 10  $\mu$ . The fine material is usually not objectionable, but the large particles would settle too rapidly in a slurry system, and they also contribute significantly to excessive wear of slurry pumps and piping.

In order to remove these large particles, use is made of Stokes' law in a simple settling-decantation system. The equipment is a series of 55-gal drums in which the oxide is first mixed with water to form a homogeneous slurry, and then the upper portion of the slurry in each drum is decanted through valves on the side of the drum to the next drum. The decantation valves are opened at time intervals such that at the time the valve is opened only particles smaller than 5  $\mu$  dia will be in the liquid above that valve. In order to reduce flocculation of small particles to clusters which would act as large particles, it has been found necessary to add a dispersing agent such as oxalic acid to the slurry.

This separation results in the removal of a major portion of the larger particles. Generally, the product will contain about 0.25 wt % of oxide with a particle diameter greater than 10  $\mu$ . (The fraction of particles with a diameter greater than 10  $\mu$  was chosen as the specification listing even though the settling separation is based on a theoretical removal of all particles above 5  $\mu$  dia.)

### 3.8 Centrifugation

To recover the solids from the slurry formed in the classification step, the slurry is fed to a 12-in-dia laboratory basket centrifuge. A filter could probably be used, but the centrifuge has proved satisfactory. The centrifuge is operated at 1150 rpm, which is sufficient to produce a clear effluent with a slurry feed rate of 500 cc/min. A hold tank is provided for the effluent from the centrifuge so that a visual check can be made for solids in the effluent.

### 3.9 Drying

The centrifuge cake is unloaded by hand and dried in fused silica trays at 650°C in the same way as described previously for the first calcination.

### 3.10 Product Handling

The final dry product oxide is packaged in plastic freezer bags which are put into fiber cartons. It should be mentioned that extensive use is made of the plastic freezer bags for storing dry oxide between any of the steps in the process. The bags are used double, one inside the other, as a safeguard against spillage in the event of bag leakage.

## 4.0 PROCESS VARIABLES<sup>3</sup>

In determining the suitability of a thorium or thorium-uranium preparation for use as a reactor slurry one important specification is its average particle size and the particle size distribution. Since no grinding is attempted on the oxide, the product particle size is established in the precipitation step. It is known that in the oxalate precipitation the size of the particles formed is dependent on the thorium nitrate and oxalic acid concentrations, the rate of mixing the reagents, the precipitation temperature, the degree of agitation, and possibly other factors. Preliminary data from laboratory studies indicated that satisfactory operating conditions could be determined by choosing a set of operating conditions that produced material near the desired size range and then fixing all the known variables except one. For simplicity of operation in the oxide facility the rate of addition of oxalic acid to the thorium nitrate solution was chosen as the variable. The fixed conditions were:

Oxalic acid solution	0.7 ± 0.02 M,	257 gal
Thorium nitrate solution	0.7 ± 0.02 M,	117 gal
Precipitation temperature	30 ± 1°C	
Agitation:	431 rpm, 8-in.-dia semiturbine impeller in draft tube with side slots completely open and bottom area 50% open <sup>2</sup>	

The thorium oxalate was precipitated by pumping the oxalic acid solution at a steady rate into an agitated tank containing the thorium nitrate solution. Both solutions were adjusted to 30°C before mixing and the precipitation tank was maintained at 30 ± 1°C during the acid addition by means of refrigeration. After precipitation the oxalate slurry was digested

for either 48 hr at 85°C or 6 hr at 95°C. The slurry was then filtered and the thorium oxalate cake converted to the oxide by calcination at either 650 or 800°C, depending on the end use for the particular product.

From a series of preparations made in this way a graph was drawn (Fig. 4) of the variation in particle diameter with change in acid addition rate. The results showed that the acid flow rate could be used as a means of controlling the final particle size. Approximately 30 runs were made in the equipment located in Building 3019 prior to moving. The 10 runs which have been made in the relocated equipment in Building 2528 are also shown on the graph. Since these points are consistently above the line drawn through previous data, it appears that a new line is needed as is shown. The cause of this is not known as yet, but it may be caused by some minor piping change such as the exact location of the oxalic acid addition pipe with respect to the mixing impeller.

