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ABSTRACT

Nuclear grade ammonium diuranate (ADU) and UO_2 powders were produced on a pilot plant scale by the continuous single-stage precipitation of ADU with ammonium hydroxide, dewatering with a rotary drum vacuum filter or a solid bowl centrifuge, and batch-tray drying and calcination-reduction to UO_2 powder.

Precipitation at 50°C and pH values in the range 7.2 to 8.0 produced ADU materials which could be converted to UO_2 powder by calcination and reduction at temperatures of 600 to 730°C, and fabricated into sintered pellets with densities of 10.37 to 10.77 g cm^{-3}. The lower the pH of precipitation the lower was the reduction temperature required to achieve a specified pellet density.

(Continued)

Precipitation with ammonium hydroxide at 80°C and with ammonia gas at 50°C offered no advantages over precipitation with ammonium hydroxide at 50°C. The UO_2 powders and sintered pellets produced from ADU powders precipitated by the three methods were similar.

Precipitation at pH 7.5 and 50°C is recommended since a reasonably filterable precipitate can be produced reproducibly without a need for stringent control, and considerable flexibility is available in the subsequent production of a sinterable UO_2 powder.

Dewatering of ADU slurries was carried out more efficiently using a solid bowl centrifuge rather than a rotary drum vacuum filter. Clearer discharge liquids were produced at a higher rate of throughput in the solid bowl centrifuge.

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ADU; AMMONIUM HYDROXIDES; CALCINATION; MEDIUM TEMPERATURE; PH VALUE; PILOT PLANTS; POWDERS; PRECIPITATION; PRODUCTION; REDUCTION; SLURRIES; URANIUM DIOXIDE

CONTENTS

(Continued)

1. INTRODUCTION

Pilot plant facilities were established for the production of nuclear grade natural uranium dioxide (UO_2) powder from Australian ore concentrates as part of the Australian Atomic Energy Commission's program to develop a capability for the production of fuel elements for uranium dioxide fuelled, water-cooled power reactors (Alfredson 1972). The objectives of this research and development work were to establish the necessary technology using conventional techniques and to make improvements to processes and equipment where possible.

Several steps are involved in converting uranium ore concentrate (yellow cake) to uranium dioxide powder; these include the dissolution of yellow cake, purification by solvent extraction, precipitation of ammonium diuranate (ADU), filtration, drying, calcination and reduction to give uranium dioxide powder. This report describes the investigation of the processes for precipitation, filtration and drying of ADU. The behaviour of the ADU in subsequent process steps, particularly calcination and reduction, was also considered in assessing its quality. The importance of the ADU precipitation conditions on the properties of UO_2 powders and pellets was previously reported (Janov, Alfredson & Vilkaitis 1971), and therefore the ADU powders were assessed from the quality of the subsequent UO_2 powder and pellet products.

The essential properties of sinterable UO_2 powder are chemical purity and sinterability, that is the ability to sinter reproducibly to a high density at relatively low temperatures in as short a time as possible. For example, the Canadian specification (Chalder 1961) requires, among other things, that the powder be pressed at not more than 276 MPa, and sintered in a hydrogenous atmosphere for not more than 1.5 h at a temperature not exceeding 1650°C to give a coherent pellet of density not less than 10.4 g cm^{-3}. In this work, densities as high as 10.6 g cm^{-3} were of interest and the allowable sintering time was four hours. In addition, the Canadian specification requires that the microstructure of sintered pellets be homogeneous and free of large defects. The UO_2 powder should therefore be homogeneous and free from tightly bound agglomerates. In particular, the uniformity of the powder and the reproducibility of its behaviour during fabrication are important factors in determining the reject rate of the pellets and the cost of fabrication.

Continuous single-stage precipitation using ammonium hydroxide was chosen for the pilot plant production of ADU, because previous work in smaller equipment (Janov, Alfredson & Vilkaitis 1971) had shown that although two-stage precipitation gave more flexibility in operation and required less stringent control than single-stage precipitation, these advantages were offset by the additional complexity of the two-stage system. Two methods for dewatering ADU slurries were investigated: rotary drum vacuum filtration and the use of a solid bowl centrifuge. The wet ADU cake was dried in trays in an electrically heated oven. Reduction of ADU to UO_2 was carried out in a batch-tray furnace using process cycles developed on the half-kilogram scale (Alfredson & Janov 1971), and UO_2 pellets were fabricated by standard procedures described by E. Ramm *et al.*,(AAEC unpublished report).

2. DESCRIPTION OF PILOT PLANT

An equipment flowsheet for ADU precipitation with ammonium hydroxide, dewatering and drying is shown in Figure 1 and a general view of the precipitation and filtration equipment is shown in Figure 2. All the equipment which came into contact with the reagents or product was made from stainless steel unless otherwise stated.

2.1 Precipitator

The precipitation vessel, 0.3 m dia. x 0.7 m high, had a working volume of 25 litres. A variable speed stirrer was mounted centrally. Purified uranyl nitrate and ammonium hydroxide were fed to the precipitation vessel by gravity from storage tanks located seven metres above it. The flow rate of uranyl nitrate through the 13 mm feed-line was set manually while the flow rate of ammonium hydroxide was controlled automatically to give the desired pH.

The uranyl nitrate was released into the precipitation vessel through a sparge ring of diameter 0.15 m (Figure 3). The 6 mm ammonium hydroxide feed-line was terminated above the impeller of the stirrer to facilitate rapid mixing with the contents of the precipitation vessel. The precipitation vessel was heated by electrical immersion coils with a total rating of two kilowatts. The current in each of the two elements was varied separately by a variable transformer to maintain the desired temperature in the precipitation vessel. The ADU product slurry overflowed from the precipitation vessel into a delay tank, 0.6 m dia. x 0.7 m high, with a working volume of 85 litres where it was maintained in suspension by a paddle rotating at 1 Hz. A one kilowatt heating coil was provided to keep the slurry warm prior to dewatering.

The pH of the ADU slurry products was measured by electrodes mounted in a polyvinyl chloride electrode holder. The whole of the assembly was immersed in the ADU overflow stream. The electrodes were connected to a pH meter and then through a transducer to a pneumatic recorder-controller. This provided proportional plus derivative control at the desired pH setting. The proportional band gain was set at 10 per cent and a reset rate of 0.1 repeats per minute was used. Further details of the pH control system are given in the Appendix A.

Some ADU precipitations were carried out using gaseous ammonia instead of ammonium hydroxide to establish whether there were differences in the product. The ammonia and diluent air were proportioned through rotameters and mixed in a simple tee junction before being released into the precipitator. The ammonia was supplied from anhydrous liquefied gas cylinders at 163 kPa (absolute), and the ammonia flow rate was controlled manually to determine the pH of precipitation. The hollow cylindrical distributor, through which the diluted ammonia entered the reactor, was 79 mm dia. x 25 mm high and was positioned centrally 50 mm below the stirrer. It had holes, 0.8 mm dia. and 6.3 mm apart, drilled through the top surface.

2.2 Rotary Drum Vacuum Filter

ADU slurry was pumped from the delay tank to the rotary drum vacuum filter by a variable speed slurry pump (Mono, model SB15) of maximum capacity 150 litres per hour. The drum of the vacuum filter (International Combustion Products Ltd, model ROVAC) had an area of 0.3 m^2 and was divided into three separate segments. Vacuum could be applied separately to two segments while the segment at which the filter cake discharged could be operated either under vacuum, with no vacuum applied, or with air blown from inside the drum to assist the removal of the filter cake. A double layer of multifilament 3/1 twill nylon cloth (The Eimco Corporation, NY-319F; 95 x 47 threads per cm) was used as the filter septum on the drum. The air permeability of the cloth was 1.2 to 1.5 cubic metres of air per minute per square metre when a pressure difference of 250 Pa was applied across it. ADU slurry in the trough of the filter was maintained in suspension by a reciprocating agitator connected to the drive mechanism of the rotating drum. The drum speed was adjustable to a maximum speed of three revolutions per minute. The rate of agitation was proportional to the drum speed.

2.3 Centrifuge

A continuous centrifuge (International Combustion Products Ltd, model 612 Dynacone) was also investigated for dewatering ADU slurries (Figure 4). It consisted of a solid bowl, cylindro-conical in form, with an internal screw conveyor rotated at a slightly higher speed (84 Hz). The feed was admitted to the machine by means of a stationary feed pipe which discharged into the centre tube of the conveyor. From this centre tube, the ADU slurry was discharged through ports into the bowl of the machine. The rotation of the bowl imparted an angular momentum to the liquid/solid suspension, the resultant high centrifugal force caused the solids to settle on the surface of the bowl, and the liquid formed a cylindrical solid of revolution.

