

AUSTRALIAN ATOMIC ENERGY COMMISSION

RESEARCH ESTABLISHMENT

LUCAS HEIGHTS

PREPARATION AND EVALUATION OF AN ADU-DERIVED

CERAMIC GRADE UO₂ POWDER

by

E. J. RAMM

S. T. QUAASS

ABSTRACT

The method and equipment used to prepare a ceramic grade uranium dioxide powder are described, together with relevant characteristics of the intermediate and final products. The method chosen followed the well established ammonium diuranate route involving continuous precipitation from uranyl nitrate solution using gaseous ammonia. Conversion of the ammonium diuranate to uranium dioxide was effected by heating in a hydrogen/nitrogen atmosphere and following this with a low temperature stabilisation treatment.

Various physical tests were carried out on the resultant powder, and finally, specimens were pressed and sintered over a wide range of pressures and temperatures. The tests indicated that the powder was 'sinterable' and that the method of preparation produced a ceramic grade powder exhibiting consistent properties and behaviour.

CONTENTS

	Page
1. INTRODUCTION	1
2. DESCRIPTION OF METHOD AND EQUIPMENT FOR UO ₂ POWDER PREPARATION	2
2.1 Outline of Method	2
2.2 Starting Materials	3
2.3 Equipment	2
2.3.1 Construction material	3
2.3.2 Nitrate tank	3
2.3.3 Precipitation tank	4
2.3.4 Flow meters	4
2.3.5 Filter	4
2.3.6 Drying oven	5
2.3.7 Calcination - reduction and stabilisation	5
3. EVALUATION OF A STANDARD PRODUCT	7
3.1 Standard Conditions and Testing Procedure	7
3.1.1 Standard conditions	7
3.1.2 Testing programme	7
3.1.3 Standard tests	8
3.2 Results of Standard Tests	9
3.2.1 Wet ADU cake	9
3.2.2 Dried ADU cake	9
3.2.3 UO ₂ Powder	10
3.2.4 Pressed pellets	10
3.2.5 Sintered pellets	10
4. CONCLUSIONS	11
5. ACKNOWLEDGEMENTS	12
6. REFERENCES	12
APPENDIX	Equipment Details and Standard Operating Conditions
Table 1	Spectrographic Analysis of Eldorado Mining and Refining Company Nuclear Grade Uranyl Nitrate Hexahydrate
Table 2	Spectrographic Analysis of Six Batches of Wet ADU and Uranium Nitrate Hexahydrate Crystals

Continued...

CONTENTS (Continued)

Table 3	Analysis of Six Batches of Dried ADU Precipitate
Table 4	Comparison Between X-ray Diffraction d -Values (\AA) of ADU from this Study and those Listed in the A.S.T.M. Index
Table 5	Spectrographic Analysis of Six Batches of Reduced UO_2 Powder
Table 6	B.E.T. Surface Areas of Six Batches of Reduced UO_2 Powder
Table 7	Pour and Tap Densities of -100 Mesh UO_2 Powder (Blended Batches)
Table 8	Green Densities of Pressed UO_2 Pellets (Blended Batches)
Table 9	Spectrographic Analysis of Sintered UO_2 Pellets Pressed at 15 tons/in ² (Blended Batches)
Table 10	Densities of UO_2 Sintered at Four Different Temperatures
Table 11	Densities of UO_2 Sintered for Four Hours at 1,600°C Six Separate Furnace Runs (Blended Batches)
Table 12	Densities of Six Separate Precipitation Batches of UO_2 Sintered in the Pusher Furnace in the Same Run at 1,500°C for Four Hours in Hydrogen
Table 13	Grain Sizes of UO_2 Pellets Sintered for Four Hours
Figure 1	Equipment Flow Sheet for the Preparation of Uranium Dioxide Powder
Figure 2	General View of the Equipment Used for the Preparation of Uranium Dioxide Powder
Figure 3	Precipitation Tank, pH Cell and Conditioning Tank (Schematic)
Figure 4	The Precipitator, pH Cell and Conditioning Tank
Figure 5	pH of Precipitation Versus Ammonia Flow
Figure 6	The Filter Shown Schematically
Figure 7	The Filter
Figure 8	The Reduction Furnace
Figure 9	A Typical Heating Curve in the Reduction Stage
Figure 10	Electron Micrographs of Wet ADU Dispersed in Alcohol
Figure 11	Typical Microstructures of UO_2 Isopressed at 20 tons/in ² and Sintered for Four Hours at Various Temperatures

1. INTRODUCTION

Uranium dioxide in the form of sintered pellets is the accepted fuel material for a number of important nuclear power reactor types including PWR, BWR, PHW (CANDU), AGR, and the newer SGHW and CANDU-BLW systems. The fuel fabrication cost, which is important in determining the overall economics of power production, depends on a variety of factors, including the basic cost of the ceramic grade powder, the number and complexity of steps required to fabricate it to the required shape, the ratios of output rate to capital investment and output rate, labour requirements, and the reject rates at particular stages. In general, the simplest process with the smallest reject rate will, for a fixed output requirement, lead to the lowest as-fabricated cost of the powders.

The difficulty and thus the cost of fabricating a UO_2 powder depends on its physical properties, such as particle size and size distribution, aggregate structure, surface area, and crystallite size, but may also depend on some as yet unknown factors. These properties are critically dependent on the conditions used to prepare the powder. The most commonly used route for ceramic grade UO_2 powder includes the precipitation of an ammonium uranate from aqueous uranyl nitrate using ammonia, followed by reduction to UO_2 in hydrogen, either directly or after calcination of the filtered and dried product. The uranate is usually referred to as 'ADU' but it seldom has the required formula for ammonium diuranate, $(NH_4)_2U_2O_7$. There are numerous plants throughout the world producing ceramic grade UO_2 by the ADU route and many details of these are available from the published literature. The various plants differ in many respects, and in some cases important differences in powder properties can result from apparently minor changes in equipment design and process variables. In general, the inter-relationship between process and equipment variables and final product is not always understood, and therefore it is virtually impossible to design and construct a production plant which will assuredly produce a required grade of UO_2 without experimentation on or modification of the completed plant. The present work should help to develop Australian expertise in the preparation of ceramic grade UO_2 and sintered UO_2 .

The work reported here formed the first phase of a project which had the following specific aims:

- (i) To prepare a wide range of UO_2 powders using various values of process variables, to study their fabrication behaviour, and to relate this to their preparative history and physical properties.

AUSTRALIAN ATOMIC ENERGY COMMISSION

RESEARCH ESTABLISHMENT

LUCAS HEIGHTS

PREPARATION AND EVALUATION OF AN ADU-DERIVED

CERAMIC GRADE UO₂ POWDER

by

E. J. RAMM

S. T. QUAASS

ABSTRACT

The method and equipment used to prepare a ceramic grade uranium dioxide powder are described, together with relevant characteristics of the intermediate and final products. The method chosen followed the well established ammonium diuranate route involving continuous precipitation from uranyl nitrate solution using gaseous ammonia. Conversion of the ammonium diuranate to uranium dioxide was effected by heating in a hydrogen/nitrogen atmosphere and following this with a low temperature stabilisation treatment.

Various physical tests were carried out on the resultant powder, and finally, specimens were pressed and sintered over a wide range of pressures and temperatures. The tests indicated that the powder was 'sinterable' and that the method of preparation produced a ceramic grade powder exhibiting consistent properties and behaviour.

CONTENTS

	Page
1. INTRODUCTION	1
2. DESCRIPTION OF METHOD AND EQUIPMENT FOR UO ₂ POWDER PREPARATION	2
2.1 Outline of Method	2
2.2 Starting Materials	3
2.3 Equipment	2
2.3.1 Construction material	3
2.3.2 Nitrate tank	3
2.3.3 Precipitation tank	4
2.3.4 Flow meters	4
2.3.5 Filter	4
2.3.6 Drying oven	5
2.3.7 Calcination - reduction and stabilisation	5
3. EVALUATION OF A STANDARD PRODUCT	7
3.1 Standard Conditions and Testing Procedure	7
3.1.1 Standard conditions	7
3.1.2 Testing programme	7
3.1.3 Standard tests	8
3.2 Results of Standard Tests	9
3.2.1 Wet ADU cake	9
3.2.2 Dried ADU cake	9
3.2.3 UO ₂ Powder	10
3.2.4 Pressed pellets	10
3.2.5 Sintered pellets	10
4. CONCLUSIONS	11
5. ACKNOWLEDGEMENTS	12
6. REFERENCES	12
APPENDIX	Equipment Details and Standard Operating Conditions
Table 1	Spectrographic Analysis of Eldorado Mining and Refining Company Nuclear Grade Uranyl Nitrate Hexahydrate
Table 2	Spectrographic Analysis of Six Batches of Wet ADU and Uranium Nitrate Hexahydrate Crystals

Continued...

CONTENTS (Continued)

Table 3	Analysis of Six Batches of Dried ADU Precipitate
Table 4	Comparison Between X-ray Diffraction d -Values (\AA) of ADU from this Study and those Listed in the A.S.T.M. Index
Table 5	Spectrographic Analysis of Six Batches of Reduced UO_2 Powder
Table 6	B.E.T. Surface Areas of Six Batches of Reduced UO_2 Powder
Table 7	Pour and Tap Densities of -100 Mesh UO_2 Powder (Blended Batches)
Table 8	Green Densities of Pressed UO_2 Pellets (Blended Batches)
Table 9	Spectrographic Analysis of Sintered UO_2 Pellets Pressed at 15 tons/in ² (Blended Batches)
Table 10	Densities of UO_2 Sintered at Four Different Temperatures
Table 11	Densities of UO_2 Sintered for Four Hours at 1,600°C Six Separate Furnace Runs (Blended Batches)
Table 12	Densities of Six Separate Precipitation Batches of UO_2 Sintered in the Pusher Furnace in the Same Run at 1,500°C for Four Hours in Hydrogen
Table 13	Grain Sizes of UO_2 Pellets Sintered for Four Hours
Figure 1	Equipment Flow Sheet for the Preparation of Uranium Dioxide Powder
Figure 2	General View of the Equipment Used for the Preparation of Uranium Dioxide Powder
Figure 3	Precipitation Tank, pH Cell and Conditioning Tank (Schematic)
Figure 4	The Precipitator, pH Cell and Conditioning Tank
Figure 5	pH of Precipitation Versus Ammonia Flow
Figure 6	The Filter Shown Schematically
Figure 7	The Filter
Figure 8	The Reduction Furnace
Figure 9	A Typical Heating Curve in the Reduction Stage
Figure 10	Electron Micrographs of Wet ADU Dispersed in Alcohol
Figure 11	Typical Microstructures of UO_2 Isopressed at 20 tons/in ² and Sintered for Four Hours at Various Temperatures

1. INTRODUCTION

Uranium dioxide in the form of sintered pellets is the accepted fuel material for a number of important nuclear power reactor types including PWR, BWR, PHW (CANDU), AGR, and the newer SGHW and CANDU-BLW systems. The fuel fabrication cost, which is important in determining the overall economics of power production, depends on a variety of factors, including the basic cost of the ceramic grade powder, the number and complexity of steps required to fabricate it to the required shape, the ratios of output rate to capital investment and output rate to power requirements, and the reject rates at particular stages. In general, the simplest process with the smallest reject rate will, for a fixed output requirement, lead to the lowest as-fabricated cost of the powders.

