



**AUSTRALIAN ATOMIC ENERGY COMMISSION
RESEARCH ESTABLISHMENT
LUCAS HEIGHTS**

**PILOT PLANT DEVELOPMENT OF PROCESSES FOR THE PRODUCTION
OF NUCLEAR GRADE URANIUM OXIDE**

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P.G. ALFREDSON

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ABSTRACT

Most types of nuclear power reactors use fuel in the form of high density uranium dioxide pellets clad in Zircaloy. Sinterable uranium dioxide powder is usually produced via the ammonium diuranate (ADU) route. This involves dissolution of uranium ore concentrates (yellow cake) in nitric acid, purification by solvent extraction using tributyl phosphate in kerosene, precipitation of ADU, filtration, drying, calcination and reduction with hydrogen to give uranium dioxide powder.

The AAEC has carried out pilot plant development of these processes to demonstrate the production of nuclear grade uranium dioxide from Australian yellow cake and to improve the processes and technology wherever possible.

ABSTRACT (Cont'd.)

This paper describes the processes and equipment with particular reference to the improvements which have been made. The nitric acid requirements in the solvent extraction process have been substantially reduced and a pulsed fluidised bed reactor has been developed for the continuous calcination-reduction of ADU to uranium dioxide. The influence of the conditions for precipitation of ADU on its rate of filtration and on the fabrication behaviour of the uranium dioxide powder is also described.

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ADU; CALCINATION; FABRICATION; FLUIDISED BED; PILOT PLANTS;
PRECIPITATION; REDUCTION; SOLVENT EXTRACTION; URANIUM DIOXIDE

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1. INTRODUCTION

Most types of nuclear power reactors use fuel in the form of high density, sintered pellets of uranium dioxide, about 10 mm diameter by 10 mm long, which are held in Zircaloy tubes. These tubes of fuel pellets, or fuel rods, are arranged in various arrays to form fuel elements.

Depending on the design of the reactor, natural uranium dioxide or enriched uranium dioxide may be used as the fuel material. Natural uranium contains 0.7 per cent of the fissile ^{235}U isotope whereas enriched uranium fuel used in present power reactors typically contains 2 to 4 per cent ^{235}U . Currently the only economical way of producing enriched uranium is the multi-stage, gaseous diffusion process based on uranium hexafluoride in which the lighter ^{235}U hexafluoride diffuses through a porous barrier more rapidly than does the heavier ^{238}U hexafluoride. However considerable effort is now being devoted to alternative techniques such as the gas centrifuge and nozzle processes (Nucl. Eng., 1968, Avery and Kehoe, 1970).

Sinterable uranium dioxide powder is usually produced via the ammonium diuranate (ADU) route. In the production of natural uranium dioxide powder from uranium ore concentrates (yellow cake), this involves dissolution of yellow cake in nitric acid, purification by solvent extraction, precipitation of ADU, filtration, drying and calcination and reduction with hydrogen. If enriched uranium dioxide powder is required, the enriched uranium hexafluoride product from the diffusion plant is hydrolysed to uranyl fluoride solution and precipitated as ADU. It is then converted to uranium dioxide using a calcination-reduction process similar to that for natural uranium, at the same time ensuring complete removal of occluded fluoride by pyrohydrolysis with steam.

As part of the Research Establishment's program to establish the technology for the production of nuclear fuel elements from indigenous raw materials, Chemical Engineering Section has carried out pilot plant studies to demonstrate the production of nuclear grade uranium dioxide from Australian yellow cake and to improve the processes and technology wherever possible (Alfredson 1970). While this program was oriented towards natural uranium dioxide, it was equally relevant to the production of uranium dioxide for conversion to uranium hexafluoride and the conversion of enriched uranium hexafluoride to uranium dioxide powder.

This paper describes the processes and equipment which were developed and the improvements which have been made.

2. URANIUM DIOXIDE SPECIFICATION FOR PELLET FABRICATION

Uranium dioxide pellets are fabricated by cold pressing and sintering

techniques. Specification of the uranium dioxide powder includes requirements of chemical purity and sinterability. The chemical purity required by the Canadian specification for natural uranium dioxide powder, for example, is given in Table I (Chalder 1961). Some impurities in the pellets (e.g. boron and cadmium) are undesirable since they wastefully absorb neutrons which would otherwise be available for fission of the ^{235}U atoms in the reactor, whereas others (e.g. carbon and fluorine) may have a deleterious effect on the fabrication of the fuel or its performance under irradiation.

Specifications for nuclear grade, sinterable uranium dioxide powder (Chalder 1961, Forscher 1965) do not define the required physical properties of the powder, or the process to be used in its preparation, but give fabrication conditions which should be used in testing the powder. For example, the Canadian specification states:

"A compact of not less than 0.72 in. (18.3 mm) in diameter and 1.0 in. (25.4 mm) in length obtained by pressing the powder to not more than 40,000 lb/in² (276 MPa) shall have a density between 4.75 and 5.50 g/cm³. The pressed sample complying with the above requirements, after sintering in a hydrogenous atmosphere for not more than 1.5 hr at a temperature not exceeding 1650°C, shall form a coherent pellet of density not less than 10.4 g/cm³. The rate of heating of the sample during the sintering cycle shall not be less than 200°C/hr and the density shall be determined by appropriately accurate geometric and weight determinations".

In practice, a wide range of uranium dioxide powders, with surface areas generally in the range 3 to 9 m²/g, can be fabricated into acceptable pellets and the deciding factors in the choice of powder are its cost and fabrication properties. Sinterability is not the major consideration. More important features are probably its uniformity and reproducibility in behaviour and whether the number and complexity of fabrication steps can be reduced, especially those related to the need for binders and lubricants as aids in the pressing of pellets. The ideal powder flows readily, presses without the need for binders or lubricants, sinters to the required density, and gives rise to low reject rates at all stages of fabrication (Reeve, AECC private communication).

The cost of conversion of yellow cake to uranium dioxide powder is less than 10 per cent of the total cost of Canadian fuel elements and approximately 60 per cent of the cost of pellet fabrication. Marginal reductions in conversion costs will not have much effect on total fuel cost. Reductions are more likely to be achieved by improving the homogeneity of the uranium dioxide

powder and its suitability for automatic pressing, thus reducing the rate of rejects in fabrication, than by making technical innovations in the conversion process *per se* (Alfredson 1970).