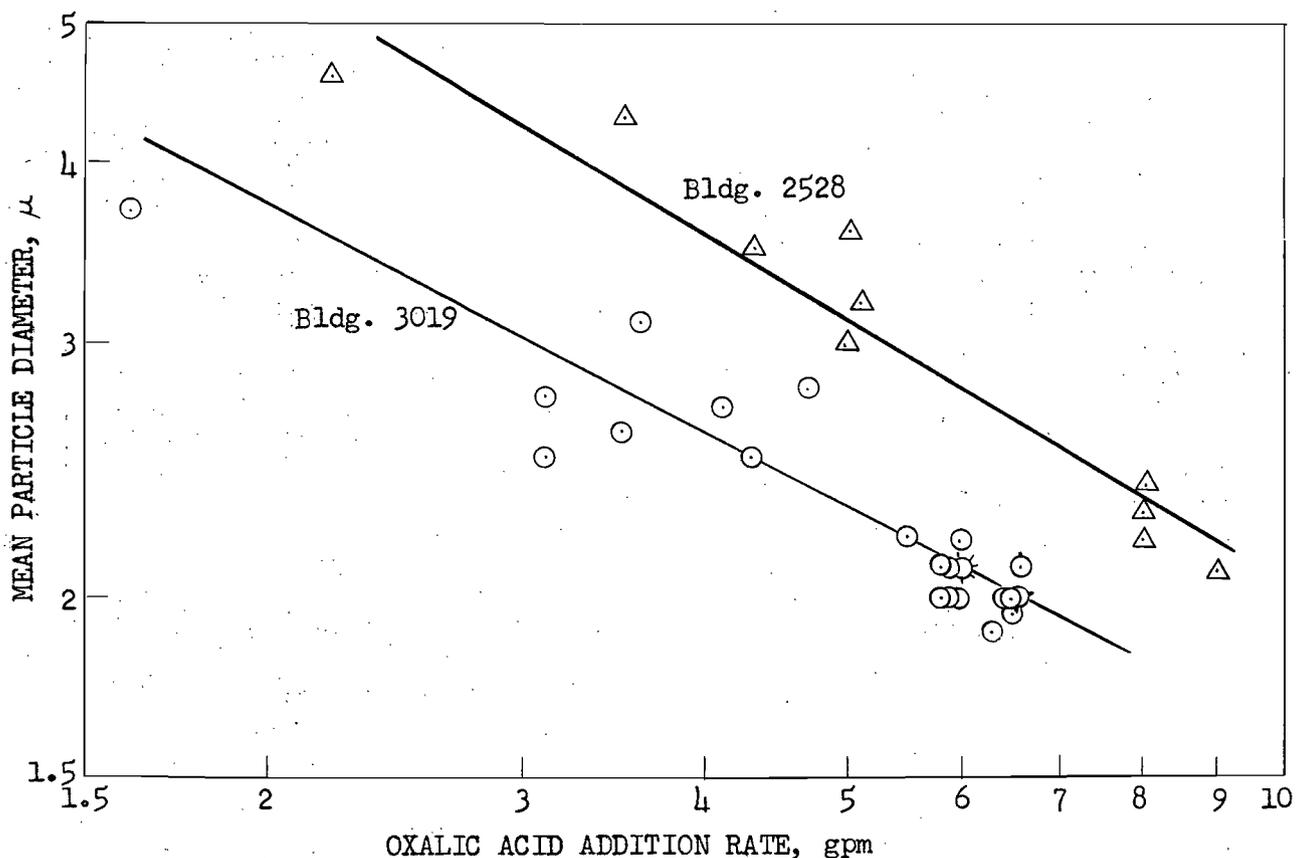


Fig. 4. Effect of acid addition rate on particle size.

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6.0 APPENDIX

6.1 Specifications for and Analysis of Thorium Oxide Product

The physical property specification is that no more than 0.5 wt % of the particles shall be more than 10  $\mu$  dia. The nominal\* value for the product as shown by analysis has been 0.25 wt %. The chemical impurity specifications and analyses are:

<u>Impurity</u>	<u>Max Allowable, ppm</u>	<u>Nominal Analysis, ppm</u>
Cl	10	< 10
F	10	< 10
CO <sub>3</sub>	3000	500
NO <sub>3</sub>	10	< 10
SO <sub>4</sub>	100	25
PO <sub>4</sub>	50	40
Si	10	< 10
Fe	50	20
Al	10	4
Mg	50	4
Ni	50	< 10
Cr	50	< 10
Pb	10	< 10
Na	100	15
K	100	< 10
Li	100	< 10
Ca	100	30

6.2 Thorium Oxide Particle Size Analysis

Since the particle size of the thorium oxide is an important factor in the suitability of a particular product for nuclear reactor use, accurate size determinations must be made. Also, it is desirable to have available a rapid size determination method for use in process control. Methods suitable for each of these purposes are in routine use at Oak Ridge National Laboratory.<sup>4</sup>

Process control is obtained by use of a "pipet method" and a "clinker test" method of size analysis. The pipet method uses a gravity sedimentation technique in which the sample is dispersed in a suitable medium and stirred until the suspension is homogeneous. Stirring is then stopped and the particles are allowed to fall freely. A pipet mounted in the sedimentation tube at a given distance from the top of the liquid is used to remove samples from the suspension at specific times. The natural radioactivity of each sample is measured by a gamma scintillation counter. The amount of radioactivity of each aliquot is related to the radioactivity of the suspended portion so that the concentration of particles of a given size may be calculated. The clinker test method has been developed to assay for particles having a diameter of greater than 10  $\mu$ , which are considered oversized or "clinkers." This method consists essentially in shaking a thorium oxide sample with a dispersant in a long tube and then

\*These values are an average of a number of runs and are given merely to represent a typical oxide calcined to 1050°C.

allowing it to settle for a time long enough for the 10- $\mu$  or larger particles to reach the bottom (according to Stokes' law). The unsettled oxide is withdrawn and the natural radioactivity of the unsettled material counted for gross gamma activity. By comparing this count with that of a sample of the same oxide taken prior to settling, the concentration of particles  $> 10 \mu$  can be calculated.