When the liquid reached a predetermined depth, it overflowed through discharge ports at the larger end of the bowl. The settled ADU was conveyed out of the liquid to the smaller end of the bowl, where it was progressively dewatered while being conveyed up the incline of the centrifuge and finally discharged.

The centrifuge bowl was driven at 83 Hz by a 5.36 kW main motor, and the conveyor was carried on the output shaft of a planetary gear-box which rotated with the bowl. The input shaft of the gear-box was driven by a 1.34 kW conveyor control motor. The relative differential speed between the screw conveyor and the bowl was then obtained by arranging a speed difference between gear-box input shaft and the machine.

2.4 Drying Oven

Moist ADU filter cake was collected in stainless steel trays, 0.5 m x 0.45 m x 45 mm deep, and then placed in an electrically heated oven. The drying space in the oven accommodated eight trays on horizontal shelves.

2.5 Calcination - Reduction Furnace

The ADU was converted to UO_2 in batch-tray calcination-reduction equipment previously described in detail by Alfredson & Janov (1971). It consisted of a closed reaction vessel, constructed of 321 AISI stainless steel, which was lowered into an electrical resistance furnace. Fourteen trays (0.29 m dia. x 32 mm deep) could be accommodated on the framework suspended from the top of the reaction vessel. The top section and the main body were bolted together with a Teflon gasket between them. The process gases were introduced through the top of the reaction vessel and directed *via* two tubes to the bottom of the vessel where they were released. The gases left the reaction vessel through a port in the top cover.

3. OPERATING PROCEDURE

3.1 Precipitation

Uranyl nitrate solution containing 80-120 g ℓ^{-1} of uranium was purified by solvent extraction with tributyl phosphate in kerosene (Alfredson *et al.* AAEC unpublished report). Analytical grade ammonium hydroxide (28 weight per cent) was used for ADU precipitation, but laboratory grade could possibly be used without increasing the impurity level of the uranium powders above specification. Typical impurity concentrations in the uranyl nitrate and the

Canadian specification for UO_2 powders are shown in Table 1. Table 2 gives the specifications of analytical grade and laboratory grade ammonium hydroxide (Ajax Chemicals Ltd., Sydney).

The precipitator was operated at throughputs of uranium in the range 4.8 to 7.2 kg h^{-1}, depending on variations in concentration and flow rate of uranyl nitrate. The range of reactant flow rates, concentration, temperature of precipitation and rate of stirring are shown in Table 3. The residence time of the reactants in the precipitator was 20 to 24 minutes. The duration of precipitation runs varied but generally 20-30 kg of ADU was produced per run.

3.2 Dewatering ADU Slurries

Filtration was commenced as soon as ADU slurry began to flow into the product delay tank. As the rate of filtration was slower than the rate of precipitation (Table 4), ADU slurry accumulated in the delay tank and filtration had to be completed after precipitation was concluded. In the standard method of operating the filter, a vacuum of 90 kPa was applied to two segments of the drum but not to the segment required for filter cake removal (see Section 2.2). Through this segment, air was blown from inside the drum every ten minutes to completely dislodge the filter cake which had built up on the drum. The scraper for continuous removal of the filter cake was set three millimetres from the surface of the filter drum. The temperature of the slurry during filtration was 35-40°C. The filter cake was not washed with demineralised water in the standard method of filtration. The filter drum was generally operated at 0.043 Hz.

The solid bowl centrifuge was operated over a range of conditions (Figure 5), but for normal production of ADU the weir height was 22 mm and the slurry temperature was 50°C. ADU slurry was fed to the solid bowl centrifuge at 150 ℓ h^{-1}. This throughput was greater than the rate of ADU production (72 ℓ h^{-1}) and hence dewatering of ADU was not commenced until the ADU slurry delay tank was almost full.

3.3 Drying

Wet ADU filter cake was dried in an oven at 110°C for approximately 36 hours. About 8 kg of wet ADU was loaded per tray to a depth of 40 mm. To assist drying, the ADU in the trays was turned over with a hand scoop from time to time.

3.4 Calcination - Reduction

Generally, seven kilograms of ADU per batch was reduced to UO_2. The ADU was loaded into seven trays without any prior crushing or granulation.

The depth of powder in the trays was 30 mm. The calcination-reduction cycle, described by Alfredson & Janov (1971), involved heating the ADU to the desired temperature in a stream of nitrogen and then reducing the calcined oxide (U_3O_8 or UO_3) in a 30 volume per cent hydrogen/nitrogen mixture at that temperature. Approximately 4.2 times the amount of hydrogen theoretically required to convert U_3O_8 to UO_2 was metered into the furnace in two hours. Reduction temperatures from 600 to 730°C were used, depending on the surface area of UO_2 required.

Freshly reduced stoichiometric UO_2 powder was cooled to room temperature in nitrogen and then stabilised with 2 volume per cent oxygen in nitrogen. The stabilisation process was continued for 16 hours (overnight) and twice the amount of oxygen required to increase the oxygen/uranium ratio to 2.10 was used.

3.5 Evaluation of UO_2 Powders

Representative samples of UO_2 powder for surface area measurement and sinterability tests were obtained by riffling. Both the classical BET method (Brunauer, Emmett & Teller 1938) and the continuous flow method developed by Nelsen & Eggertsen (1958) were used for measuring the surface area of UO_2 powders as described previously (Janov, Alfredson & Vilkaitis 1971).

The standard procedure used by the AAEC Ceramics Section (Ramm *et al.*, AAEC unpublished report) for fabricating UO_2 pellets was as follows:

- the stabilised UO_2 powder was crushed to -100 mesh BSS;
- precompacted at 69 MPa gauge;
- granulated to size -22 + 100 mesh BSS;
- pressed into pellets at 309 MPa gauge;
- sintered in hydrogen at 1600°C for four hours; and
- the sintered pellets were ground to the final size in a centreless grinder.

No binders were added to the UO_2 powder, but a stearic-acid trichloroethylene solution was used to lubricate the walls of the die during pellet formation. Instead of crushing the UO_2 powder to -100 mesh BSS, some powders were first micronised in a high speed rotary microniser to give a maximum particle size of 5-10 μm.

4. PRODUCTION EXPERIENCE AND PRODUCT ASSESSMENT

4.1 Precipitation

4.1.1 Effect of pH on properties of ADU precipitates

Precipitation of ADU was carried out at three different values of pH during the course of this work - 7.2, 7.5 and 8.0. At pH values less than

7.2, the solubility of uranium increased rapidly and there was a risk of incomplete precipitation and consequent loss of uranium. Above pH 8.0, the ADU slurry was so difficult to filter that it did not appear economically attractive for production. Table 5 gives properties of ADU slurries precipitated at these pH values; data for three runs at pH 7.2, eight at pH 7.5 and three at pH 8.0 are incorporated in these results. The accuracy with which the pH of the system could be controlled was ± 0.15, and this was the main reason for the spread in the values of the slurry properties. Variations of $\pm 10 \text{ g } \ell^{-1}$ also occurred in the concentration of the ADU slurry and this would have resulted in small variations of settling rate, settled volume and filtration rate, but no correction for this has been applied to the data in Table 5. The values for ADU settling rate have been normalised for slight variations in the measurement temperature by allowing for the change in liquid viscosity with temperature.

As the pH of precipitation increased, the slurry settled more slowly and was more difficult to filter because smaller agglomerates were formed at higher pH (Janov, Alfredson & Vilkaitis 1971). With increasing pH, the volume to which the ADU slurry settled increased and the per cent moisture left in the filter cake also increased.

The settling rate of ADU slurries was useful for checking that the pH equipment was operating correctly. A problem encountered in the early stages of this work was the tendency for the pH electrodes to become coated with ADU, thus giving incorrect pH readings. The accumulation of ADU around the electrodes was eliminated by redesigning the trough in which the electrodes were located, but slurry samples were always taken to check that the settling rate of the slurry was that expected for the pH of precipitation.

A production facility for producing ADU could be operated satisfactorily at any of these three pH values. Precipitation at pH 7.2 produces an ADU slurry with the best filtering and settling characteristics, but careful control of pH is required and the properties vary appreciably with small changes in conditions of precipitation. The quality of the ADU precipitate at pH 7.5 can be reproduced more reliably and the precipitate is still quite filterable. Precipitation at pH 8.0 can be readily controlled but the precipitate is not as filterable as that produced at pH 7.5 and therefore, from a comparison of ADU properties only, precipitation at pH 7.5 (50°C) is recommended.