The difficulty and thus the cost of fabricating a UO_2 powder depends on its physical properties, such as particle size and size distribution, aggregate structure, surface area, and crystallite size, but may also depend on some as yet unknown factors. These properties are critically dependent on the conditions used to prepare the powder. The most commonly used route for ceramic grade UO_2 powder includes the precipitation of an ammonium uranate from aqueous uranyl nitrate using ammonia, followed by reduction to UO_2 in hydrogen, either directly or after calcination of the filtered and dried product. The uranate is usually referred to as 'ADU' but it seldom has the required formula for ammonium diuranate, $(NH_4)_2U_2O_7$. There are numerous plants throughout the world producing ceramic grade UO_2 by the ADU route and many details of these are available from the published literature. The various plants differ in many respects, and in some cases important differences in powder properties can result from apparently minor changes in equipment design and process variables. In general, the inter-relationship between process and equipment variables and final product is not always understood, and therefore it is virtually impossible to design and construct a production plant which will assuredly produce a required grade of UO_2 without experimentation on or modification of the completed plant. The present work should help to develop Australian expertise in the preparation of ceramic grade UO_2 and sintered UO_2 .

The work reported here formed the first phase of a project which had the following specific aims:

- (i) To prepare a wide range of UO_2 powders using various values of process variables, to study their fabrication behaviour, and to relate this to their preparative history and physical properties.

(ii) Ultimately, to specify in as much detail as possible the physical characteristics required in a ceramic grade UO_2 powder and to suggest the most important process variables which should be controlled during its preparation.

(iii) To set up standard assessment procedures for new UO_2 powders.

A necessary preliminary phase of this work was the setting-up of facilities for preparing ceramic grade UO_2 in kilogram quantities. A decision was made to use an ammonia-ADU route, because there is more documentation in the literature on this route than on its variants such as urea-ADU, and because the ammonia route can be relied upon to produce sinterable UO_2 without too much experimentation. The scale required for the precipitation facilities was similar to that of the enriched UO_2 plant described in some detail by Bourns and Watson (1961) as part of the Canadian heavy water reactor programme, and this design was followed quite closely in the present work on natural UO_2 .

Having established such facilities, it was necessary to determine the uniformity and ceramic fabrication behaviour of the standard powder made using fixed values of all process variables. In this assessment work, the emphasis was placed on purity, uniformity and sinterability rather than on pressing behaviour. Ultimately, pressing behaviour during automatic steel-die pressing is extremely important in determining the acceptability of a UO_2 powder for cold pressing and sintering into fuel pellets. However, since a suitable automatic press was not available at this stage, sinterability was assessed using pellets made by isostatic pressing rather than die-pressing. Later work will concentrate on automatic steel die pressing.

A description of the equipment, process, standard powder and the results of an assessment of this powder forms the basis of this report.

2. DESCRIPTION OF METHOD AND EQUIPMENT FOR UO_2 POWDER PREPARATION

2.1 Outline of Method

In setting-up ADU precipitation facilities along the lines described by Bourns and Watson (1961), a change from an aqueous ammonia precipitant to gaseous ammonia was made. The precipitation of ADU with NH_3 appeared a simpler process, eliminating the preparation of standard NH_4OH solutions. It is difficult from the results available in the literature to choose between the use of NH_3 or NH_4OH in the precipitation stage. However, Watson (1957) has reported preparing a sinterable UO_2 powder from ADU precipitated with NH_3 and considers a satisfactory

process could be developed by this method.

Figure 1 shows the equipment flow sheet. The uranyl nitrate tank containing uranyl nitrate of the required concentration is pressurised with air to 15 lb/in². The solution flows from the tank through a flow meter into the precipitator and reacts with a metered flow of gaseous ammonia. The resultant precipitate is discharged and filtered on a revolving vacuum drum filter; the process to this stage is designed for continuous operation. The wet ADU precipitate is oven-dried in trays and subsequently calcined, reduced and stabilised; these latter stages are batch processes. Calcination-reduction can be carried out either in one step or separately in different atmospheres, for example, air calcination followed by N_2/H_2 reduction is possible. Stabilisation of the as-reduced powders is effected by controlled oxidation of the powder before it is exposed to atmosphere. A general view of the equipment is shown in Figure 2.

2.2 Starting Materials

The uranyl nitrate hexahydrate used throughout this work was an Eldorado Mining and Refining Company nuclear grade product. Table 1 shows the impurities listed in the Eldorado data sheet for this material. An A.A.E.C. analysis (Table 2) however indicated a much higher copper content. The reason for this discrepancy is not known.

All solutions were made using demineralised water. The ammonia was standard anhydrous commercial grade.

2.3 Equipment

2.3.1 Construction material

The valves, tanks, piping and all components in contact with the uranium liquors were made from either 18/8 stainless steel or polythene.

2.3.2 Nitrate tank

The nitrate tank has a working capacity of approximately 25 litres and can be pressurised up to 50 lb/in² with filtered air from the laboratory supply. The solution level is observed from a sight-gauge and the nitrate solution flow is stopped before the tank empties to prevent splashing if air is blown through the system. The nitrate flow is metered through a flow meter and frequent adjustment of the control valve is required to maintain a constant flow. Variations in the flow rate are due to the decreasing height of the level of solution in the tank and small variations in the pressurisation.

2.3.3 Precipitation tank

The precipitation tank is shown schematically in Figure 3 and as a general view in Figure 4. An impeller (situated below the ammonia inlet) is attached at the lower end of the drive shaft. The upward thrust from the impeller causes both reactants to impinge against the perforated spreader disc where intimate mixing occurs; the speed of rotation of the drive shaft is variable by means of a variable speed motor. The precipitation tank is surrounded by a water jacket through which hot or cold water can be circulated to vary the temperature of precipitation if desired.

The precipitate flows through the side opening near the top of the tank into the pH cell which contains glass and reference electrodes. The precipitate is discharged via the pH cell into the dump tank until precipitation conditions have been stabilised, and thereafter the slurry is fed into the conditioning tank and overflows into the filter trough. The conditioning tank, which is continuously agitated, evens out small variations in the precipitate and enhances uniformity of the filter cake. With no water flowing through the jacket surrounding the precipitation tank the temperature of precipitation becomes constant at about 45 to 50°C when a nitrate solution of concentration 150 g U/litre is fed into the precipitation tank at 270 ml/min and precipitated at pH 7.2.

2.3.4 Flow meters

Liquid ammonia is allowed to vaporise in a small buffer tank at a constant pressure, which can be varied between 5 and 25 lb/in². The flow is measured with a flow meter which has been calibrated by measuring the volume of kerosene displaced in a given time at various ammonia flow rates.

To measure the nitrate flow modifications were made to the float of a standard flow meter and the meter was calibrated by direct displacement using a uranyl nitrate solution containing 150 g U/litre.

The effect on the pH of precipitation of a varying ammonia flow rate with a constant flow rate of nitrate solution (150 g U/litre) is shown in Figure 5.

2.3.5 Filter

The filter is shown schematically in Figure 6 and as a general view in Figure 7. The unit consists of a continuously revolving drum fabricated from stainless steel, having circular ends and a framework covered with stainless steel mesh round which a terylene filter cloth is wrapped. Vacuum inside the drum is obtained from a vane-type pump and the slurry is picked up by the cloth

as the drum rotates. The drum is driven by a variable speed motor and a speed is selected to permit satisfactory filtering. A perforated pipe across the top of the drum allows a metered flow (usually 160 ml/min) of demineralised water to flow onto the cake to remove the major portion of soluble salts such as NH₄NO₃. The drum normally rotates at 1½ rev/min. The applied vacuum of approximately 120 mm of mercury below atmosphere is controlled by a bleed valve in the vacuum line. A polythene blade continuously scrapes the cloth and the filtered cake falls directly into an enamel tray. The slurry level is maintained about 1½ in. above the bottom of the drum and a discharge outlet near the top of the trough allows excess slurry to overflow into a tank below if the filtering rate becomes inadequate or if failure occurs in the filter system.

2.3.6 Drying oven

The oven used is a conventional laboratory air oven of inside dimensions 18 in. high x 15 in. x 15 in.

The ADU cake is loaded directly into flat enamel trays, measuring 13 in. x 10½ in. x 2½ in, to a depth of 1½ in, and dried for specified times at the desired temperatures; when cool, the dried cake is loaded into a stout polythene bag and lightly crushed into lumps approximately ¼ in. in size.

2.3.7 Calcination - reduction and stabilisation

The reduction furnace can be used either for air or controlled atmosphere calcination followed by hydrogenous atmosphere reduction, or for direct reduction without prior calcination. The initial runs were all made by direct reduction and this is the process described.

The inner tray assembly of the furnace and a general view of the reduction facility is shown in Figure 8. The tray assembly holds approximately 2 kg of dried ADU and produces approximately 1.5 kg UO₂ in 24 hours. The stainless steel tray supports are attached to the top flange of the furnace tube cover permitting the loaded assembly to be inserted and withdrawn without difficulty. Three platinum/platinum-13%-rhodium couples pass through the top flange and indicate the temperature in the bottom, middle and top trays. The furnace tube is heated in a conventional circular upright resistance furnace, manually controlled, with appropriate power supply and voltage control. The control thermocouple is situated between the furnace tube and the wire-wound muffle. A typical heating cycle of the three thermocouples inside the furnace tube is shown in Figure 9.

The stainless steel 'cake stand' assembly contains ten 5 in. dia x 1½ in. deep

unglazed porcelain dishes which are loaded with ADU to a depth of about 1 in. The thermocouples are placed directly on top of the powder in various trays. The inner assembly is then loaded directly into the furnace tube or reduction chamber, the top flanges are bolted together, the reduction chamber is introduced into the cold furnace, and the gas lines are connected.

The following method of operation, including heating rates, gas compositions, etc., is based closely on that used by Bourns and Watson (1961), except that the maximum temperature to which the powder is heated in H₂ after reduction is not fixed at 600°C but can be held anywhere in the range, 500 to 900°C. Provision is made for controlled in situ partial re-oxidation of the as-reduced UO₂ to prevent pyrophoric behaviour on exposure to the atmosphere.

The furnace tube is flushed with dry nitrogen before admitting a nitrogen-10%-hydrogen gas mixture; the tube is then heated at about 100°C per hour to 450°C and held at this temperature for one hour. The gas mixture is increased to equal volumes of hydrogen and nitrogen and, if no increase in temperature is observed in the powder, pure hydrogen is then admitted. The tube temperature is raised at approximately 100°C per hour to a chosen maximum temperature and held for the chosen time. The tube is then flushed with pure nitrogen for 10 minutes, pressurised to 20 lb/in² and the inlet and outlet valves are closed. Flexible hoses are coupled at the flanges and the inlet valve is opened to maintain a positive nitrogen pressure of 20 lb/in² during cooling. The tube assembly is lifted from the furnace by means of a crane and lowered into a cooling tank where cold water is circulated until the tube and contents reach water temperature. The water is drained from the cooling tank and dry ice is packed around the tube to reduce the powder temperature to 0°C or lower. A mixture of nitrogen with 10 per cent of dry air is then flushed through the tube before removing it from the cooling tank and allowing the temperature to rise to ambient. The air-nitrogen mixture is gradually changed to 100 per cent air; if stabilisation is effective, no further increase in the powder temperature should be observed.