3. RESEARCH AND DEVELOPMENT WORK

Pilot plant facilities were constructed with a throughput such that the experimental data could be used with confidence in the design of a subsequent production facility.

3.1 Dissolution

The dissolution step was designed to process yellow cake as well as recycled uranium materials, e.g. ADU and uranium dioxide powder and pellets, and to permit dilution and adjustment of acidity of the solutions. In general, a dissolver product solution containing 300 g U/litre and 0.5 to 4M nitric acid was required as the feed for the solvent extraction process.

An existing 0.1 m³ dissolver, constructed of AISI 321 stainless steel, heated via steam coils and agitated by sparging with air, was used. A reflux condenser was mounted on top of the dissolver and served to minimise loss of nitric acid fumes from the dissolver, recover some of the nitrogen oxide off-gases produced during dissolution, and allow removal of the exothermic heat of dissolution. The off-gases from the condenser were scrubbed with 10 wt. % sodium carbonate or hydroxide solution in a packed column before being discharged through de-entrainment separators to the building ventilation system.

Yellow cake and ADU in batches of up to 25 kg of contained uranium dissolved readily within one hour at 100°C. Dissolution of uranium dioxide powder was strongly exothermic and care in the addition of the nitric acid was essential. With UO₂ pellets, some material remained undissolved even after 12 hours.

Yellow cake may contain up to 10 wt. % silica (Page, Shortis and Dukes 1960), although the Rum Jungle material used in this work contained only 0.25 wt. %. Some of this silica dissolves and may subsequently cause emulsion problems during solvent extraction. The insoluble silica is in a gelatinous form which is difficult to filter. These problems can be minimised by 'ageing' the dissolver solution at 95°C for 2 hours (Page, Shortis and Dukes 1960). The silica precipitates in a semi-crystalline form which is more readily filtered. For these reasons, standard dissolution conditions of 4 hours at 100°C were used. In this work, the silica was not filtered from the dissolver solution and no difficulties were encountered during solvent extraction. Tests with a solid bowl centrifuge indicated that the silica could be readily removed if necessary.

3.2 Solvent Extraction

Purification of the uranium was accomplished by solvent extraction using 20 vol. % tri-butyl phosphate (TBP) in odourless kerosene (OK) as the solvent and mixer-settler contactors, following UKAEA practice (Page, Shortis and Dukes 1960). Initially the flowsheet shown in Figure 1 was adopted. The feed solution contained 300 g U/litre and 4M free acid and was contacted with the organic solvent in 6 stages. The loaded organic was scrubbed with 1M HNO₃ in 10 stages and the purified uranium was stripped from the solvent using dilute nitric acid solution in 16 stages.

3.2.1 Design of mixer-settler equipment

Two identical 16-stage mixer-settler units were used, one for extraction and scrubbing and one for stripping. The design of the mixer-settler units is shown in Figure 2 and a general view of the equipment in Figure 3. Each mixer was 63 mm x 63 mm x 93 mm deep and each settler was 63 mm x 203 mm x 165 mm deep, corresponding to design residence times of 30 seconds in the mixer and 180 seconds in the settler. These parameters corresponded to a total phase flowrate of 47 litre/hr in the stripping unit, equivalent to a throughput of 1.5 kg U/hr. The cross-sectional area of the settler was based on a settling rate of approximately 1 mm/s. Each mixer was agitated with a centrifugal pump-mix impeller with additional mixing blades. The agitators in each 16-stage unit were driven through a gear train by an electronically controlled D.C. motor. An impeller speed of 700 rev/min was used in the extraction-scrubbing unit and 600 rev/min in the stripping unit.

The organic extractant, scrub and strip solutions were fed by gravity from head tanks and the flowrates controlled by means of needle valves and flowmeters. The uranium feed solution was supplied through a positive displacement metering pump. The level of the aqueous phase in the final stage of each unit was controlled with an adjustable, external, overflow weir. The organic phase overflowed a fixed outlet weir in the final stages. Mist separators were provided on all outlet streams to allow separation of secondary haze.

3.2.2 Process optimisation

Two aspects of this solvent extraction system were considered: the acid consumption and the throughput of the mixer-settler units. Essentially all of the free acid in the feed solution and that added in the scrubbing stages is discharged in the raffinate waste stream and must be recovered for an economic, large-scale operation. The effect of free acid concentration in the feed on uranium extraction was investigated in the range 0.5 to 4M HNO₃. Uranium

equilibrium data are shown in Figure 4 as a function of acid concentration in the aqueous phase (Apelblat and Faraggi 1965). Uranium distribution is sensitive to acid concentration especially at low uranium concentrations. The number of ideal extraction stages required was calculated using the McCabe-Thiele method as described for solvent extraction systems by Varteressian and Fenske (1936).

The number of ideal extraction stages to give a raffinate concentration less than 0.1 g U/litre is 5, 4 and 3 for free acid concentrations of 0.5, 1.0 and 4.0M respectively. Figure 4 illustrates these calculations for 0.5M free acid in the feed and uranyl nitrate solution (95 g U/litre) as the scrub liquor as described below. The situation is actually more complicated than shown in Figure 4 because both uranium and nitric acid are coextracted. Wood and Williams (1960) have reported a method of calculation which allows for this coextraction. Under typical operating conditions, the nitric acid concentration in the extraction stages exceeds the concentration in the feed solution. Some free acid is essential in the feed solution if low uranium values in the raffinate are to be achieved because of the inflection in the equilibrium curve for zero acid. With eight actual extraction stages available, operation with 0.5M free acid was practicable.

In the scrubbing stages, the uranium concentration in the organic phase does not vary greatly and is maintained as high as possible to enhance the separation of impurities from the uranium. For efficient and stable operation, a 'pinch' must be obtained, that is, the equilibrium and operating lines should cross or be tangential (see Figure 4). Under these conditions, changes in the flowrates of the aqueous and organic phases or in the number of stages have little effect on the uranium concentration in the loaded organic. The use of nitric acid scrubbing was eliminated following the work of Littlechild (1967) by recycling part of the purified product solution as the scrub liquor. This was also advantageous in further increasing the uranium concentration in the scrubbing stages and in the loaded organic (from 60 to 70 g U/litre). Eight actual stages were used for scrubbing with the low acid flowsheet.