4.1.2 Effect of temperature of precipitation on the properties of ADU precipitates

Precipitation at 80°C was investigated and compared with that at the standard temperature of 50°C. The ADU precipitated at pH 7.5 and 80°C was similar to that produced at pH 8.0 and 50°C (Table 6). It settled more slowly than ADU precipitated at pH 7.5 and 50°C, was more difficult to filter, and gave a wetter filtered product. The amount of ammonium hydroxide required at pH 7.5 and 80°C was approximately the same as at pH 8.0 and 50°C; consequently there does not appear to be any justification for operation at the higher temperature.

4.1.3 Precipitation using ammonia gas

Two batches (15 kg each) were precipitated using gaseous ammonia rather than ammonium hydroxide. The precipitations were carried out at pH 7.5 and 50°C, and the ammonia was diluted with three times its volume of air to aid dispersion in the uranyl nitrate. The ADU slurry produced at these conditions had properties essentially similar to those produced using ammonium hydroxide as precipitant, although the ADU did settle more rapidly but filtered slightly more slowly (Table 7). The resulting filter cake was slightly drier.

The small effect that the form of ammonia precipitant has on the properties of the ADU slurry would not be an important consideration in choosing between the use of ammonia gas and ammonium hydroxide in a production facility. This decision would be made solely with regard to comparative costs, ease of handling on a large scale, and influence (if any) on pellet fabrication.

4.2 Dewatering of ADU Slurries

4.2.1 Rotary drum vacuum filter

The operational features of the rotary drum vacuum filter were investigated with ADU slurries precipitated at pH 7.5 and 50°C. Theoretically, the rate of filtration can be described by Equation (1)

$$V = \left[\frac{2\ P\ A^2\ x}{\mu\ r_1\ C\ T}\right]^{0.5} \qquad \ldots \quad (1)$$

where V = the rate of filtration,
T = the time for one revolution of the filter drum,
P = the pressure drop applied across the filter,
A = the area of the filter,
x = the fraction of the filter area submerged in the slurry of concentration C,
μ = the viscosity of the filtrate, and

r_1 = the specific filtration resistance of the slurry.

Experimentally, the rate of filtration was observed to increase with slurry temperature (Table 8) and was inversely proportional to the square root of the viscosity of the filtrate, in agreement with Equation (1). Increasing the speed of rotation of the drum also increased the filtration rate (Table 9) in accordance with Equation (1). The moisture content of the filter cake was unaffected.

When the thickness of filter cake on the drum was decreased from 4.5 to 2 mm, the rate of filtration increased from 24 to 36 $\ell\ h^{-1}$ at 40° C. Various methods of removing the filter cake from the drum were also examined (Table 10), since the filter cloth gradually became blocked with fine ADU particles. The maximum rate of filtration (44 $\ell\ h^{-1}$) was achieved by removing all the ADU filter cake at the end of each revolution of the filter drum by continuously blowing air from the inside of the drum. However, this procedure caused 200 mg of uranium per litre of filtrate to be lost. When the filter cake was blown off only every ten minutes, the loss was reduced to 50 mg per litre.

These results were obtained using a single layer of the filter cloth. When a double layer of filter cloth was used and the filter cake was blown off every ten minutes, the loss of uranium was reduced to 10 mg per litre of filtrate without reducing the rate of filtration, and this was later adopted as the standard procedure.

4.2.2 Centrifuge

The performance of the solid bowl centrifuge was investigated using a uniform large batch of ADU slurry precipitated at pH 7.5 and 50°C. The amount of uranium in the discharge liquid is shown in Figure 5 as a function of slurry temperature, rate of feed and height of the overflow weir in the centrifuge.

At 50°C, the centrifuge could be operated at the maximum speed of the slurry feed pump (150 $\ell\ h^{-1}$), and the amount of uranium in the discharge liquid (<10 mg ℓ^{-1}) was still less than in the filtrate from the rotary drum vacuum filter which had a throughput of 40 $\ell\ h^{-1}$ when producing ADU filter cake of the same residual water content. In addition, the high separating force in the centrifuge should make it possible, with an improved design, to obtain a drier filter cake than is possible with a rotary drum vacuum filter.

The centrifuge and rotary drum vacuum filter were of comparable physical size and capital cost. The performance of the centrifuge, however, was superior to the rotary drum vacuum filter in terms of throughput and clarity of discharge liquid, while the ADU from each unit contained approximately the same amount of residual moisture.

4.3 Drying of ADU

Figure 6 shows the relationship between moisture content in ADU and time of drying for an ADU precipitated under standard conditions at a pH of 7.5. The results were obtained in the drying oven loaded with eight trays of wet ADU filter cake. The temperature in the oven decreased from 115°C in the top tray to 75°C in the bottom tray but, as can be seen in Figure 6, this did not reduce the amount of moisture removed from the ADU. Indeed, the greatest loss in weight occurred in ADU on the bottom tray at 75°C. The rate of drying was the same at 75°C and 115°C (Figure 6) but the middle tray dried more slowly at 90°C than the top or bottom trays. This was probably due to the close stacking of trays in the oven, which resulted in poor air flows across the middle trays.

In a well designed batch-tray drying oven, the drying of ADU could be completed in 24 hours at approximately 100°C. With mechanical agitation of the ADU, this time could probably be reduced.

4.4 Calcination - Reduction

A temperature variation of approximately 30°C along the vertical axis of the batch-tray furnace resulted in a difference of approximately 0.5 $m^2\ g^{-1}$ in the surface areas of UO_2 powders reduced on the top (coolest) and the middle (hottest) trays. The surface areas quoted in this report are for riffled samples of UO_2 representative of the whole furnace load.

The dependence of UO_2 surface area on the temperature of reduction in the range 600 - 730°C was in good agreement with that found in smaller-scale developmental work (Figure 7). As found previously (Janov, Alfredson & Vilkaitis 1971), the pH of ADU precipitation did not affect the surface area of the UO_2 powders and the average UO_2 surface areas shown in Figure 7 include powders prepared from ADU precipitated at pH 7.2, 7.5 and 8.0. Nor did precipitation with ammonia gas or precipitation at 80°C affect the surface area of the subsequent UO_2 powder.

The reproducibility of UO_2 surface area was demonstrated in nineteen identical calcination - reduction runs (Table 11). The same ADU (pH 7.5) was reduced at 630°C in each case. The average surface area of the nineteen powders was 4.3 $m^2 g^{-1}$ with a standard deviation of 0.6 $m^2\ g^{-1}$. The average O/U ratio of the powders (measured one to four days after exposure to the atmosphere) was 2.10 with a standard deviation of 0.03.

Only slight temperature excursions were experienced using the standard operating conditions. At the commencement of reduction, a rise of up to 20°C occurred on occasions and lasted for approximately ten minutes. During stabilisation of the UO_2 powder, temperature rises (5 - 10°C) were also noted. Generally, however, the equipment and procedures adopted were quite satisfactory and UO_2 powders with specified surface areas could be made reproducibly.

4.5 Product Assessment

Typical impurity levels of uranyl nitrate, ADU and UO_2 produced in the pilot plant are compared with the Canadian specification for UO_2 powder in Table 1. Comparing the second and third columns with column one, it can be seen that nickel was the only impurity whose level was increased significantly during precipitation and calcination-reduction. In other batches the levels of chromium, copper or iron were sometimes increased slightly during precipitation of the ADU or its calcination-reduction to UO_2. Generally, these increases were slight and the UO_2 powder produced in the pilot plant met the Canadian specification (Table 1, column 4).

The densities of sintered UO_2 pellets produced from ADU precipitated at pH 7.2, 7.5 and 8.0 (at 50°C), and subsequently calcined and reduced in the batch-tray furnace, are summarised in Figure 8. The density increased with increasing pH of precipitation of the precursor ADU and with decreasing temperature of reduction (lower UO_2 surface area). Thus UO_2 pellets with the required density of at least 10.4 g cm^{-3} can be produced over a range of combinations of pH of precipitation and temperature of reduction. Micronising the UO_2 powder increased the density of sintered pellets slightly (<0.05 g cm^{-3}) compared to those produced from UO_2 powder crushed to -100 mesh BSS.

UO_2 powder produced at 650°C from ADU precipitated at 80°C and pH 7.5 produced pellets with densities in the range 10.65 - 10.70 g cm^{-3} after sintering at 1600°C. These densities are approximately the same as those produced from ADU precipitated at pH 8.0 and 50°C.