The tube is finally replaced in the cooling tank, in which warm water is circulated until the powder temperature is about 40°C. If no rise in the powder temperature occurs there is little chance of subsequent uncontrolled oxidation taking place under normal handling conditions. The furnace reduction tube is removed and placed in a fume hood where the cake stand assembly is removed; the trays are blended and the powder lightly crushed to pass a 100 mesh screen. This powder was in a suitable form for isostatic pressing. For assessment by die-pressing, further treatment to give a free-flowing, granular material would have

been required, but as stated earlier it was not intended to employ die-pressing in the present work. An assessment of the standard -100 mesh powder made using fixed values of the precipitation, calcination and reduction variables is now reported.

3. EVALUATION OF A STANDARD PRODUCT

3.1 Standard Conditions and Testing Procedure

3.1.1 Standard conditions

The following conditions were chosen for assessment. In arriving at these, Bourns and Watson's (1961) best conditions for a sinterable UO₂ powder were used as a guide.

U concentration in uranyl nitrate solution	150 g/litre
pH of precipitation	7.2 ± 0.2
Drying temperature	100°C
Drying time	24 hours
Maximum temperature in H ₂	600°C
Time at maximum temperature in H ₂	1 hour
Powder treatment	Crushed to -100 mesh
Pressing procedure	Low pressure die-forming into ½ in. dia. pellets, then wet bag isostatic pressing; no binder or lubricant addition.
Isostatic Pressing Pressures	7, 10, 15 and 20 tons/in ² .
Sintering temperatures	1,400, 1,500, 1,600, and 1,700°C.
Sintering time	4 hours
Sintering atmosphere	Hydrogen

3.1.2 Testing programme

The basic scheme of the study was to carry out each of three critical stages six times and assess the reproducibility of each stage before proceeding to the next. The three stages designated as 'critical' were:

- (A) Precipitation and drying
- (B) Calcination - reduction and stabilisation
- (C) Sintering

In practice, Stage A was carried out six times to produce six dried batches of ADU. After making characterisation tests, the batches were blended and then

redivided into six parts before proceeding to Stage B. Similarly, the six batches from Stage B were finally blended before pressing and sintering was carried out. The details of pressing and sintering are discussed below.

In addition to this procedure, a small part of each of the precipitation batches was processed separately to form UO_2 powder and finally sintered specimens.

At the pressing stage, each combination of 4 pressing pressures and 4 sintering temperatures was assigned a group of 20 identical specimens. These were formed at 1,000 lb/in² in $\frac{1}{2}$ in. dia. steel dies and then isostatically pressed at the required pressure in sealed and evacuated rubber latex tubing. Sintering was carried out in a hydrogen atmosphere in a molybdenum resistance-heated pusher furnace. The specimens were loaded onto sintered alumina boats and pushed through the furnace at a rate such as to maintain the maximum temperature for 4 hours.

Sintering runs were as follows:

- (i) The blended batch from Stage B was pressed at 7, 10, 15 and 20 tons/in² and sintered at 1,400, 1,500, 1,600 and 1,700°C (total of 320 specimens).
- (ii) The blended batch from Stage B was pressed at 7, 10, 15 and 20 tons/in² and sintered at 1,600°C on six different days (total of 480 specimens). This constituted the assessment of reproducibility of Stage C.
- (iii) Material from each of the six batches from Stage A, separately processed to UO_2 powder, was pressed at 10 tons/in² and sintered at 1,500°C. Ten specimens from each of the six batches were sintered, together with 10 from the blended batch from Stage B.

3.1.3 Standard tests

The following tests were made at the various stages:

(i) Wet ADU Cake

Spectrographic analysis for selected cations, and electron microscopic examination of the dispersed precipitate.

(ii) Dried ADU

Spectrographic analysis for selected cations. Chemical analysis for NH_3 , NO_3 and U. X-ray diffraction powder pattern.

(iii) UO_2 Powder (-100 mesh)

Spectrographic analysis for selected cations.

Four density.

Tap density.

B.E.T. Surface Area (N_2 adsorption).

X-ray diffraction powder pattern.

(iv) Pressed Pellets

Green density measured on 5 pellets at each pressing condition.

(v) Sintered Pellets

Chemical analysis to determine O/U ratio.

Spectrographic analysis for selected cations.

Bulk density on all pellets from each pressing and sintering condition.

X-ray diffraction pattern.

Metallographic examination for grain size and porosity distribution.

3.2 Results of Standard Tests

3.2.1 Wet ADU cake

Spectrographic analyses of the uranyl nitrate and of the six individual precipitation batches are given in Table 2. Negligible contamination is picked up in the precipitation stage and a slight decrease in the initial copper content appears to have occurred.

Electron microscopy of the alcohol dispersed material from each batch revealed loosely agglomerated crystallites and typical fields are shown in Figures 10a and b. In each case the crystallites appeared as thin hexagonal plates varying in maximum dimensions from about 0.5 μm to 0.025 μm with a mean overall dimension of approximately 0.25 μm . The plates are observed to be very thin as the images of others can be observed behind several of the larger plates.

3.2.2 Dried ADU cake

The Fe, Cr and Ni contents of the six individual batches are shown in Table 3. These were the specific elements sought in the spectrographic analysis to check the relative contamination picked up from the stainless steel tanks, piping, etc. The uranium contents of the precipitates (Table 3) determined by gravimetric analysis show considerable variation and no simple relationship exists between the uranium, nitrate and ammonia contents. A non-uniform moisture content and insufficient washing during filtering may have contributed to these variations.

X-ray diffraction patterns of the six separate batches determined with Cu K α radiation, were found to be consistent. A comparison between the lines obtained and the lines listed in the A.S.T.M. index for an ADU composition $\text{UO}_3 \cdot \frac{1}{2} \text{NH}_3 \cdot 2 \text{H}_2\text{O}$ is given in Table 4. The agreement shown is reasonably good, and there were no identified extra lines.

The precipitate when pulverised and screened through 100 mesh was found to have a tap density of approximately 1.1 g/cm^3 .

3.2.3 UO₂ Powder

The spectrographic analyses for Fe, Cr and Ni are given in Table 5. As a result of reduction there was a slight increase in Fe content and possibly in the Ni and Cr. An O/U mole ratio of 2.09 ± 0.03 was found for the six reduced powder batches. X-ray diffraction patterns obtained with Cu K α radiation showed that all products were UO_2 ; no extra lines were present. Surface areas of the six batches, given in Table 6, are reasonably consistent at $5.1 \left[\begin{array}{c} + 0.6 \\ - 0.4 \end{array} \right] \text{ m}^2/\text{g}$ with the exception of Batch 4 at $3.4 \text{ m}^2/\text{g}$. However even this low figure is within the range of surface area in which UO_2 powders generally show good sinterability. This batch showed similar sinterability to the other batches (Table 12). The pour and tap densities of the six batches (Table 7) were found to be close to 1.3 and 1.9 g/cm^3 respectively.

3.2.4 Pressed pellets

The green densities of pellets isopressed at various pressures are shown in Table 8. Comparing these with the sintered densities obtained at various temperatures in Table 10, it can be seen that a pellet having a green density of approximately 5.3 g/cm^3 (that is, isopressed at approximately 17 tons/in^2) should sinter to at least 10.6 g/cm^3 at $1,500^\circ\text{C}$. The green densities obtained at each isopressing pressure may show some increase if the powder is precompact and regranulated before pressing.

3.2.5 Sintered pellets

The spectrographic and O/U analyses of sintered pellets from the blended batches pressed at 15 tons/in^2 and sintered at four different temperatures are given in Table 9. The Fe content is lower than in the reduced powder and Ni and Cr are almost the same. The O/U mole ratio is very close to 2.000 and is well within the stoichiometry requirement normally quoted for reactor grade UO_2 , that is, 2.000 to 2.005 . X-ray diffraction patterns from the surface of the sintered pellets showed an unidentified extra line at a d-spacing of 3.4 \AA , which

is close to that of an intense U_3O_8 line. U_3O_8 could not have formed in the furnace but may have formed as a surface film if specimens were removed to air without sufficient cooling. However, the water vapour content of the hydrogen atmosphere in the furnace was known to be approximately $10,000$ to $20,000 \text{ p.p.m.}$ as a result of air ingress around the door seals, and these seals were improved before further X-ray diffraction was carried out. Pellets prepared from the same blended batch, when resintered in the furnace and cooled to below 100°C before removal, gave UO_2 X-ray patterns with no extra lines.

The sintered densities of pellets pressed at $7, 10, 15$ and 20 tons/in^2 from the blended reduction batches and sintered at $1,400, 1,500, 1,600$ and $1,700^\circ\text{C}$ are shown in Table 10. Table 11 indicates that very reproducible sintered densities are obtained between different sintering runs. Table 12 shows results on the material processed from the individual precipitation batches pressed at 10 tons/in^2 and sintered at $1,500^\circ\text{C}$. There is good reproducibility between these batches. In this case the relatively low pressing pressure and sintering temperature was selected to enhance any possible variations in sinterability.

The microstructures of the blended powder when pressed at 20 tons/in^2 and sintered at $1,400, 1,500, 1,600,$ and $1,700^\circ\text{C}$ are compared in Figure 11. The microstructures reveal that the porosity is confined mainly to areas which may result from the presence of powder granules differing in sinterability. More uniformly distributed porosity would be desirable and this aspect will be studied in later phases of this work. The grain sizes of pellets pressed at $7, 10, 15$ and 20 tons/in^2 and sintered at $1,400, 1,500, 1,600$ and $1,700^\circ\text{C}$ are shown in Table 13.

The simplest method of converting the -100 mesh powder to a form suitable for die-pressing would be by precompaction and granulation without binder. The authors' previous (unpublished) experience in granulation of beryllium oxide powders of sinterability similar to that of the present UO_2 has shown that, provided the precompaction pressure is less than one-half the final pressing pressure, the sinterability is not affected and no artefacts related to precompaction appear in the microstructure. A similar situation would be expected to apply to the present UO_2 powder.

4. CONCLUSIONS

- (i) The ADU prepared in the equipment described was found to produce a sinterable or ceramic grade UO_2 powder on reduction under standard conditions. Evaluation of the sintered densities shows that 99 per

cent of all sintered pellets have densities above 10.6 g/cm^3 when isostatically pressed at 15 tons/in^2 and sintered at $1,600^\circ\text{C}$ for 4 hours.