With a uranium concentration in the loaded organic of 70 g/litre, approximately 12 ideal stages are required to give a 95 g/litre product after stripping at 25°C. Some difficulties were encountered in reducing the uranium concentration in the stripped organic below 1 g U/litre in the 16-stage stripping unit. However, increasing temperature enhances the efficiency of stripping (Rozen, Khorkhorina and Karpacheva 1962) and this problem was overcome by heating the dilute nitric acid solution used for stripping to 60°C. The

temperatures in the stripping stages varied from 60° to 30°C and the effect of this increase in temperature on the efficiency of stripping is shown in Figure 5. Under these conditions, the uranium concentration in the product increased to 120 g/litre while the uranium concentration in the stripped organic was maintained less than 0.005 g/litre. It may be noted from Figure 5 that heating the loaded organic to 60°C would be more effective in improving the efficiency of stripping than heating the strip solution.

For process control, simple, rapid methods of analysis were desirable. A gamma-absorptiometer was developed for analysis of uranium solutions in the range 10 to 400 g/litre (Yates and May 1970) and gamma-excited X-ray fluorescence was investigated for the concentration range 0.05-10 g/litre (Alfredson et al. 1970).

As mentioned previously, the mixer-settler units were designed for a throughput of 1.5 kg U/hr, corresponding to a total phase flowrate in the stripping section of 47 litre/hr. For this flowrate, the above modifications in the flowsheet increased the throughput to 2.1 kg U/hr. Hydrodynamic studies of these mixer-settlers indicated that total phase flowrates up to 75 litre/hr should be practicable before flooding occurred.

In a series of experiments using a feed solution containing 300 g U/litre and 1M HNO₃ (requiring four ideal extraction stages), the uranium throughput was increased to 2.5 kg U/hr, corresponding to a total phase flowrate of 62 litre/hr in the stripping section, with acceptable losses of uranium in the raffinate (<0.04 g U/litre corresponding to ~ 0.01% of the uranium feed). At higher throughputs, uranium losses to the raffinate were unacceptable. The maximum concentration in the stripped organic remained at a low level at all throughputs. The effect of increasing the throughput was to reduce the mass transfer efficiency of the mixer-settler stages and this rather than flooding constituted the operating limit.

The purity of the uranyl nitrate product solution was generally within the limits of the Canadian specification and was not affected by the changes in which the nitric acid consumption was reduced by 87 per cent and the uranium throughput increased by 66 per cent. The concentration of rare earths was below the detectable limits of 0.5 ppm for samarium and 0.05 ppm for europium, gadolinium and dysprosium.

3.3 Precipitation and Filtration

A variety of methods have been investigated overseas for batch and continuous precipitation of ADU. Continuous precipitation has been carried out in single-stage, two-stage and multi-stage processes. Ammonium hydroxide,

ammonia gas, and ammonia produced by the hydrolysis of urea, have been used as the precipitant. The sinterability of uranium dioxide powder depends on both the conditions of ADU precipitation and its subsequent calcination-reduction to uranium dioxide powder (Alfredson 1970).

The chemical composition and the physical nature of ADU change with the pH of precipitation. Various compositions of ammonium uranates have been reported with different $\text{NH}_3:\text{U}$ ratios (Cordefunke 1962, Stuart and Whateley 1969) but the diuranate, $(\text{NH}_4)_2\text{U}_2\text{O}_7$, probably never exists in aqueous solution (Stuart and Whateley 1969). Nevertheless the precipitate is usually referred to as ADU in the technical literature. ADU precipitated from uranyl nitrate solution inevitably also contains nitrate ions most of which can be removed by washing with water.

The size of ADU crystallites and agglomerates decreases with increasing pH of precipitation, resulting in a decrease in the settling rates and filterability of the ADU slurry. The most filterable ADU is produced at pH 3.5 where ADU is partly soluble and large crystallites and agglomerates are formed. However the pH must be increased to 6 or 7 to recover all the uranium from solution. Two-stage and multi-stage processes have been used to achieve complete recovery of uranium while producing a filterable product. For example, in two-stage precipitation, a low pH is maintained in the first precipitator to produce a readily filterable material and the pH increased above 7 in the second precipitator to ensure that all the uranium is recovered from solution (Janov, Alfredson and Vilkaitis 1971).

3.3.1 Bench-scale studies

Continuous precipitation in one and two stages was investigated on the half kilogram per hour scale to determine the effect of precipitation variables on the properties of ADU precipitates and particularly the sinterability of the subsequent uranium dioxide powders (Janov, Alfredson and Vilkaitis 1971). The two cylindrical precipitation vessels, 95 mm i.d. with overflow pipes 0.36 m from the base, were stirred with 25 mm diameter paddles at 2000 rev/min.

When operating as a two-stage precipitator, ammonium hydroxide was fed to both vessels but uranyl nitrate was fed only to the first. In the first stage, pH was essentially constant and not affected by the extent of uranium precipitation. The amount precipitated was determined by withdrawing a sample of the partially precipitated ADU/uranyl nitrate slurry, filtering out the ADU and analysing the residual uranium in solution using the gamma-absorptiometer. In the second stage, pH was controlled in the range 7 to 9. For single-stage precipitation, the second vessel was by-passed and the pH was controlled.

The settling characteristics and filterability of ADU precipitated in one stage at various values of pH are compared in Table II. Filterability was measured in a constant-pressure filtration test and characterised in terms of the specific filtration resistance (Janov, Alfredson and Vilkaitis 1971). The ADU produced at pH 3.5 settled very rapidly and filtered fast but above pH 6.6 the settling and filtration rates were reduced. In the pH range 6.6 to 7.2, the properties changed very rapidly. This region corresponds to the inflection point in the uranyl nitrate-ammonium hydroxide titration curve (Janov, Alfredson and Vilkaitis 1971) and small changes in flowrates of the reactants cause appreciable changes in the pH of the solution and in the properties of the slurry. Precipitation at pH 7.2 was recommended by Bourns and Watson (1961).

Table III shows how the filterability and settling characteristics of ADU slurries can be modified in two-stage precipitation by precipitating different amounts of uranium at pH 3.5 in the first stage and above 7 in the second stage. When less than 83 per cent of the uranium was precipitated in the first stage, the properties of the slurry were similar to those of ADU precipitated at pH 7.2 and above. When more than 90 per cent was precipitated in the first stage, the ADU was as filterable as material produced at pH 3.5. Under the latter conditions, the filterability of the ADU was not sensitive to the pH in the second stage and increased slightly with increasing residence time (Janov, Alfredson and Vilkaitis 1971).