Final product analysis is done by an activation analysis-sedimentation method. This method is a refinement of the Andreasin method, as the radioactivity induced in the thorium oxide is measured from outside the sedimentation tube. A dry sample of the oxide is irradiated in the ORNL Graphite Reactor and then made into a slurry. The slurry is allowed to settle in a long tube, and the radioactivity is measured at a point near the bottom of the tube over a period of time. The counting data are resolved by tabulating the count as a function of time against the particle size which has been calculated from Stokes' law.

The results of a typical size analysis are shown in Fig. 5.

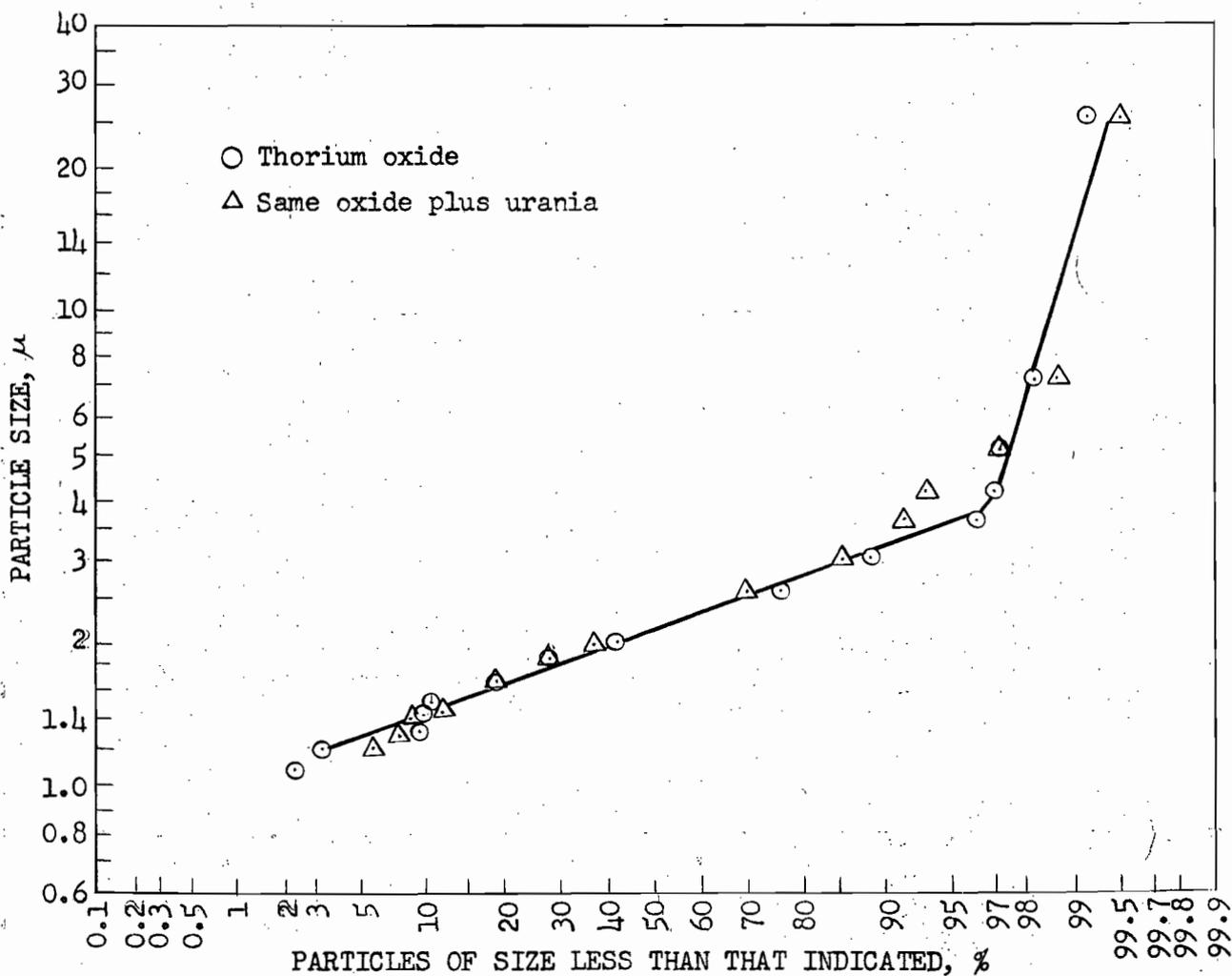


Fig. 5. Typical particle size distribution.

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