- (ii) The intermediate and final products in the three main stages, namely, precipitation and drying, calcination-reduction, and sintering, showed only minor inconsistencies between batches; these variations decreased when several batches were blended at the various stages.
- (iii) The sintered microstructure of the blended powder shows a non-uniform distribution in porosity arising from the presence of relatively hard UO_2 granules. Avoidance or removal of these granules will be studied in later phases of this work.
- (iv) Although die-pressing was not studied, it is predicted that the standard powder when converted to a die-press powder by precompaction and granulation without binder would sinter similarly to the -100 mesh powder studied here.
- (v) It has been established that the equipment constructed is capable of producing sinterable UO_2 of high purity and acceptable reproducibility. It will now be used for preparing various UO_2 powders for further study as outlined in the introduction to this report.

5. ACKNOWLEDGEMENTS

The enthusiasm and support of Mr. W. J. Wright is gratefully acknowledged.

The assistance of Mr. B. Breadner and Mr. G. Shaw with the experimental work and the service of Analytical Chemistry and X-ray Diffraction Groups is also acknowledged.

The authors thank Dr. K. D. Reeve for helpful criticism of the text and for useful discussions with him throughout the work.

6. REFERENCES

- Bourns, W. T. and Watson, L. C. (1961). - AECL 1312.
 Watson, L. C. (1957). - Fuel Element Conference. Paris, TID-7546 - Book 2.

APPENDIX

EQUIPMENT DETAILS AND STANDARD OPERATING CONDITIONS

Nitrate Tank

Height	5 ft
Diameter	6.5 in
Overall capacity	31 litres
Solution concentration	150 g of U/litre
Solution pH	1.8
Tank air pressure	15 lb/in ² (normal)

Precipitation Tank

Overall height	10 in.
Diameter	4 in.
Overall capacity	1.9 litres
Impeller blade	2 in.
Disc spreader	2½ in. dia.
Impeller speed	300 rev/min
UN flow	270 ml/min
NH ₃ flow	6.2 litre/min
Solution pH	7.2 ± 0.2

pH Cell

Overall height	5½ in
Diameter	4 in
Capacity to overflow	550 ml

Conditioning Tank and Dump Tank

Overall height	13 in.
Diameter	10 in.
Overall capacity	14.3 litres
Conditioning tank impeller	6 in. dia.
Impeller speed	100 rev/min (normal)

Filtrate Tank

Height	17 in.
Width	17 in.
Breadth	17 in.
Total capacity	81 litres

Continued...

(2)

APPENDIX (Continued)

Demineralised Water Wash Tank

Height	12 in.
Width	22½ in.
Breadth	22½ in.
Total capacity	100 litres

Filter

Diameter	9½ in.
Width	9 in.
Filter cloth	Terylene
Drum speed	Variable 1-10 rev/min
Scraper blade	Polythene
Vacuum	150 mm of Hg
Water wash	160 ml/min

Drying Oven

Internal dimensions	18 in. high x 15 in. x 15 in.
Loading	5-6 kg/24 hours
Drying temperature	100°C

Reduction Furnace

Furnace

Element	5 kW Nichrome
Chamber diameter	10 in.
Chamber depth	30 in.
Outside diameter	28 in.

Furnace Tube

Height	36 in.
Diameter	6½ in.
Uniform heating zone	18 in.
Number of trays	10
Tray diameter	5 in.
Tray height	1½ in.
Gas flow during reduction	1.5 litres/min
Capacity	1.5 kg/24 hours (UO ₂)

Continued...

(3)

APPENDIX (Continued)

Cooling Tank

Height	33 in.
Diameter	12 in.
Coolant	Circulating hot and cold water and dry ice

TABLE 1

SPECTROGRAPHIC ANALYSIS OF ELDORADO-MINING-AND-REFINING COMPANY
NUCLEAR GRADE URANYL NITRATE HEXAHYDRATE

(Eldorado Uranium Products Typical Properties Data Sheet)

Element	p.p.m. on U Basis
Ag	0.5
Al	< 10
B	0.15
Cd	< 0.2
Cr	< 10
Cu	< 1
Fe	10 (C)
Mn	< 1
Mo	< 0.5 (C)
Ni	< 5
Si	< 10
Th	< 10 (C)
V	< 10

(C) Chemical Analysis

TABLE 2

SPECTROGRAPHIC ANALYSIS OF SIX BATCHES OF WET ADU
AND URANIUM NITRATE HEXAHYDRATE CRYSTALS

Batch	p.p.m. on U basis			
	Fe	Al	Mg	Cu
1	25	15	10	85
2	10	< 10	4	35
3	10	< 10	8	20
4	15	< 10	2	45
5	10	< 10	2	8
6	10	< 10	1	8
UNH Crystals	10	< 10	10	100

p.p.m. of other elements in all cases

B < 1
 Pb < 1
 Cr < 10
 Ni < 10
 Zn < 20
 Na < 20
 Mo < 5
 Mn < 5
 Cd < 10

TABLE 3

ANALYSIS OF SIX BATCHES OF DRIED ADU PRECIPITATE

Batch	p.p.m. on U basis (Spectrographic)			wt % U (Gravimetric)	Mg/g U (Gravimetric)	
	Fe	Ni	Cr		NO ₃	NH ₃
1	15	< 10	< 20	64.7	31.4	31.8
2	25	0	0	72.4	21.6	62.7
3	10	0	0	57.8	36.9	27.3
4	20	15	0	68.6	52.1	55.8
5	15	0	0	55.3	25.7	31.8
6	20	0	0	68	33.2	30.0

0 = below level of detection by the method used

TABLE 4

COMPARISON BETWEEN X-RAY DIFFRACTION d-VALUES (Å) OF ADU
FROM THIS STUDY AND THOSE LISTED IN THE A.S.T.M. INDEX

This Study	A.S.T.M. Index Card 13-59
1.70	1.70
1.764	1.76
1.955	1.94
2.025	2.02
2.534	2.51
3.155	3.12
3.493	3.46
7.225	7.05

TABLE 5

SPECTROGRAPHIC ANALYSIS OF SIX BATCHES OF REDUCED UO₂ POWDER

Batch	p.p.m. or U basis			Molar O/U ratio
	Fe	Ni	Cr	
1	45	10	10	2.085 ± 0.003
2	40	10	10	2.110 ± 0.005
3	40	10	10	2.079 ± 0.002
4	80	10	10	2.060 ± 0.001
5	90	10	10	2.066 ± 0.004
6	30	5	10	2.120 ± 0.001

TABLE 6

B.E.T. SURFACE AREAS OF SIX BATCHES OF REDUCED UO₂ POWDER

Batch	Surface Area (m ² /g)
1	4.7
2	5.3
3	5.7
4	3.4
5	4.9
6	4.9

TABLE 7

POUR AND TAP DENSITIES OF -100 MESH UC₂ POWDER

(BLENDED BATCHES)

Mean pour density (g/cm ³)	1.31
Standard deviation (g/cm ³)	< 0.01
Sample size	6
Mean tap density (g/cm ³)	1.87
Standard deviation (g/cm ³)	< 0.01
Sample size	6

TABLE 8

GREEN DENSITIES OF PRESSED UO₂ PELLETS

(BLENDED BATCHES)

Pressing Pressure (tons/in ²)	Mean Green Density (g/cm ³)	Standard Deviation (g/cm ³)	Sample Size
7	4.63	0.02	5
10	4.84	0.03	5
15	5.20	0.07	5
20	5.43	0.04	5

TABLE 9

SPECTROGRAPHIC ANALYSIS OF SINTERED UO₂ PELLETSPRESSED AT 15 tons/in²

(BLENDED BATCHES)

Temperature °C	Impurities on U basis (p.p.m.)				O/U Ratio
	Fe	Ni	Cr	Mg	
1,400	15	5	10	10	2.000
1,500	15	10	10	10	2.000
1,600	25	10	10	30	2.001
1,700	20	10	10	10	2.001

TABLE 10

DENSITIES OF UO₂ SINTERED AT FOUR DIFFERENT TEMPERATURES

(BLENDED BATCHES)

Sintering Temperature (°C)	Pressing Pressure (tons/in ²)	Mean Density (g/cm ³)	Standard Deviation (g/cm ³)	Percentage Theoretical Density	Sample Size
1,400	7	10.15	0.05	92.6	17
	10	10.27	0.03	93.8	13
	15	10.39	0.06	95.0	17
	20	10.49	0.04	95.8	18
1,500	7	10.44	0.03	95.3	16
	10	10.49	0.05	95.8	18
	15	10.59	0.03	96.8	18
	20	10.64	0.03	97.1	18
1,600	7	10.59	0.01	96.8	104
	10	10.61	0.01	96.9	105
	15	10.67	0.02	97.4	107
	20	10.71	0.02	97.7	108
1,700	7	10.63	0.02	97.1	18
	10	10.69	0.02	97.6	18
	15	10.71	0.03	97.8	18
	20	10.78	0.02	98.4	18

TABLE 11

DENSITIES OF UO_2 SINTERED FOR 4 HOURS AT $1,600^\circ C$

SIX SEPARATE FURNACE RUNS (BLENDED BATCHES)

Furnace Run	Pressing Pressure (tons/in ²)	Mean Sintered Density (g/cm ³)	Standard Deviation (g/cm ³)	Sample Size
A	7	10.59	0.02	18
	10	10.60	0.03	18
	15	10.68	0.02	18
	20	10.68	0.04	18
B	7	10.59	0.02	18
	10	10.62	0.02	18
	15	10.65	0.02	18
	20	10.70	0.01	18
C	7	10.59	0.02	14
	10	10.61	0.02	15
	15	10.66	0.02	17
	20	10.71	0.03	18
D	7	10.59	0.03	18
	10	10.61	0.02	18
	15	10.68	0.03	18
	20	10.71	0.02	18
E	7	10.60	0.02	18
	10	10.60	0.02	18
	15	10.67	0.03	18
	20	10.70	0.01	18
F	7	10.61	0.02	18
	10	10.63	0.02	18
	15	10.70	0.01	18
	20	10.75	0.02	18
All runs combined for each pressure *	7	10.60	0.01	104
	10	10.61	0.01	105
	15	10.67	0.02	107
	20	10.71	0.02	108

* Calculated from all data for each pressure.

These are not an average mean and standard deviation.