ADU precipitated at pH 3.5 contained numerous large agglomerates 20-24 μm diameter while ADU precipitated at pH 7.2 contained agglomerates approximately 3 μm diameter. When the ADU was reduced to uranium dioxide at 600°C, the agglomerate structure of ADU was retained but differences in the surface areas of the powders were substantially reduced. The larger the agglomerates in the uranium dioxide powder, the less sinterable it was; pseudomorphs of large agglomerates were still discernible in the sintered pellets. Figure 6 shows that when less than 80 per cent of the uranium was precipitated at pH 3.5, the density of pellets sintered at 1500°C from the subsequent UO_2 powders decreased rapidly. This coincides with the marked change in filterability and settling rates of ADU slurries described above. Thus settling rate gave an early indication of the likely sinterability of the resultant UO_2 powder since both were functions of agglomerate size (Janov, Alfredson and Vilkaitis 1971).

Single-stage precipitation at pH 7.2 gave essentially complete precipitation of uranium, a reasonably filterable ADU, and the subsequent UO_2 powder

sintered at 1500°C to 10.5 to 10.6 g/cm³. Similar material was prepared by two-stage precipitation when less than 80 per cent of the uranium was precipitated in the first stage at pH 3.5 and the remainder in the second stage at pH 7 to 8. The close control required for single-stage precipitation at pH 7.2 must therefore be balanced against the less stringent control required in two-stage precipitation with its additional complexity of two precipitators and auxiliaries.

3.3.2 Pilot plant studies

A continuous single-stage precipitator was adopted for pilot plant studies and filtration was carried out using a 0.3 m² rotary drum vacuum filter (Figure 7). The precipitator, 0.3 m diameter with an overflow pipe 0.45 m above the base, was stirred with a turbine impeller at 425 rev/min. Uranyl nitrate solution (70-120 g U/litre, was fed by gravity to a sparge ring and the flowrate controlled manually to give a uranium throughput in the range 4 to 7 kg/hr. The ammonium hydroxide was introduced just above the impeller and the flowrate was adjusted automatically with a control valve to maintain the required pH. The precipitator was heated with a 2 kW electrical immersion element.

The ADU slurry overflowed through the pH electrode system into a stirred delay tank. The slurry was pumped from the delay tank to the vacuum filter. Vacuum (17 kPa) was applied to two segments of the filter and the third segment could be used for removal of the filter cake by air blow-off. The ADU was collected in stainless steel trays for drying.

The effect of pH on the properties of the ADU precipitates and on the sinterability of the subsequent UO₂ powders was examined further at pH values of 7.2, 7.5 and 8.0. With increasing pH, the ADU settled and filtered more slowly and the filter cake contained a higher moisture content (Table IV). Figure 8 shows the effect of pH of precipitation and the temperature of reduction to uranium dioxide on the density of pellets sintered at 1600°C. From this data, pH 7.5 was selected for the standard production process now used.

The effect of temperature and the use of ammonia gas as precipitant were investigated briefly. ADU precipitated at pH 7.5 (measured at 80°C) was similar to that produced at pH 8.0 (measured at 50°C). Using ammonia gas as precipitant (diluted with three times its volume of air), the ADU slurry and subsequent UO₂ powder were essentially similar to that prepared using ammonium hydroxide.

Operation of the rotary drum vacuum filter was optimised using standard

ADU slurries precipitated at pH 7.5 and 50°C. The rate of filtration increased with increasing temperature (inversely proportional to the square root of viscosity) and speed of rotation of the drum, and with decreasing cake thickness. Intermittent blow-off of the filter cake was also important in maintaining high filtration rates with a negligible loss of uranium to the filtrate (<10 mg U/litre).

3.4 Drying

ADU was dried in trays (30 mm deep) in laboratory drying ovens as a convenient standard process. At least 24 hours at 100°C was required to reach constant weight. Spray drying of representative 'slow settling' (precipitated at pH 7.2) and 'fast settling' (prepared by two-stage precipitation) slurries was also investigated using a 1 m diameter laboratory spray drier equipped for both pneumatic and centrifugal atomisation (Levins et al. 1972). Spray drying was of interest as a continuous process which produces a homogeneous product and enables the particle size to be controlled.

Pneumatic atomisation appeared to be the most suitable method of droplet dispersion. Centrifugal atomisation of slow settling slurries was possible only at relatively low feed concentrations while fast settling slurries quickly blocked the atomiser feed line near the point where the slurry first experienced the high temperature (300°C) at the inlet to the drier. The particle size of the dried ADU was typically less than 10 µm and was limited by the size of the drier. Spray drying did not adversely affect the properties of the subsequent uranium dioxide powder and pellets (Levins et al. 1972).

3.5 Calcination - Reduction

Conventional tray calcination-reduction was carried out in equipment producing 5 kg batches of uranium dioxide powder. The ADU was held as static beds, up to 25 mm deep, in a series of trays in a stainless steel vessel heated by a furnace. The powder was heated to the reduction temperature in nitrogen and hydrogen was introduced to reduce the calcined ADU to uranium dioxide. The surface area of the uranium dioxide powder was not significantly affected by the surface area of the ADU (Janov, Alfredson and Vilkaitis 1971). The reduction is exothermic: bed depth and reaction rate must be controlled to avoid temperature excursions in the static beds of powder leading to microsintering of the powder and a non-uniform product.

Stoichiometric uranium dioxide is not stable in air at ambient temperature. It absorbs oxygen in an exothermic process and the rate of absorption depends on the temperature and surface area of the powder and the oxygen partial pressure. With uranium dioxide powders of surface area greater than 3 m²/g, the

rate of oxidation may be sufficiently high to make the powder pyrophoric (Bannister 1967). It must therefore be stabilised by controlled oxidation before exposure to air, and then further oxidation proceeds slowly. Stabilisation in the batch tray furnace was carried out using 10 vol. % air in nitrogen for 16 hours (overnight) for a range of powders with surface areas in the range 3 to 10 m²/g.

The disadvantages of batch tray operation include the need for manual loading and unloading of the furnace and the possibility of non-uniform temperatures within the beds of powder described above. The susceptibility of uranium dioxide powder to microsintering under exothermic reduction conditions suggests the use of equipment with good heat transfer characteristics and efficient gas-solids contacting (Alfredson 1970). The pulsed fluidised bed technique meets these criteria and is able to handle material with a wide size distribution, including fine particles, as is the case with ceramic grade uranium dioxide powders.