Similarly, the density of UO_2 pellets produced *via* ADU precipitated using ammonia gas was the same as the density of pellets produced *via* ADU precipitated with ammonium hydroxide. UO_2 pellets (sintered at 1600°C) with an average density of 10.63 g cm^{-3} were produced *via* ADU precipitated with ammonia gas and reduced to UO_2 at 630°C. Furthermore, the micro-structures of these pellets were similar to those produced from ADU precipitated at 50°C using ammonium hydroxide.

The UO_2 pellets were generally free of structural faults such as cracks and surface defects, and they could be machined satisfactorily to the exact diameter in the centreless grinder. The internal microstructure of the pellets was fairly uniform; a typical micrograph of a radially sectioned UO_2 pellet produced by the standard procedure is shown in Figure 8. Pellets produced from micronised UO_2 powder had a slightly more homogeneous microstructure.

5. CONCLUSIONS

Nuclear grade ADU and UO_2 powders were produced on the pilot plant scale by continuous single-stage precipitation of ADU with ammonium hydroxide, dewatering with a rotary drum vacuum filter or a solid bowl centrifuge, and batch-tray drying and calcination-reduction to UO_2 powder. Approximately 1 Mg of ADU and 0.5 Mg of sinterable UO_2 were produced during this program.

Precipitation at $50^{\circ}C$ and pH values in the range 7.2 to 8.0 produced ADU materials which could be converted by calcination and reduction at temperatures of 600 to $730^{\circ}C$ to UO_2 powders and fabricated into sintered pellets with densities in the range 10.37 to 10.77 g cm^{-3}. The lower the pH of precipitation the lower was the reduction temperature required to achieve a specified UO_2 pellet density.

Precipitation of ADU at $80^{\circ}C$ offered no advantages over operation at $50^{\circ}C$, and no significant differences were found in precipitation with ammonia gas *vis a vis* ammonium hydroxide and in the subsequent UO_2 powders and sintered pellets. Precipitation at pH 7.5 and $50^{\circ}C$ is recommended since a reasonably filterable precipitate can be produced reproducibly without a need for stringent control, and considerable flexibility is available in the subsequent production of a sinterable UO_2 powder.

Dewatering of ADU slurries was carried out more efficiently using a solid bowl centrifuge rather than a rotary drum vacuum filter. Clearer discharge liquids were produced at a higher rate of throughput in the solid bowl centrifuge.

6. ACKNOWLEDGEMENTS

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TABLE 1

TYPICAL LEVELS OF IMPURITIES IN URANYL NITRATE, ADU AND UO_2 COMPARED WITH THE CANADIAN SPECIFICATION FOR UO_2 POWDER

(After Chalder 1961)

Element	Uranyl Nitrate ($\mu g\ g^{-1}$, U basis)	ADU ($\mu g\ g^{-1}$, U basis)	UO_2 ($\mu g\ g^{-1}$, U basis)	Canadian Specification for UO_2 Powder ($\mu g\ g^{-1}$, U basis)
Ag	0.3	0.3	< 0.1	1
Al	<10	<10	<10	25
B	0.15	< 0.3	0.15	0.3
Ca	20	n.d.	n.d.	50
Cd	0.4	n.d.	0.4	0.2
Cr	10	<10	10	15
Cu	10	15	9	10
Fe	40	10	10	50
Mg	8	4	10	5
Mn	< 1	< 1	n.d.	5
Mo	< 0.5	< 0.5	< 0.5	2
Na	50	<20	30	100
Ni	< 3	< 3	10	20
Si	80	n.d.	45	30
V	< 3	< 3	< 3	100
Zn	<15	<15	<15	100

n.d. not determined

TABLE 2

SPECIFICATIONS OF ANALYTICAL AND LABORATORY GRADE AMMONIUM HYDROXIDE

(After Ajax Chemicals Ltd., Sydney)

Property or Impurity	Analytical Grade	Laboratory Grade
Concentration (wt %)	28 - 30	27 - 30
Density (g cm^{-3})	0.89	0.89
CO_2 (μg g^{-1})	20	-
Ignition residue (μg g^{-1})	20	100
Chloride, Cl (μg g^{-1})	0.5	10
Phosphate, PO_4 (μg g^{-1})	2	-
Sulphur Compounds as SO_4 (μg g^{-1})	2	30
Heavy Metals as Pb (μg g^{-1})	0.5	10
Iron (μg g^{-1})	0.2	1

TABLE 3

STANDARD OPERATING CONDITIONS FOR PRECIPITATION OF ADU

Concentration of Uranyl Nitrate (g ℓ^{-1})	80 - 120
Free Acid Content of Uranyl Nitrate	<0.05 N
Concentration of Ammonium Hydroxide (wt %)	28
pH of Precipitation	7.2, 7.5, 8.0
Rate of Flow of Uranyl Nitrate (ℓ min^{-1})	1.0 - 1.2
Rate of Flow of Ammonium Hydroxide (cm^3 min^{-1})	75 - 85
Temperature of Precipitation (^{o}C)	50 ± 2
Rate of Stirring (Hz)	7.1 ± 0.1

TABLE 4

APPROXIMATE THROUGHPUT OF UNITS AT STANDARD OPERATING CONDITIONS

Unit	Uranium Throughput (kg h^{-1})
Precipitator	7.0
Filter	3.4 *
Solid Bowl Centrifuge	18.0
Drying Oven	0.7
Calcination - Reduction Furnace	0.2

* *ADU precipitated at pH 7.5*

Note: Oven drying and calcination-reduction were batch processes.

TABLE 5

EFFECT OF pH ON PROPERTIES OF ADU PRECIPITATES

Temperature of Precipitation 50°C Stirrer Speed 7.1 Hz

Residence Time in Precipitator 21 min.

Property of ADU Precipitate	pH 7.2	pH 7.5	pH 8.0
Settling Rate Measured at 40°C (mm s^{-1})	0.09-0.22	0.06-0.11	0.05-0.06
Settled Volume (%)	21-25	23-36	40-49
Filtration Rate (ℓ h^{-1})	48-70	40-45	33-40
Moisture Content of Filter Cake, on Wet Basis (wt %)	36-42	42-47	53-62

TABLE 6

EFFECT OF TEMPERATURE OF PRECIPITATION ON THE PROPERTIES OF ADU PRECIPITATES

Stirrer Speed 7.1 Hz   Residence Time in Precipitator 21 min.

Property of ADU Precipitate (Averaged values)	Precipitation Conditions		
	pH 7.5 at 50°C	pH 8.0 at 50°C	pH 7.5 at 80°C
Settling Rate (mm s^{-1})	0.09	0.06	0.067
Filtration Rate (ℓ h^{-1})	43	37	38
Moisture Content of Filter Cake, on Wet Basis (wt %)	44	59	50

TABLE 7

EFFECT OF PRECIPITANT ON PROPERTIES OF ADU PRECIPITATES

pH of Precipitation 7.5 — Stirrer Speed 7.1 Hz

Temperature of Precipitation 50° C — Residence Time in Precipitator 21 min.

NH_3 - two batches of 15 kg

Property of ADU Precipitate	Precipitant		
	NH_3	NH_3	NH_4OH
Settling Rate (mm s^{-1})	0.12	0.12	0.09
Filtration Rate (ℓ h^{-1})	36	39	43
Settled Volume (%)	27	31	30
Moisture Content of Filter Cake, on Wet Basis (wt %)	38	39	44

TABLE 8

EFFECT OF TEMPERATURE ON RATE OF FILTRATION

ADU Precipitated at pH 7.5 at 50°C

Temperature ($^{\circ}C$)	Filtration Rate ($\ell\ h^{-1}$)	Moisture Content (wt %)
25	29	52
35	30	52
47	42	53
48	44	50
55	46	46

TABLE 9

EFFECT OF DRUM SPEED ON RATE OF FILTRATION

ADU Precipitated at pH 7.2 at 50°C

Drum Speed (rev min^{-1})	Rate of Filtration at 40°C ($\ell\ h^{-1}$)	Moisture Content (wt %)
2.0	47	42
4.0	66	42

TABLE 10

EFFECT OF METHOD OF REMOVING FILTER CAKE ON FILTRATION PERFORMANCE

ADU Precipitated at pH 7.5 at 50°C

Method of Removal	Filtration Rate at 40°C ($\ell\ h^{-1}$)	Uranium Concentration in Filtrate ($mg\ \ell^{-1}$)	Moisture Content (wt %)
No Blow Off	39	10	47
Blow Off Every 10 min.	42	50	44
Continuous Blow Off	44	200	46