TABLE 12

DENSITIES OF SIX SEPARATE PRECIPITATION BATCHES OF UO_2 SINTERED INTHE PUSHER FURNACE IN THE SAME RUN AT $1,500^\circ C$ FOR 4 HOURS IN HYDROGEN

Batch	Sintered Density (g/cm ³)	Standard Deviation (g/cm ³)	Percentage Theoretical Density	Sample Size
1	10.56	0.01	96.5	9
2	10.57	0.01	96.5	10
3	10.58	0.01	96.6	10
4	10.59	0.01	96.8	6
5	10.55	0.01	96.4	7
6	10.50	0.01	95.9	7
Blended batches 1 to 6	10.56	0.02	96.4	8

TABLE 13

GRAIN SIZES OF UO_2 PELLETS SINTERED FOR 4 HOURS

Sintering Temperature (°C)	Pressing Pressure (tons/in ²)	Mean Grain Size (μm)
1,400	7	2
	10	4
	15	6
	20	5
1,500	7	6
	10	6
	15	5
	20	9
1,600	7	9
	10	12
	15	9
	20	9
1,700	7	14
	10	14
	15	16
	20	18

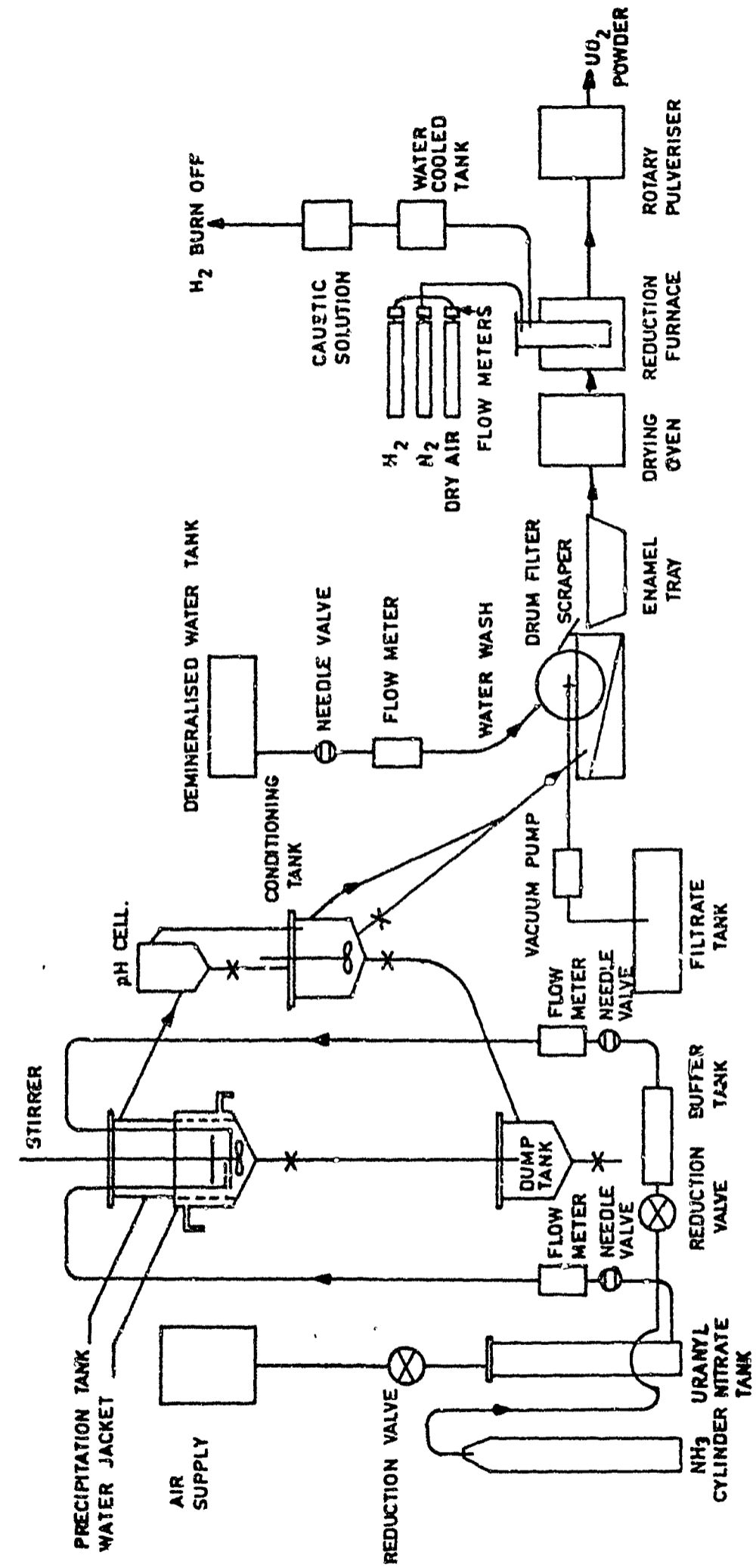


FIGURE 1. EQUIPMENT FLOW SHEET FOR THE PREPARATION OF URANIUM DIOXIDE POWDER

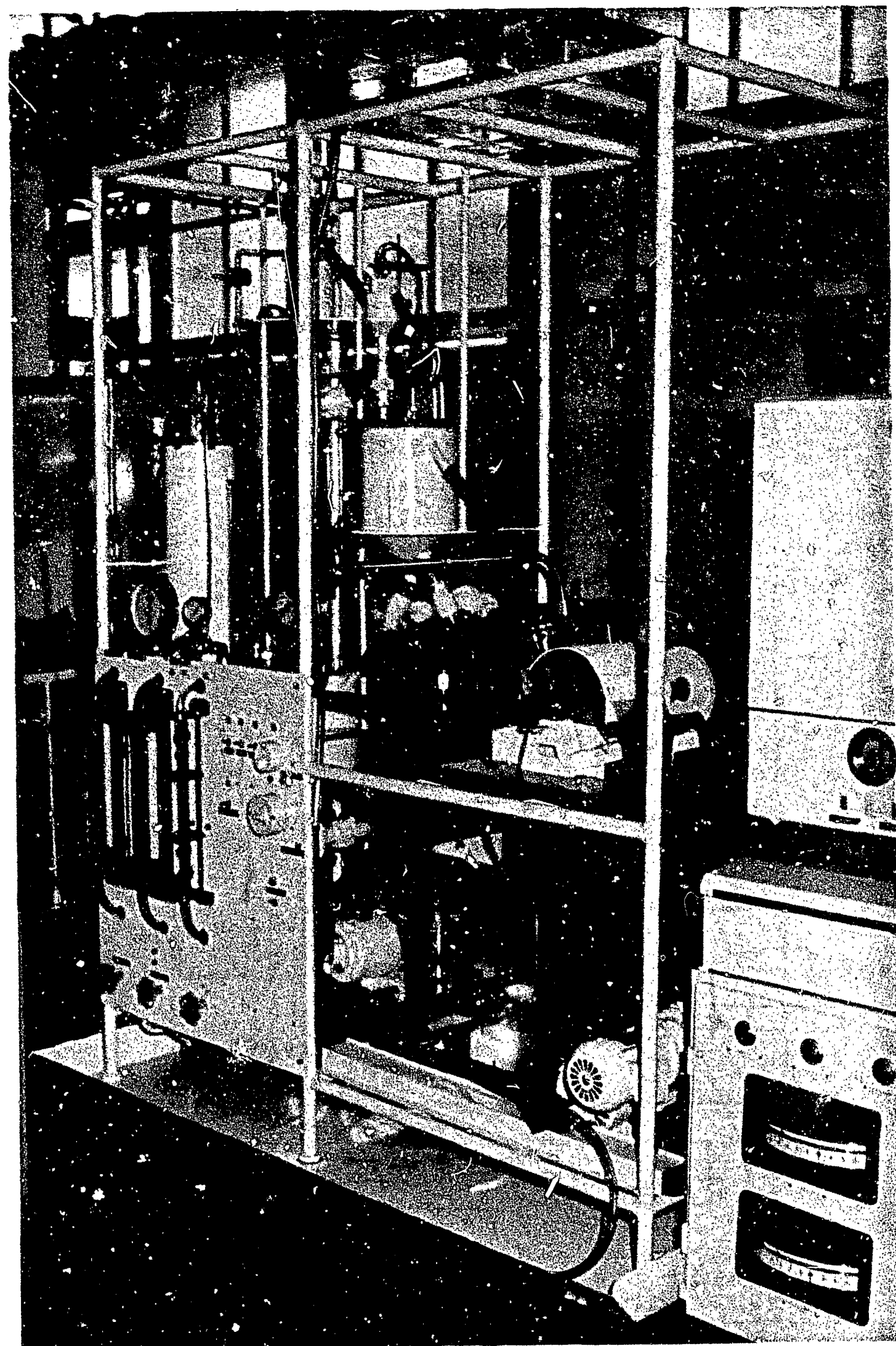


FIGURE 2. GENERAL VIEW OF THE EQUIPMENT USED FOR THE PREPARATION OF URANIUM DIOXIDE POWDER

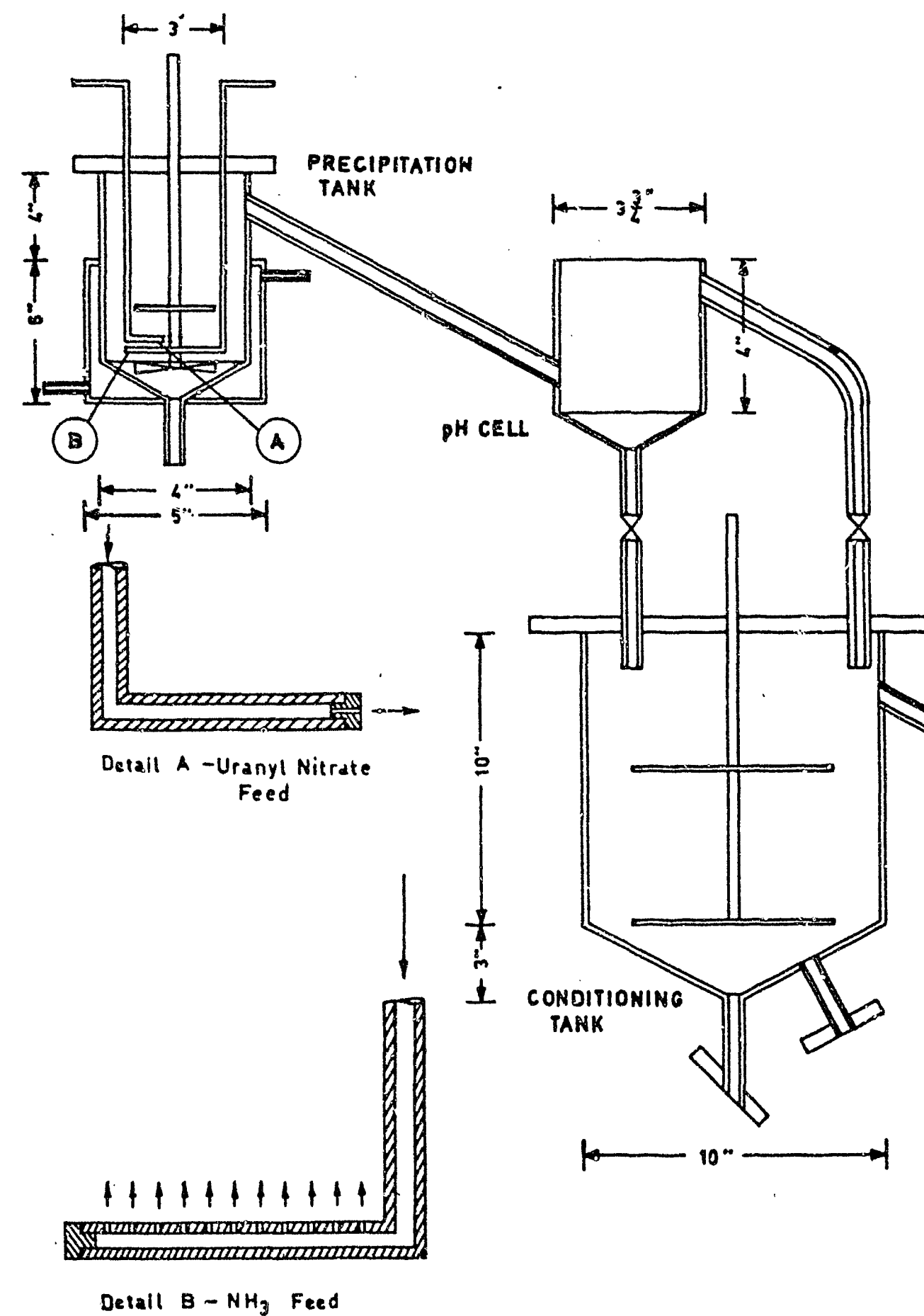


FIGURE 3. PRECIPITATION TANK, pH CELL AND CONDITIONING TANK (SCHEMATIC)