With this technique, the fluidising gas is introduced as a series of pulses by pressurising a chamber isolated by solenoid valves and discharging the contents through the bed. The behaviour of the bed is then largely determined by the pulse frequency, the volume of the pulse chamber and the pressure to which it is filled, which influence the pulsed gas velocity and duration of the pulse (Alfredson and Doig 1970). The quality of fluidisation was found to be important since microsintering of the powder occurred if poor fluidisation resulted in the formation of hot-spots.

3.5.1 Pulsed fluidised bed reactor system

The pulsed fluidised bed reactor system is shown schematically in Figure 9 and Figure 10 is a general view of the equipment. The reactor was fabricated from a 130 mm diameter Schedule 40 pipe, approximately 1 m long, having a conical gas inlet system and a 260 mm diameter disengaging section housing four sintered metal filters. Initially porous bed support plates were used but subsequently these were removed. Electrical heating elements were wrapped around the reactor and the two heating zones were controlled with on-off controllers.

The reaction gases entered through a heated pipe from the pulse chamber. Measurement of the gas flowrates was facilitated by the use of differential flow controllers which eliminated pulsations at the flowmeters. The off-gases left the reactor via the filters and passed through a backup filter before discharging to the ventilation system. Fine powder which accumulated on the filters was periodically returned to the reactor by blowback of the filters.

Various methods of feeding solids to and removing them from the reactor were used with different modes of operating the system as discussed below. Figure 9 shows the equipment for continuous feeding and removal in which ADU was fed via a screw feeder and rotary valve to the top of the reactor and the uranium dioxide product was removed through the bottom cone via a sealed vibratory feeder.

A separate reactor was used for stabilisation of the uranium dioxide product. It had similar features to the calcination-reduction reactor but was designed for operation at ambient temperature. The body of the reactor was a 152 mm i.d. glass pipe, 1.5 m long.

Three different modes of operation of the pulsed fluidised bed reactor system have been investigated: batch, batch-continuous and continuous operation.

- Batch operation

Initially, batch operation using a process cycle similar to that for tray calcination-reduction was demonstrated. A 4 to 7.5 kg batch of ADU (crushed -20 BSS) was charged pneumatically to the cold reactor, heated and calcined in nitrogen over 2 hours before hydrogen was introduced for 40 minutes. The uranium dioxide product, either hot or after cooling, was pneumatically removed from the reactor using a 'gulper' technique (Heidt, Levey and Hamrin 1966).

The throughput of the system was obviously low under those conditions and was increased by pneumatically charging the ADU into the hot reactor. Thus three batches of approximately 2 kg ADU each were charged sequentially to the reactor which was maintained at the reduction temperature, generally in the range 600 to 700°C depending on the required surface area. Rapid calcination occurred and was complete within 20 minutes and hydrogen was then introduced for the reduction reaction, followed by pneumatic removal of the product. By this means a throughput of 6 kg ADU per hour was achieved.

- Batch-continuous operation

With this mode of operation, ADU was fed continuously to the top of the reactor with a vibratory feeder, the bed was fluidised with hydrogen-nitrogen at all times, and calcination and reduction occurred simultaneously in the reactor. The bed of uranium dioxide powder was allowed to build up to a maximum level, then the ADU feed was shut off and the hydrogen flow continued for 5 to 10 minutes to ensure complete reduction of the ADU in the reactor. The uranium dioxide product was removed from the reactor pneumatically. In later experiments, when the bed support plate was removed, the product was discharged through the bottom of the reactor via a sealed vibratory feeder. A portion of

the bed was retained in the reactor for the next continuous feeding period. Batch-continuous operation takes advantage of the contraction in volume in the conversion of ADU to uranium dioxide and has low labour requirements compared to sequential batch operation.

An average production rate of 6 kg uranium dioxide per hour was demonstrated with batch-continuous operation. In one experiment lasting 10.5 hours, 65 kg of uranium dioxide powder was produced in eight batches. The reproducibility of the surface area of the individual batches of powder and the densities of the sintered pellets was very good. Pellets pressed at 309 MPa (20 tons/in²) and sintered at 1600°C in hydrogen for 4 hours had densities in the range 10.66 to 10.70 g/cm³.

- Continuous operation

Continuous operation potentially improves the consistency of product quality and reduces the labour requirements. In demonstrating this mode of operation, ADU was fed to the top of the reactor and the product removed through the cone bottom as described previously. Since fluidised beds approach perfect mixing conditions, each particle in the bed has an equal chance of leaving and this is undesirable because any unreacted ADU will give rise to porosity in the subsequent uranium dioxide pellets. To minimise this problem, the average residence time of particles in the bed is very much greater than the time required for reaction. Also since ADU has a lower density than uranium dioxide, feeding ADU to the top and removing the product from the bottom, instead of vice versa, takes advantage of any tendency to segregation (due to the difference in densities) to minimise short circuiting of ADU through the system.

To gain some insight into the operation of the continuous pulsed fluidised bed reactor, an attempt is being made to model reactor performance by combining the kinetics of the conversion of ADU to uranium dioxide with the residence time characteristics of the system. The time required for reaction is a function of temperature and hydrogen concentration and is approximately 2 minutes under the conditions of interest.

In residence time studies of the passage of particles through the bed, particular attention was paid to the 'toe' of the distribution curve since it is those particles which escape before being completely reacted which are of concern. These studies showed that the pulsed fluidised bed reactor is equivalent to 1.12 continuous stirred tank reactors (CSTRs). This deviation from ideal behaviour is particularly significant: for an average residence time in the bed of 60 minutes, 3.3% of the particles leave the bed within 2 minutes in

a single CSTR compared with 0.5% in 1.12 CSTRs.

Experimental studies have shown that uranium dioxide powder which sinters to a density of 10.7 g/cm^3 at 1600°C , can be produced continuously in the pulsed fluidised bed reactor at throughputs up to 10 kg uranium dioxide per hour corresponding to a residence time of 60 minutes.

It is of interest to note that all the uranium dioxide powders produced in the pulsed fluidised bed reactor have been much more readily pelletised and have shown a lower incidence of cracking and pellet defects than powders produced by batch-tray calcination-reduction. Comparison of these powders in detail has failed to reveal the basic reason for this difference in behaviour (Ramm, AAEC private communication). It is however most satisfying that the pulsed fluidised bed reactor has produced a superior powder and at the same time represents an improved reactor concept compared to batch-tray operation.