TABLE 11

REPRODUCIBILITY OF UO_2 SURFACE AREA

pH of ADU Precipitation 7.5   Temperature of Reduction 630°C

Batch No.	UO_2 Surface Area ($m^2\ g^{-1}$)	O/U ratio
CE 123	5.0	n.a.
124	4.8	2.15
125	5.2	2.12
126	4.2	2.13
127	4.6	2.13
128	4.2	2.08
129	3.1	2.07
130	3.7	2.06
131	4.1	2.06
132	3.8	2.06
133	3.3	2.11
134	4.2	2.12
135	3.7	2.07
137	4.7	2.10
138	5.1	2.11
139	4.5	2.10
141	4.5	2.11
142	4.6	2.18
143	5.3	2.10

n.a. = *not available*

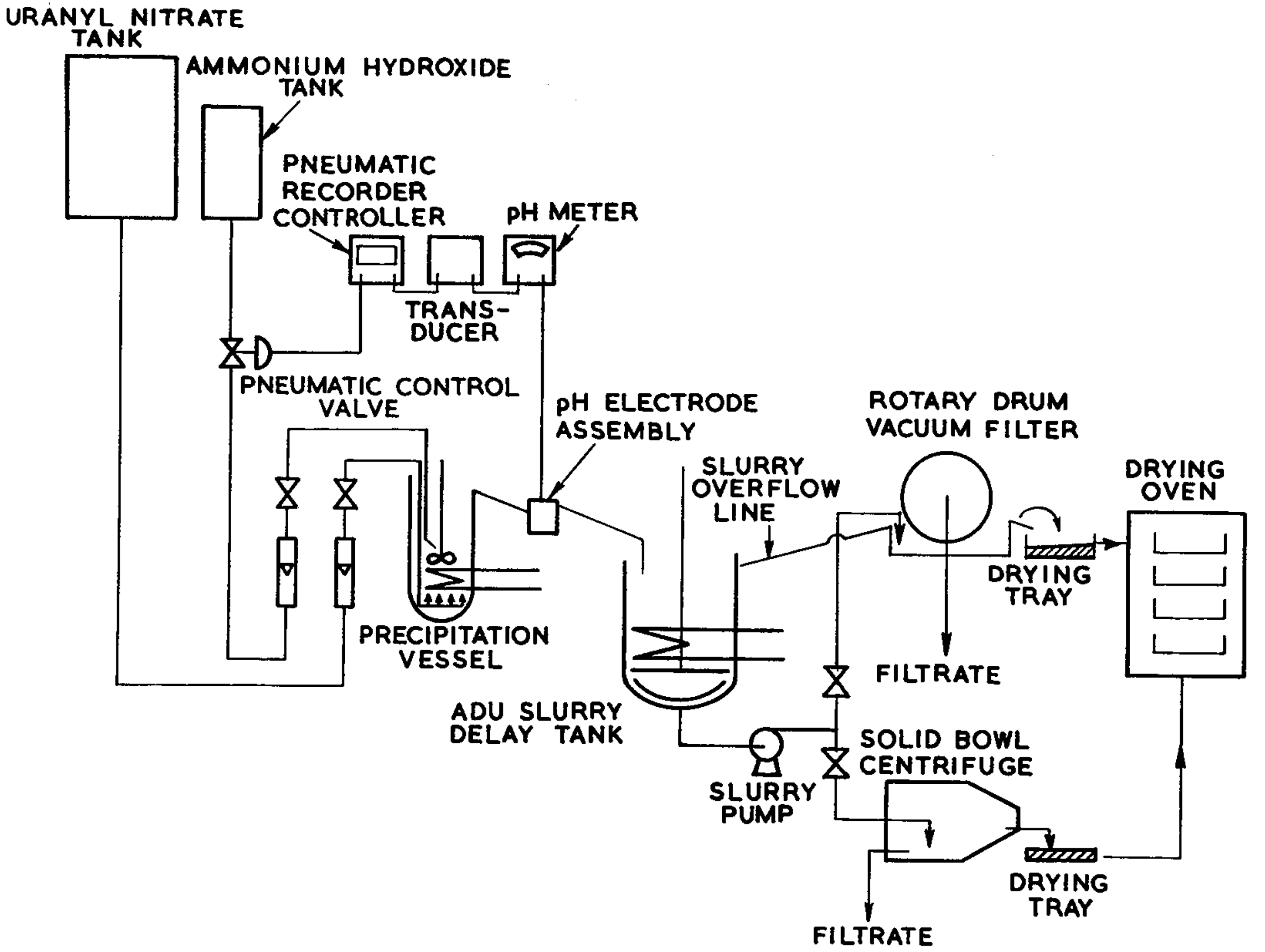


FIGURE 1. EQUIPMENT FLOWSHEET FOR PRECIPITATION, DEWATERING AND DRYING OF ADU

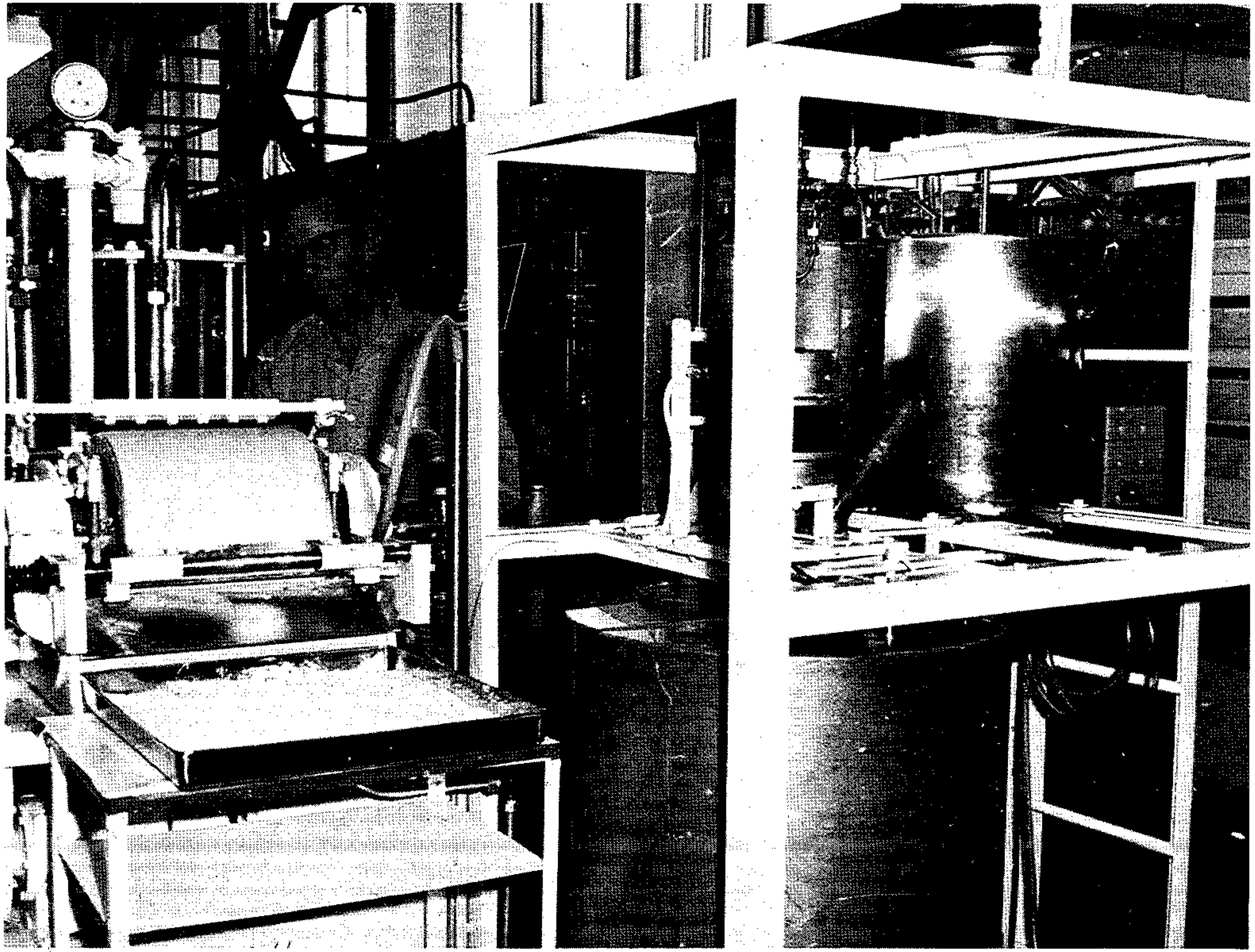


FIGURE 2. PRECIPITATION AND FILTRATION EQUIPMENT

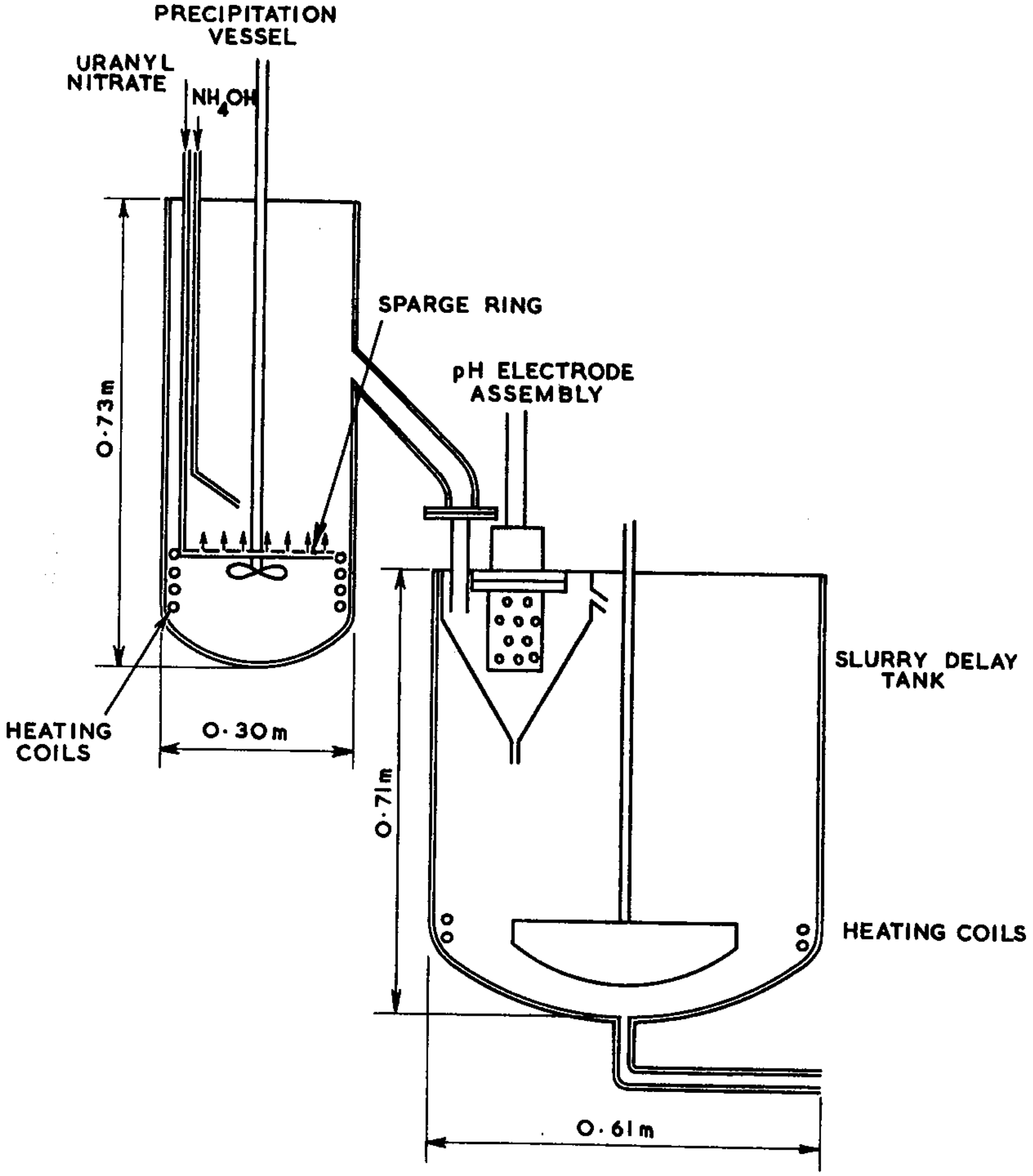
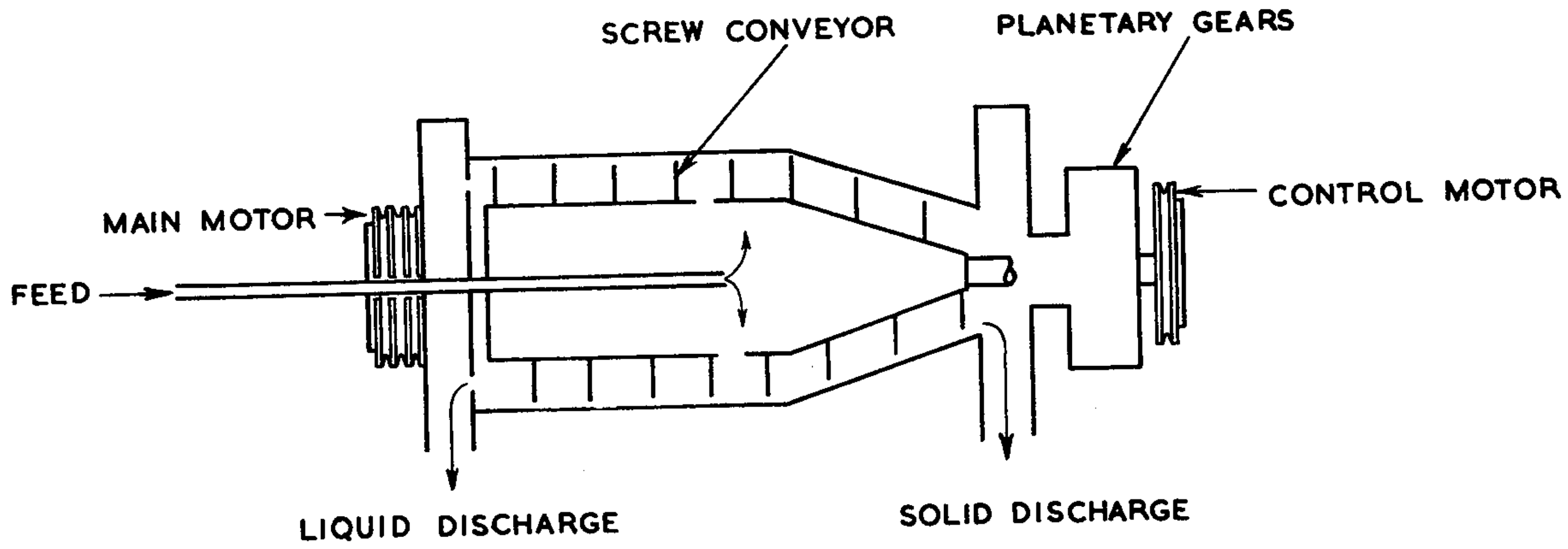