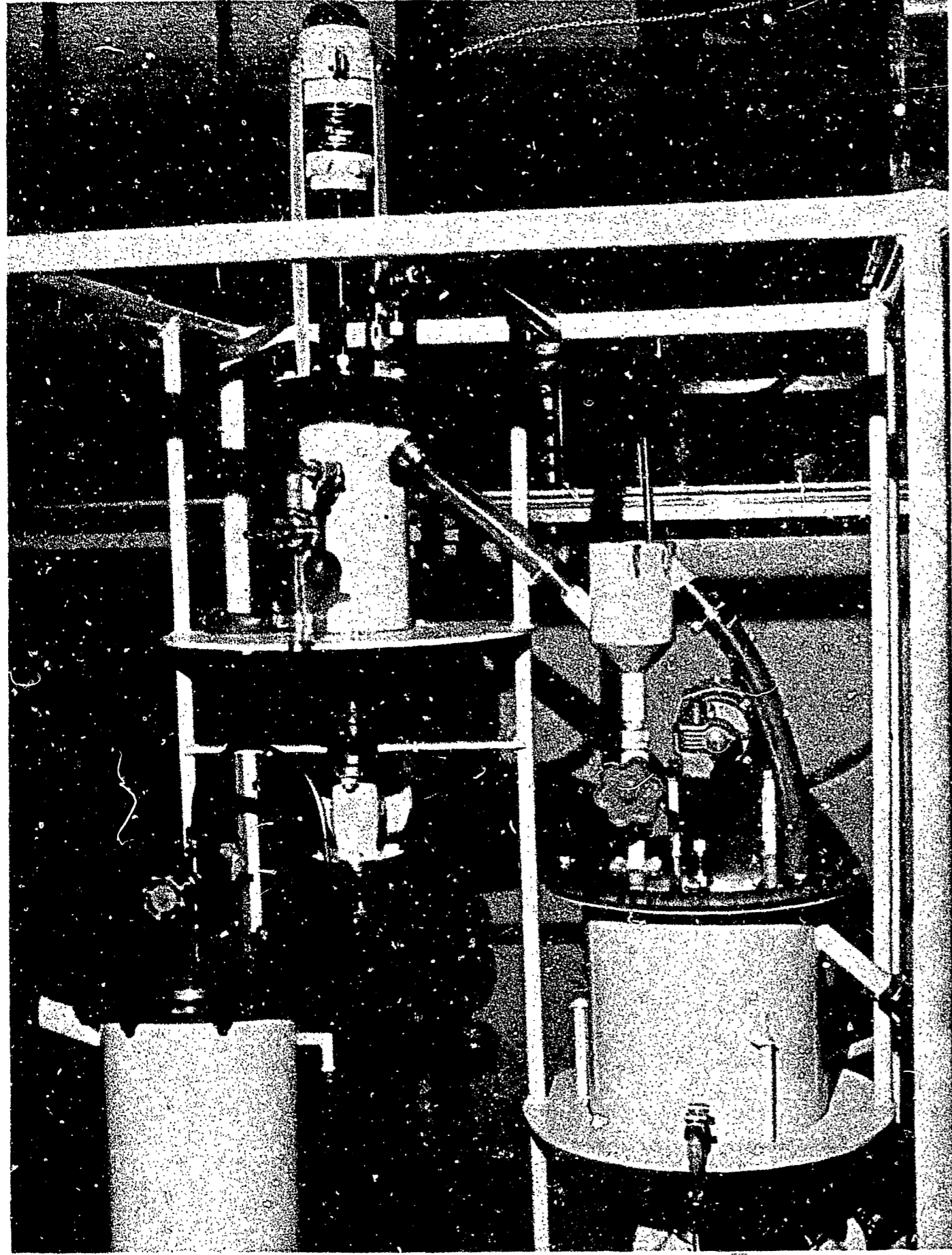


FIGURE 4. THE PRECIPITATOR, pH CELL AND CONDITIONING TANK

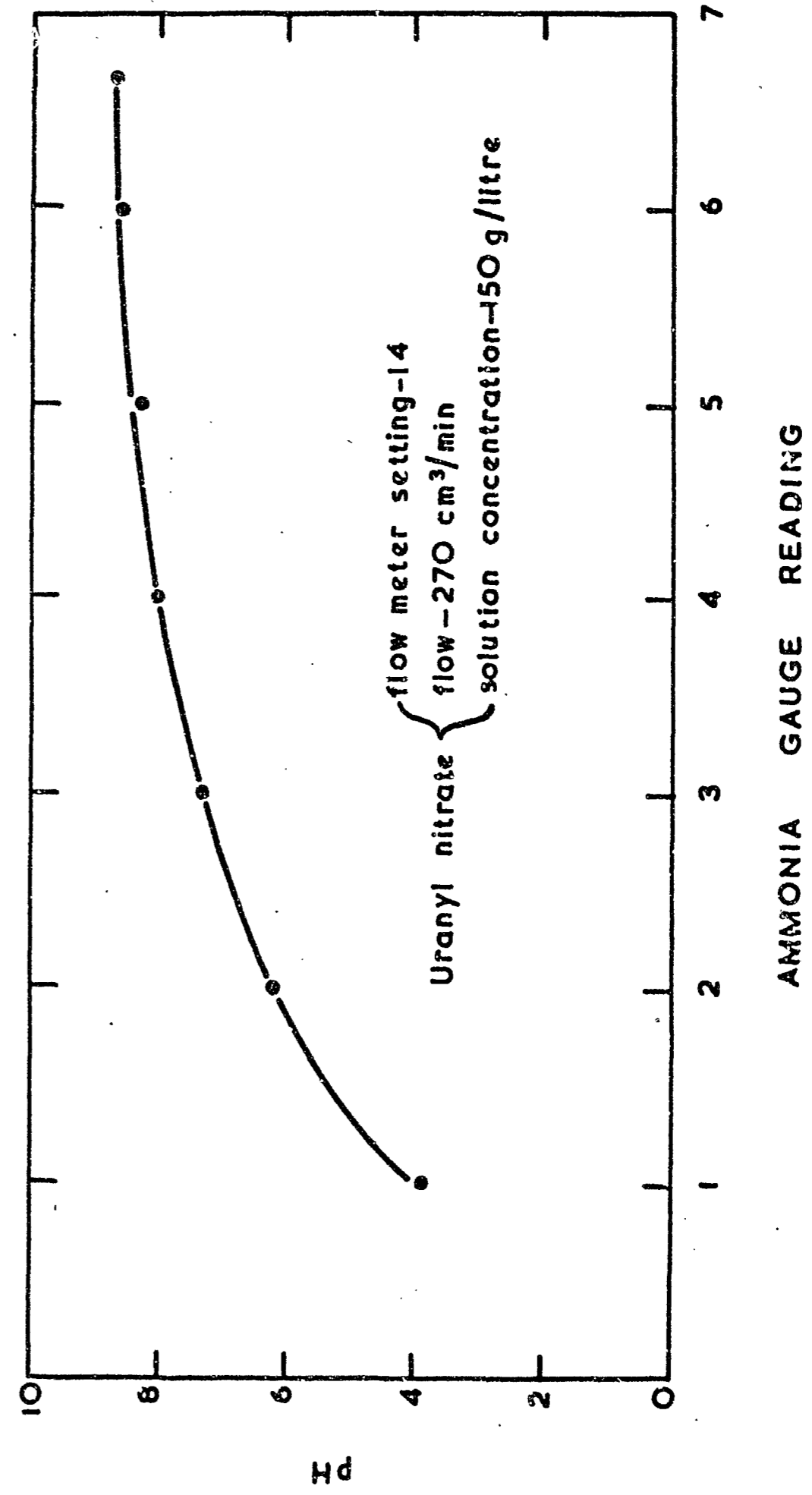


FIGURE 5. pH OF PRECIPITATION VERSUS AMMONIA FLOW

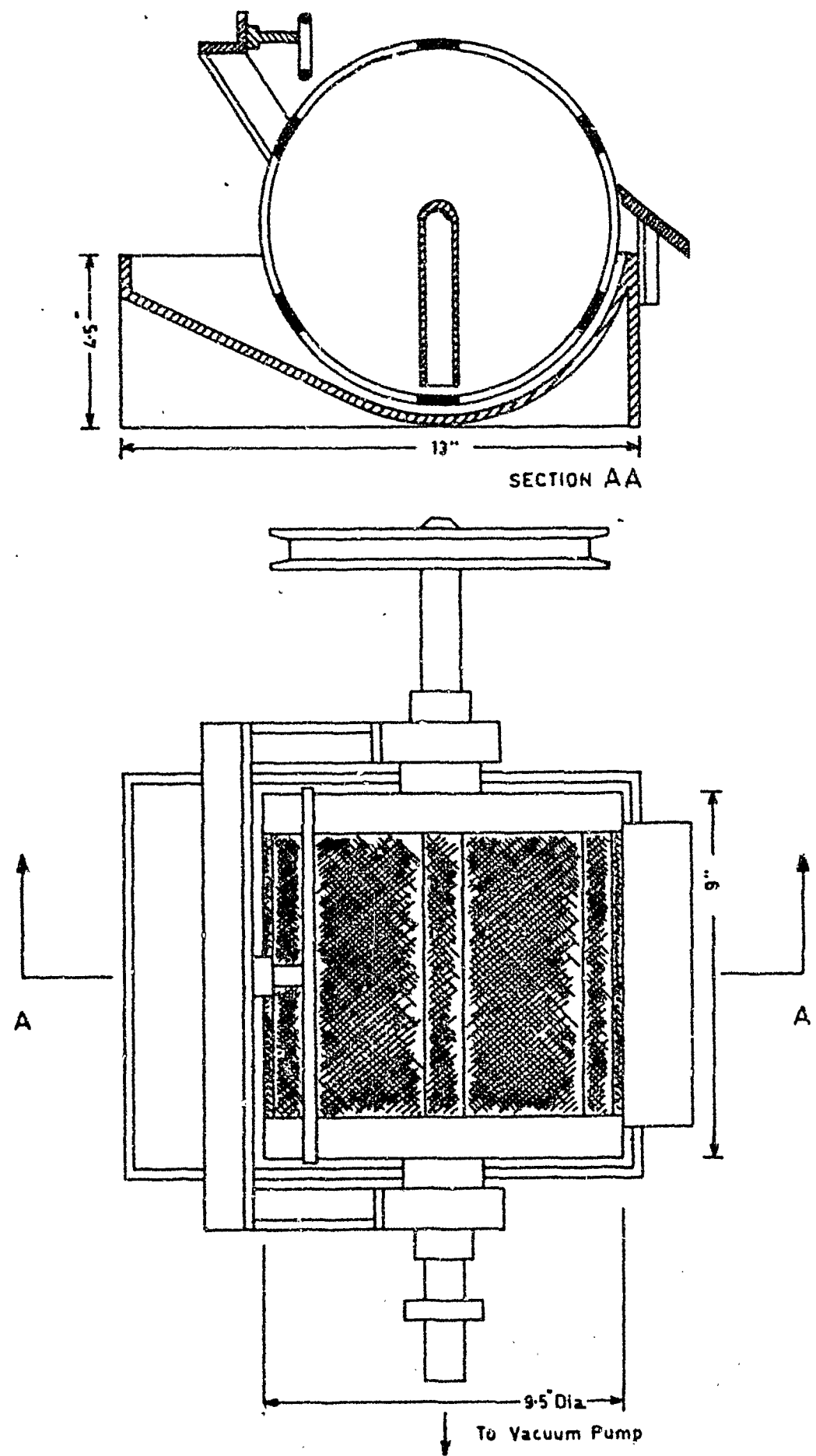


FIGURE 6. THE FILTER SHOWN SCHEMATICALLY

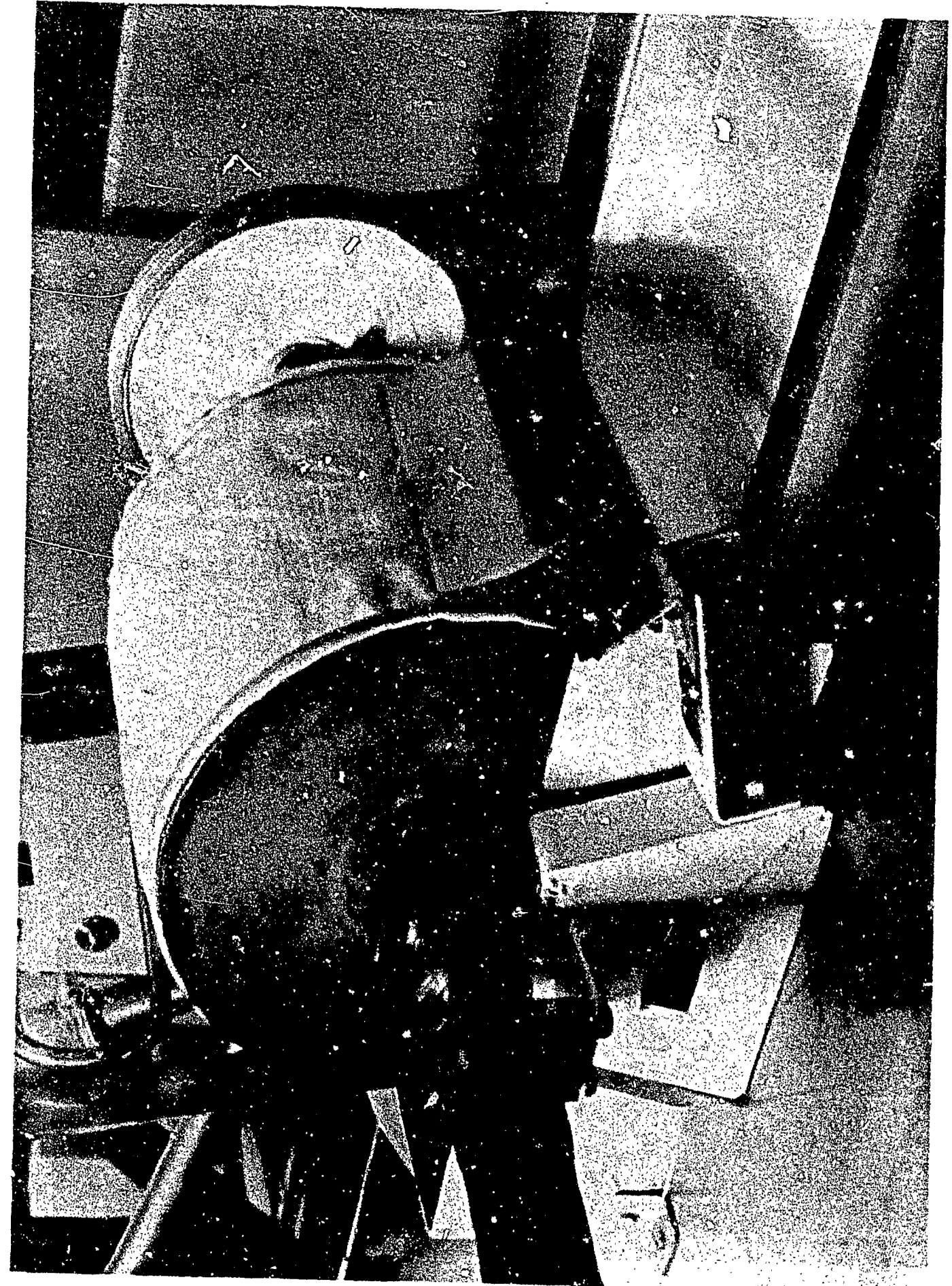