4. CONCLUSIONS

In the research and development program outlined in this paper, approximately 1500 kg of yellow cake has been processed to uranium dioxide powder. This work has established the technology required to design a plant for the production of uranium dioxide powder, made significant improvements in some processes and equipment, and generally optimised each of the process steps.

5. ACKNOWLEDGEMENT

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TABLE I MAXIMUM IMPURITY LEVEL - CANADIAN SPECIFICATION
FOR URANIUM DIOXIDE POWDERS (CHALDER 1961)

Symbol	Name	Maximum Impurity Level p.p.m. by Weight on U Basis Including Analytical Error
Ag	Silver	1
Al	Aluminium	25
B	Boron	0.3
C	Carbon	200
Ca	Calcium	50
Cd	Cadmium	0.2
Cr	Chromium	15
Cu	Copper	10
Dy	Dysprosium	0.15
F	Fluorine	50
Fe	Iron	50
Gd	Gadolinium	0.10
Mg	Magnesium	10
Mn	Manganese	5
Mo	Molybdenum	2
Ni	Nickel	20
Si	Silicon	30

The content of individual impurities in the powder shall not exceed the levels shown in the above table, and not more than 100 p.p.m. of any other element except uranium and oxygen.

TABLE II EFFECT OF pH ON THE FILTERABILITY OF ADU
PRECIPITATED IN ONE STAGE

Temperature of precipitation 50°C
 Residence time 8 min.
 Stirrer speed 2000 rev/min.

pH of Precipitation (measured at 50°C)	Specific Filtration Resistance m/g	Initial Settling Rate of ADU slurry mm/s
8.4	7.84 x 10 ⁸	0.02
7.2	1.93 x 10 ⁸	0.07
7.2	0.52 x 10 ⁸	0.18
7.1	1.00 x 10 ⁸	0.19
6.6	0.13 x 10 ⁸	0.90
3.5	0.16 x 10 ⁸	rapid (>0.90) but no clear interface

TABLE III EFFECT OF PERCENTAGE OF URANIUM PRECIPITATED IN
STAGE ONE ON THE FILTERABILITY OF ADU PRECIPITATED IN TWO STAGES

Total residence time 34 min.
 pH in Stage Two 8.0 ± 0.1
 Temperature of precipitation 50°C

Percentage Uranium Precipitated in Stage One	Specific Filtration Resistance m/g	Initial Settling Rate mm/s
55	4.5 x 10 ⁸	0.07
80	1.9 x 10 ⁸	0.15
83	1.05 x 10 ⁸	0.18
90	0.24 x 10 ⁸	0.83
95	0.10 x 10 ⁸	1.37

TABLE IV EFFECT OF pH ON PROPERTIES OF ADU PRECIPITATES

Temperature of precipitation 50°C

Stirrer Speed 425 rev/min.

Property	pH 7.2	pH 7.5	pH 8.0
Settling rate, mm/s	0.10 - 0.22	0.06 - 0.09	0.05 - 0.06
Filtration rate, litre/hr	48 - 70	40 - 45	33 - 40
Moisture content of filter cake, wt % on wet basis	36 - 42	42 - 47	53 - 62