FIGURE 3. PRECIPITATION VESSEL, pH ELECTRODE ASSEMBLY AND SLURRY DELAY TANK



BOWL SPEED	83 Hz
DIFFERENTIAL SPEED	1 Hz
CONVEYOR SCREW SPEED	84 Hz

FIGURE 4. SOLID BOWL CENTRIFUGE

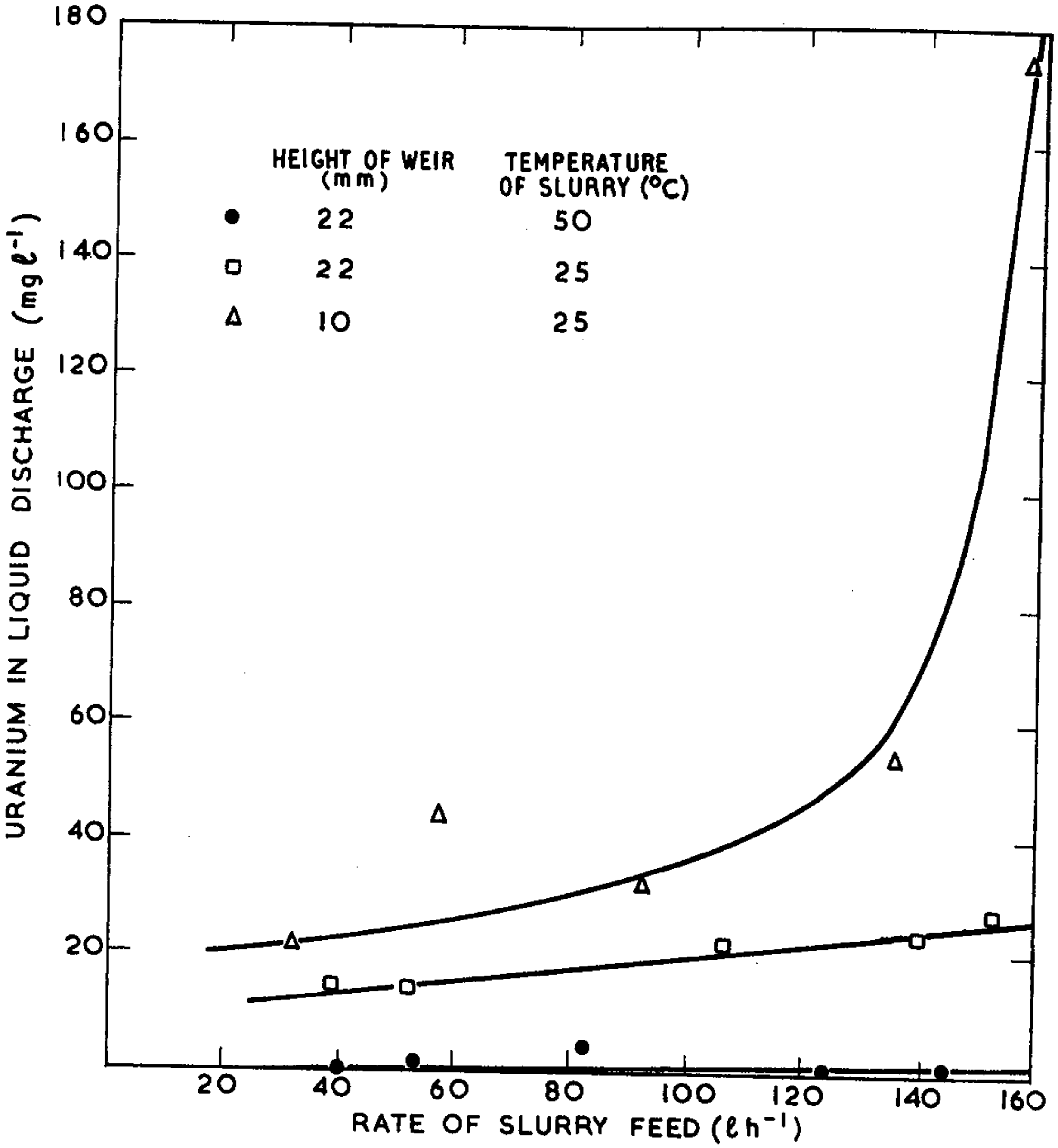


FIGURE 5. EFFECT OF OPERATING CONDITIONS ON THE CLARITY OF LIQUID DISCHARGED FROM THE SOLID BOWL CENTRIFUGE

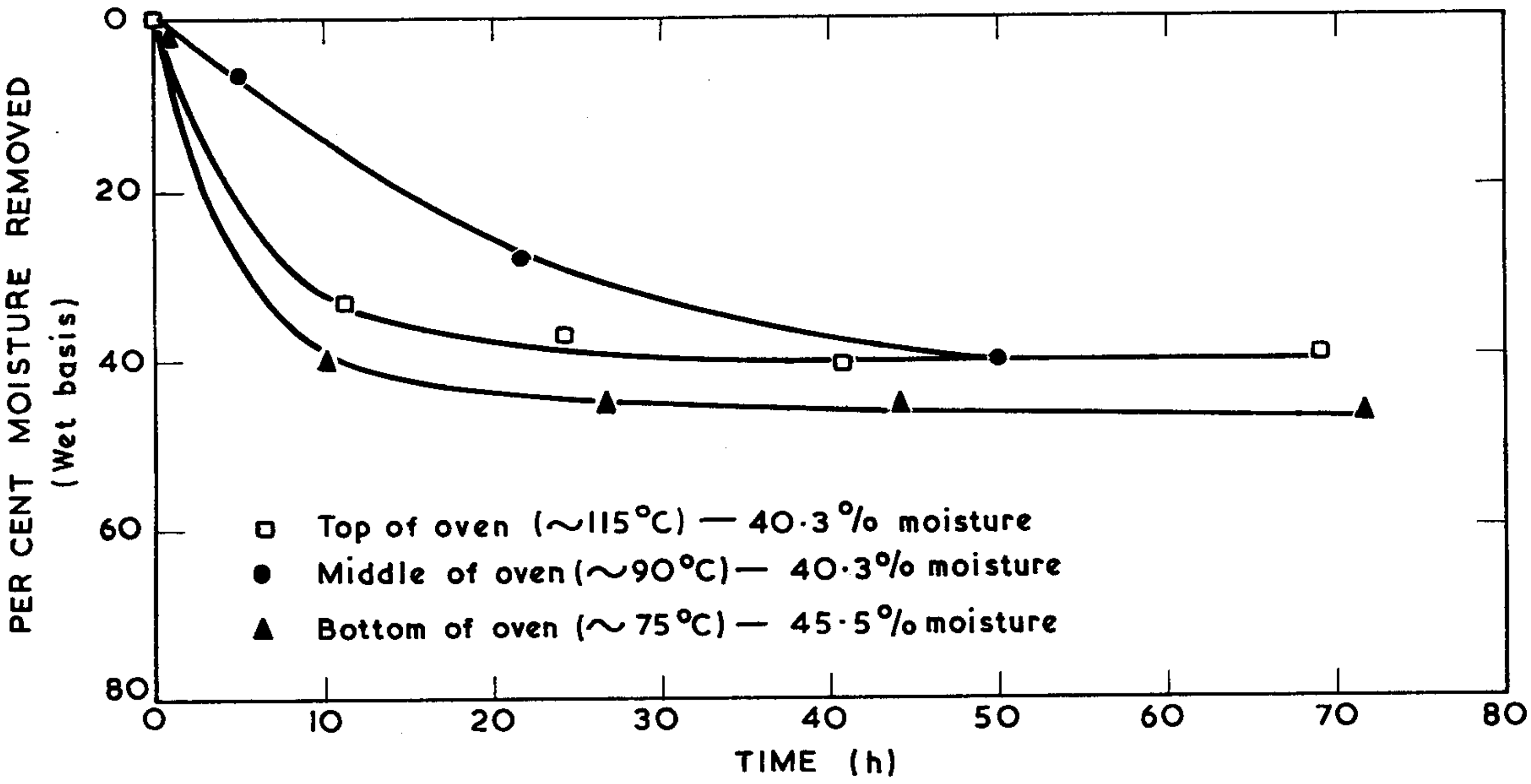


FIGURE 6. MOISTURE CONTENT OF ADU VERSUS DRYING TIME

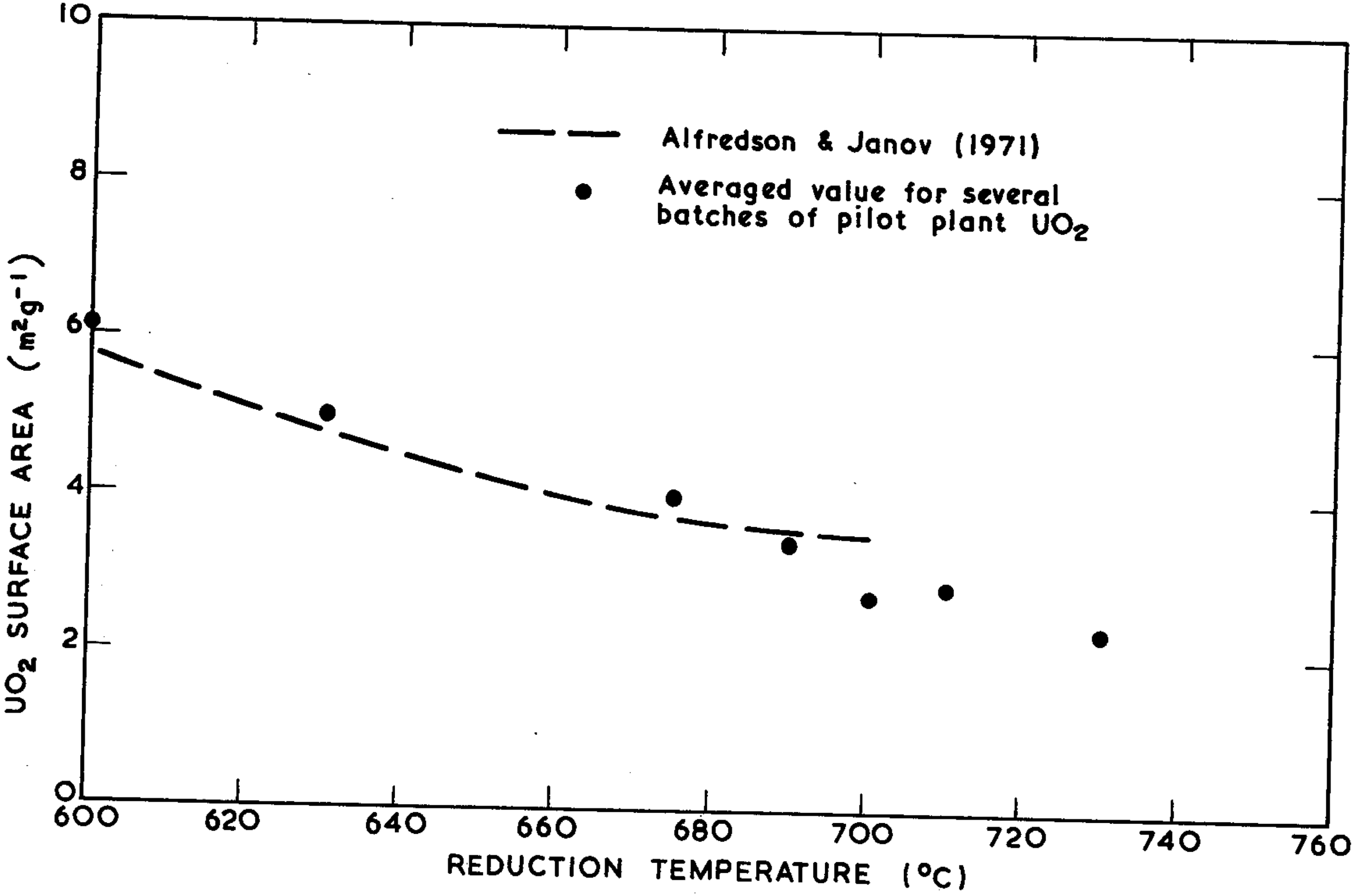


FIGURE 7. UO_2 SURFACE AREA VERSUS TEMPERATURE OF REDUCTION

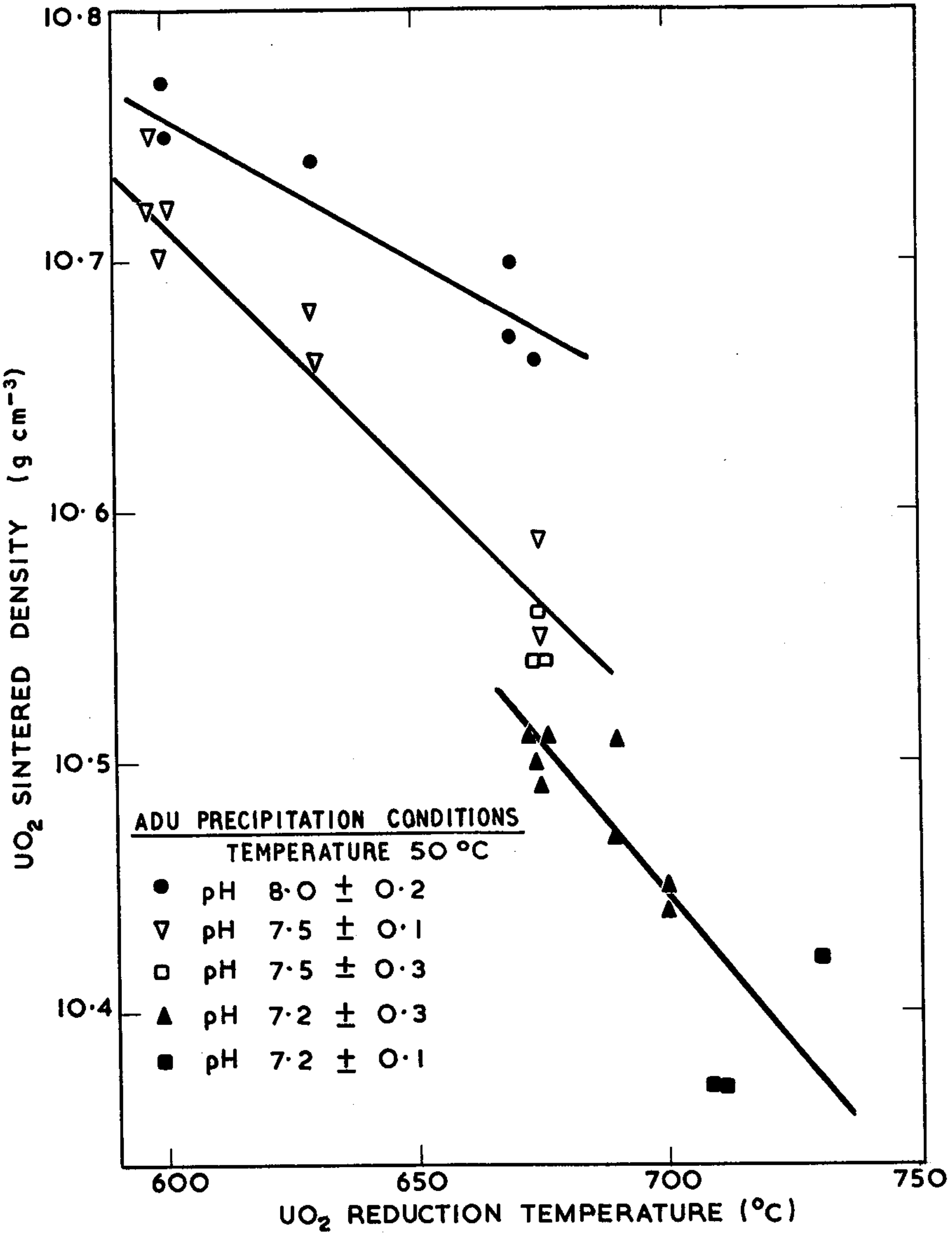


FIGURE 8. DENSITY OF UO_2 PELLETS VERSUS pH OF PRECIPITATION AND TEMPERATURE OF REDUCTION

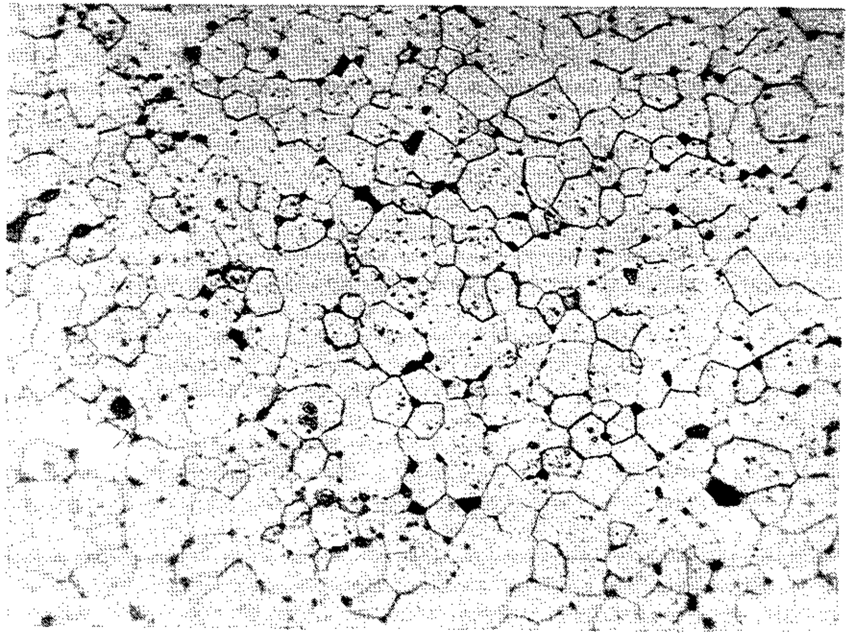


FIGURE 9. SINTERED UO_2 PELLET. DENSITY 10.70 g cm^{-3} (× 500)

APPENDIX A

DETAILS OF pH CONTROL EQUIPMENT

Electrodes		
Manufacturer	Ohkura Electric Co. Ltd	
Model	Industrial glass electrode	HG102
	Industrial reference electrode	HR314
	Industrial temperature - compensator	T501
Holder for Electrodes		
Manufacturer	Ohkura Electric Co. Ltd	
Model	Immersion	P212
pH Meter		
Manufacturer	Ohkura Electric Co. Ltd	
Model	SHZ1	
Range	0 - 14 pH	
Output	4 - 20 mA	
Current-to-Air Transducer		
Manufacturer	Foxboro Pty Limited	
Model	69TA - 1	
Input	4 - 20 mA	
Output	122 - 205 kPa	
Recorder - Controller		
Manufacturer	Taylor Instrument Companies of Australia Pty Ltd	
Model	91SF341 (recorder) 402RF1041 (controller)	
Chart speed	0.042 mm s^{-1}	
Input	122 - 205 kPa	
Output	122 - 205 kPa	
Pneumatic Control Valve		
Manufacturer	Research Controls	
Size	$C_v = 0.006$	
End Connections	0.25 in. N.P.T.	
Pressure Required to Open	205 kPa	