FIGURE 7. THE FILTER

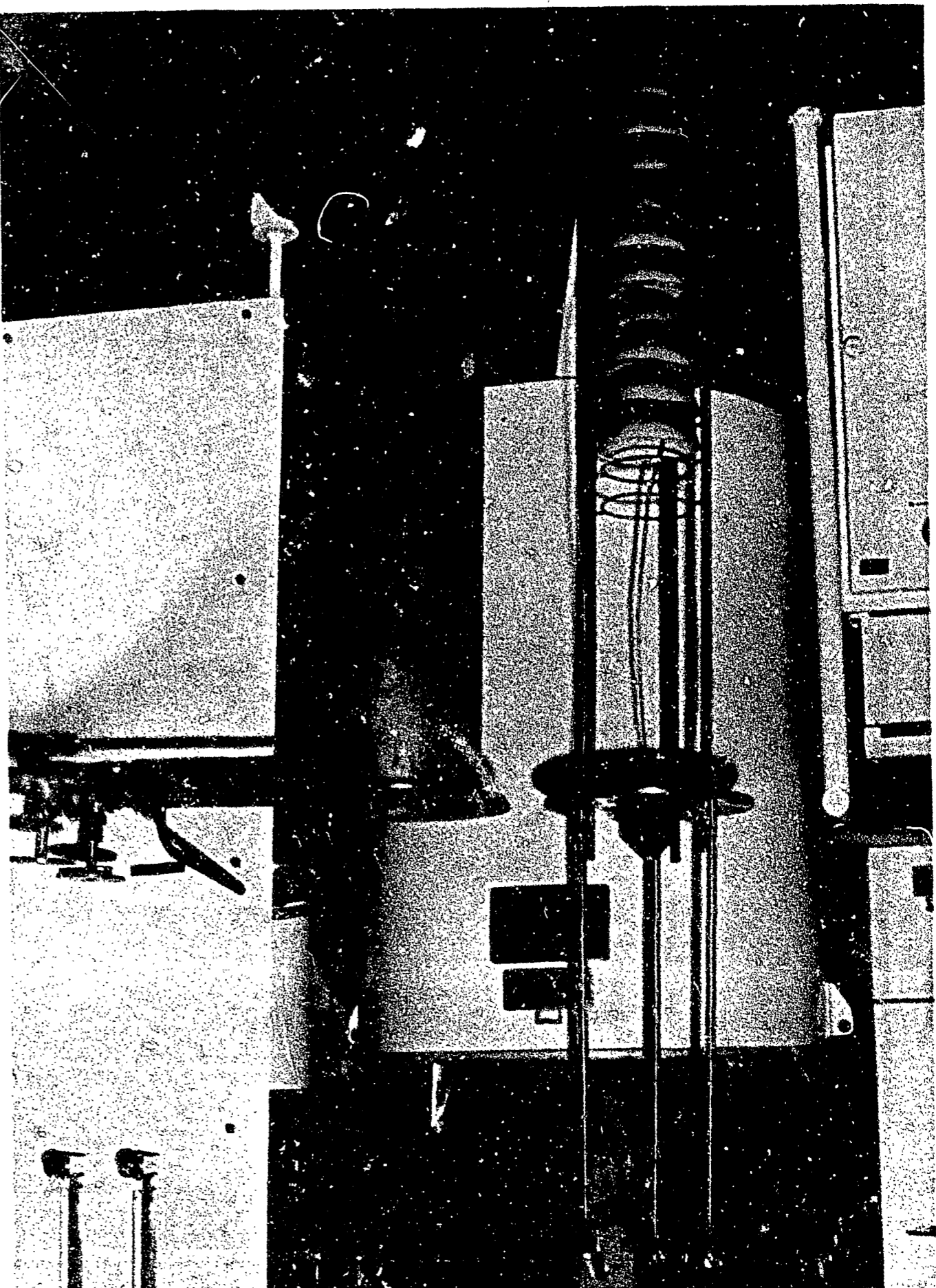


FIGURE 8. THE REDUCTION FURNACE

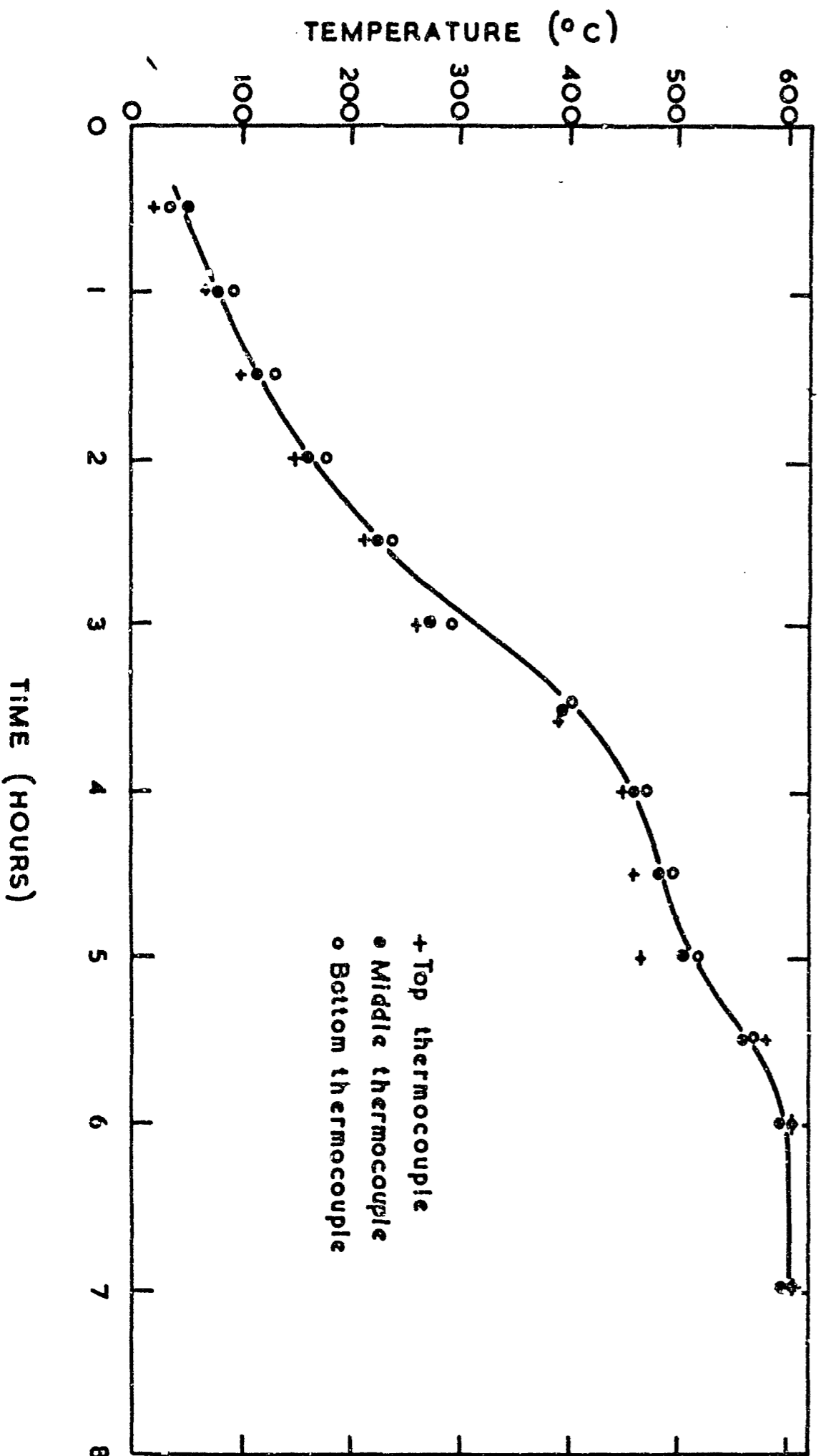
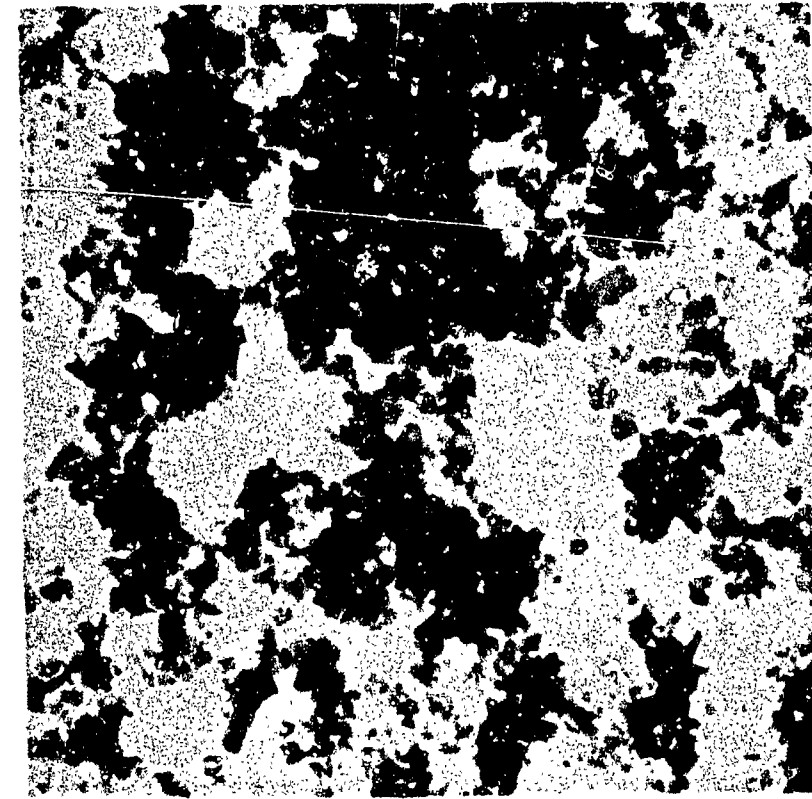


FIGURE 9. A TYPICAL HEATING CURVE IN THE REDUCTION STAGE

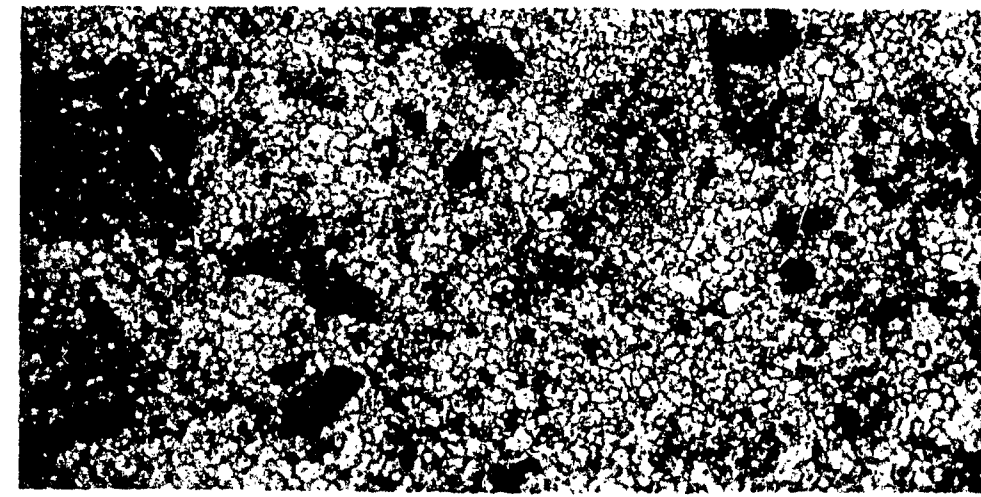
FIGURE 10. ELECTRON MICROGRAPHS OF WET ADU DISPERSED IN ALCOHOL