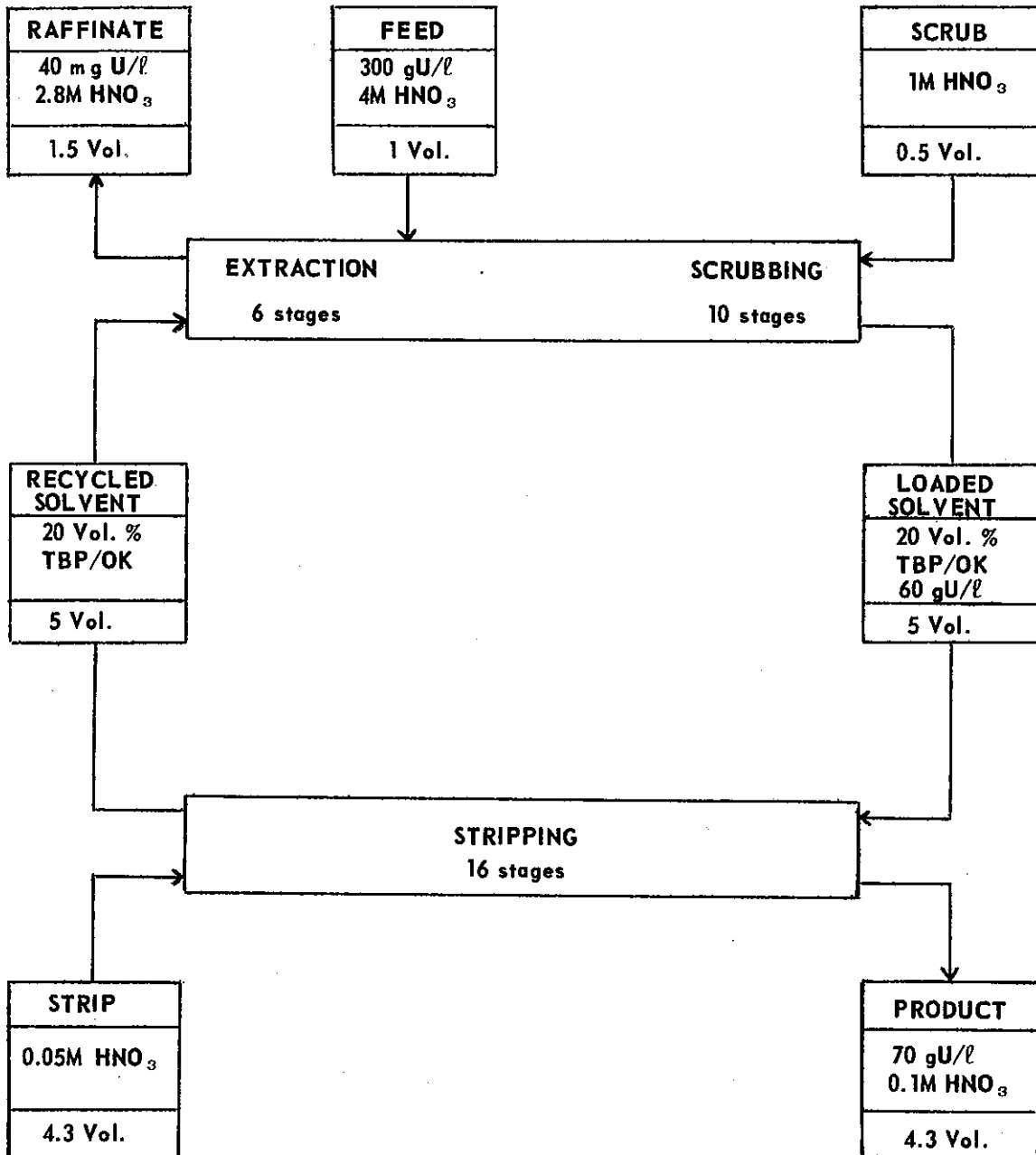


FIGURE 1. SOLVENT EXTRACTION - HIGH ACID FLOWSHEET

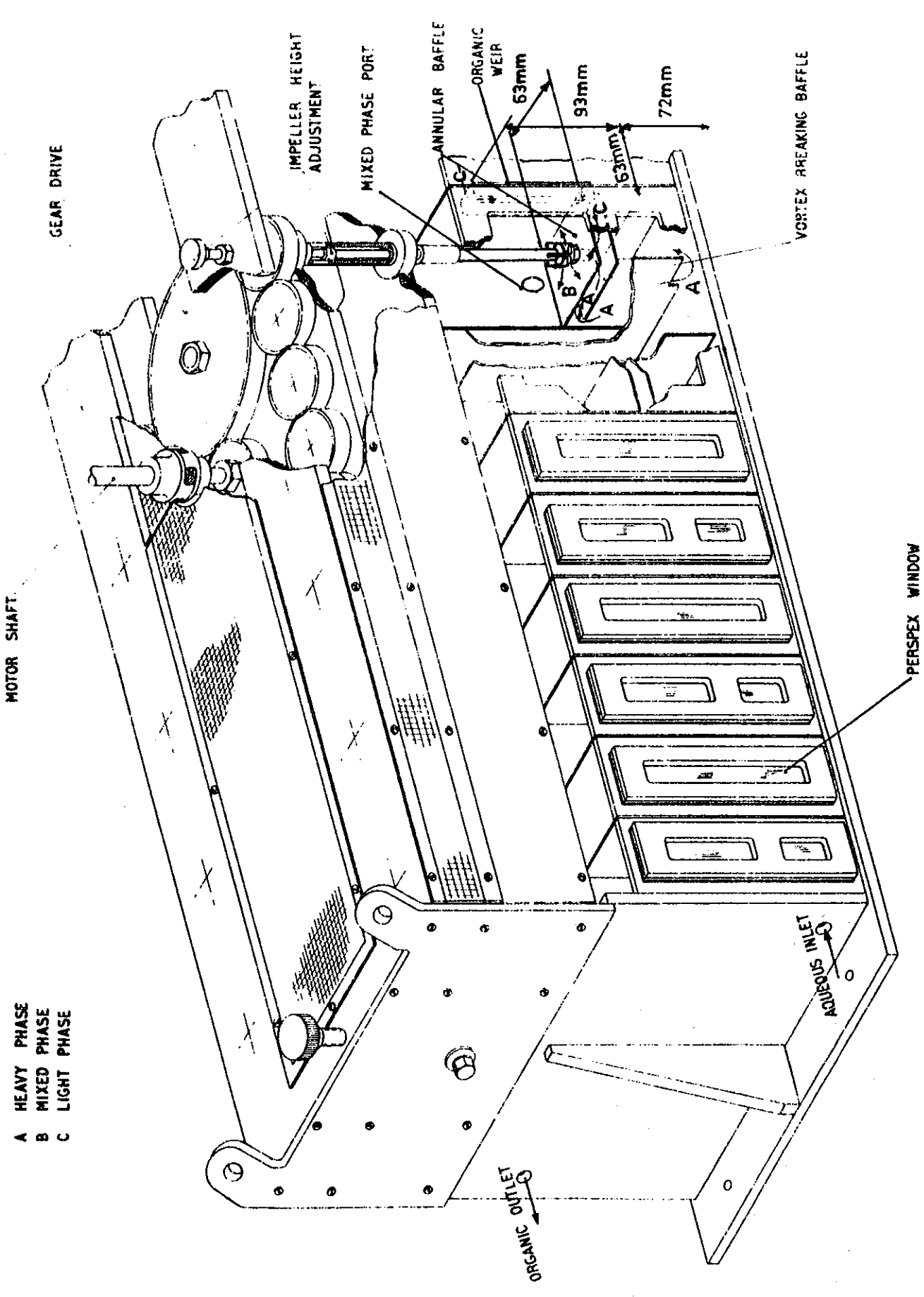


FIGURE 2. SIXTEEN STAGE MIXER-SETTLER UNIT