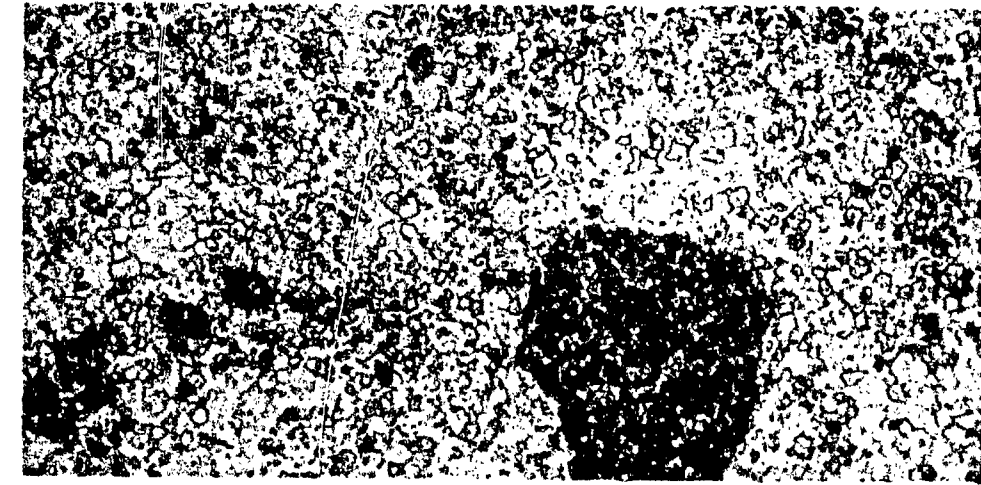
(X20,000)



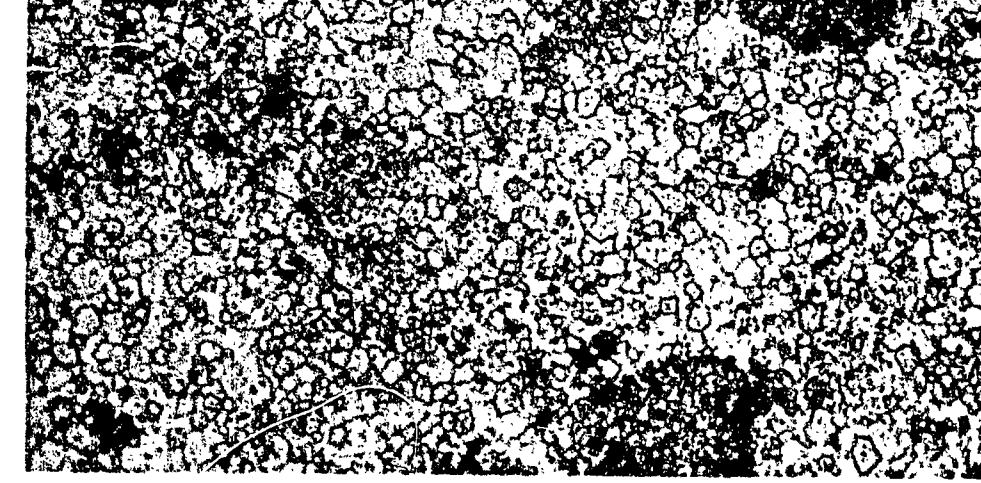
(X80,000)



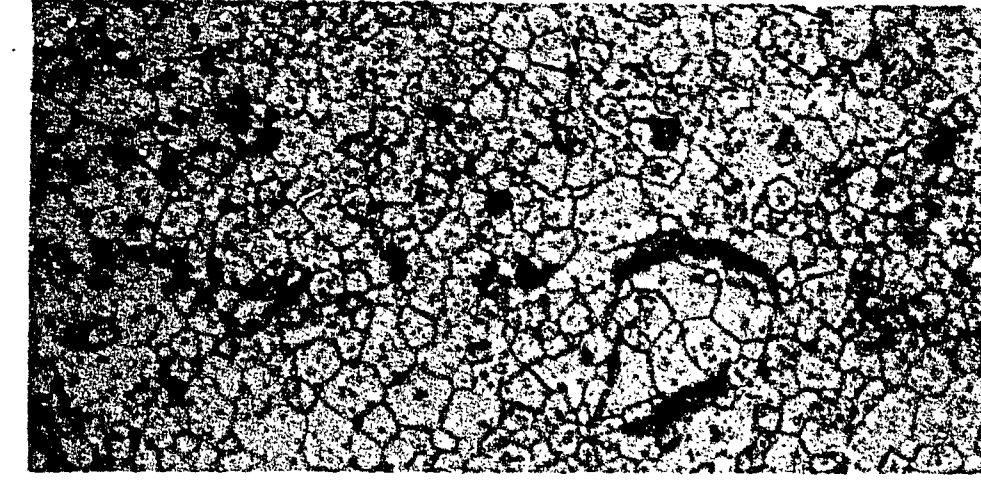
1400°C



1500°C



1600°C



1700°C

(X250)

FIGURE 11. TYPICAL MICROSTRUCTURES OF UO₂ ISOPRESSED AT 20 TONS/IN², AND SINTERED FOR 4 HOURS AT VARIOUS TEMPERATURES