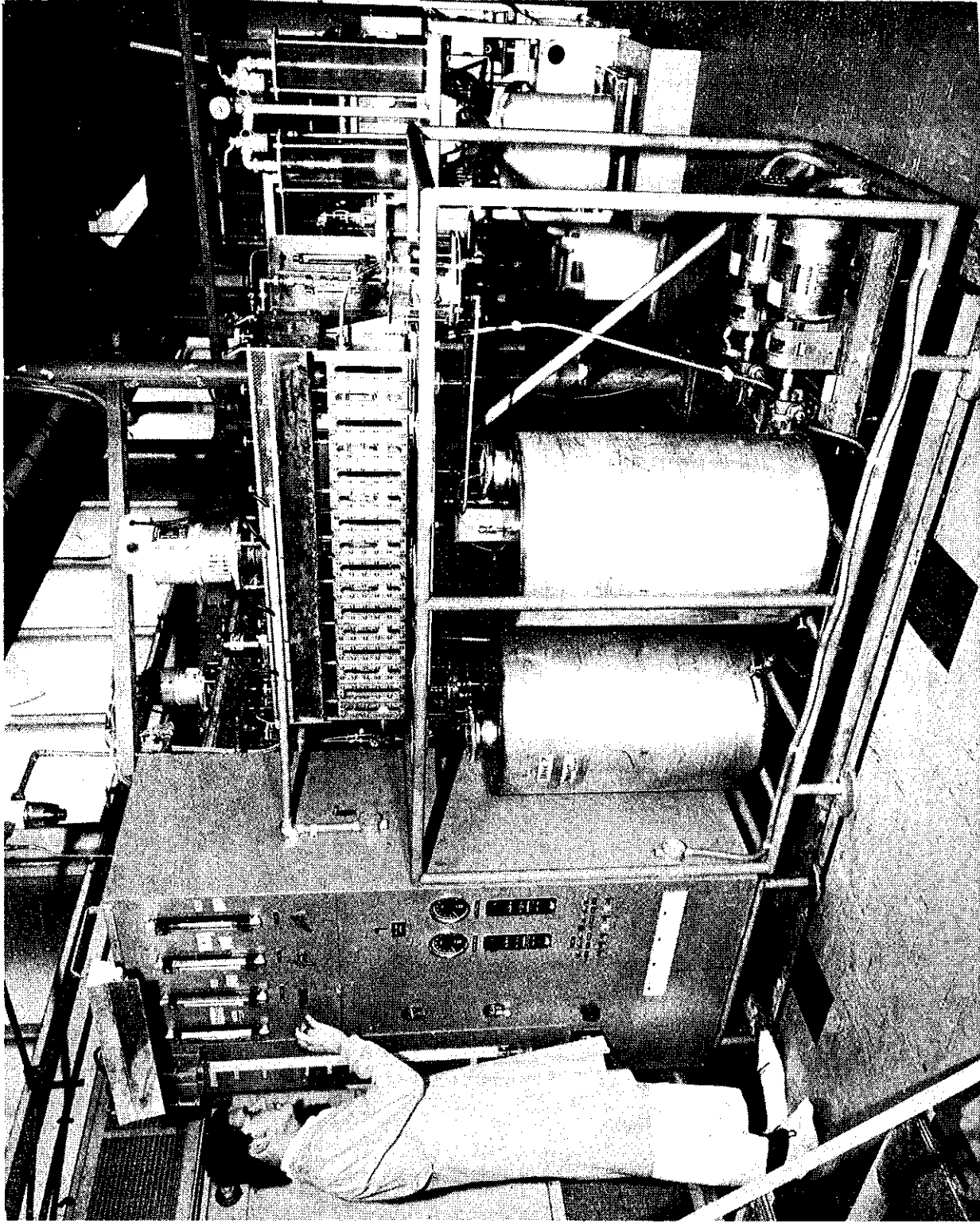


FIGURE 3 PILOT PLANT MIXER-SETTLER EQUIPMENT

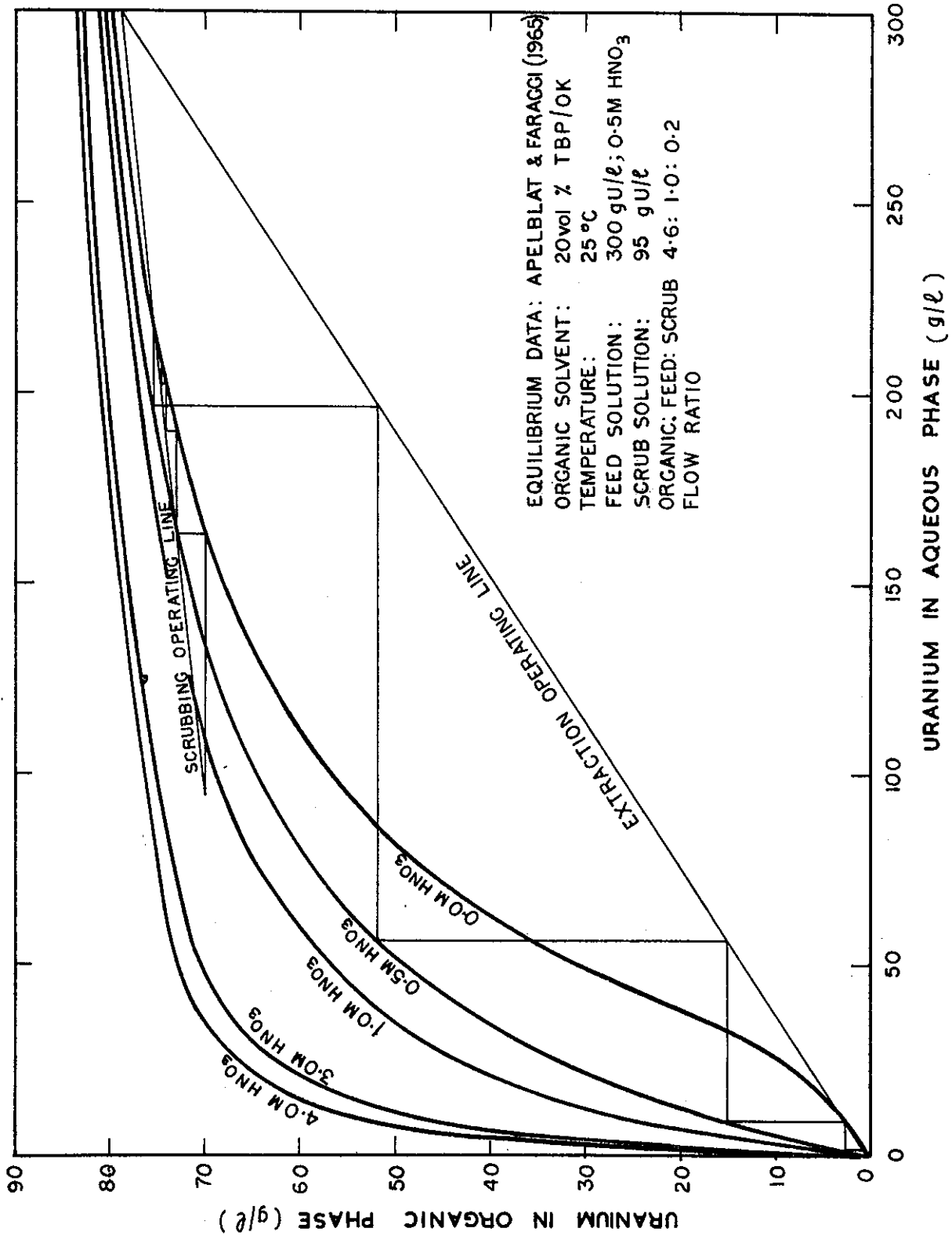


FIGURE 4. EFFECT OF FREE ACID CONCENTRATION ON URANIUM EQUILIBRIUM DATA

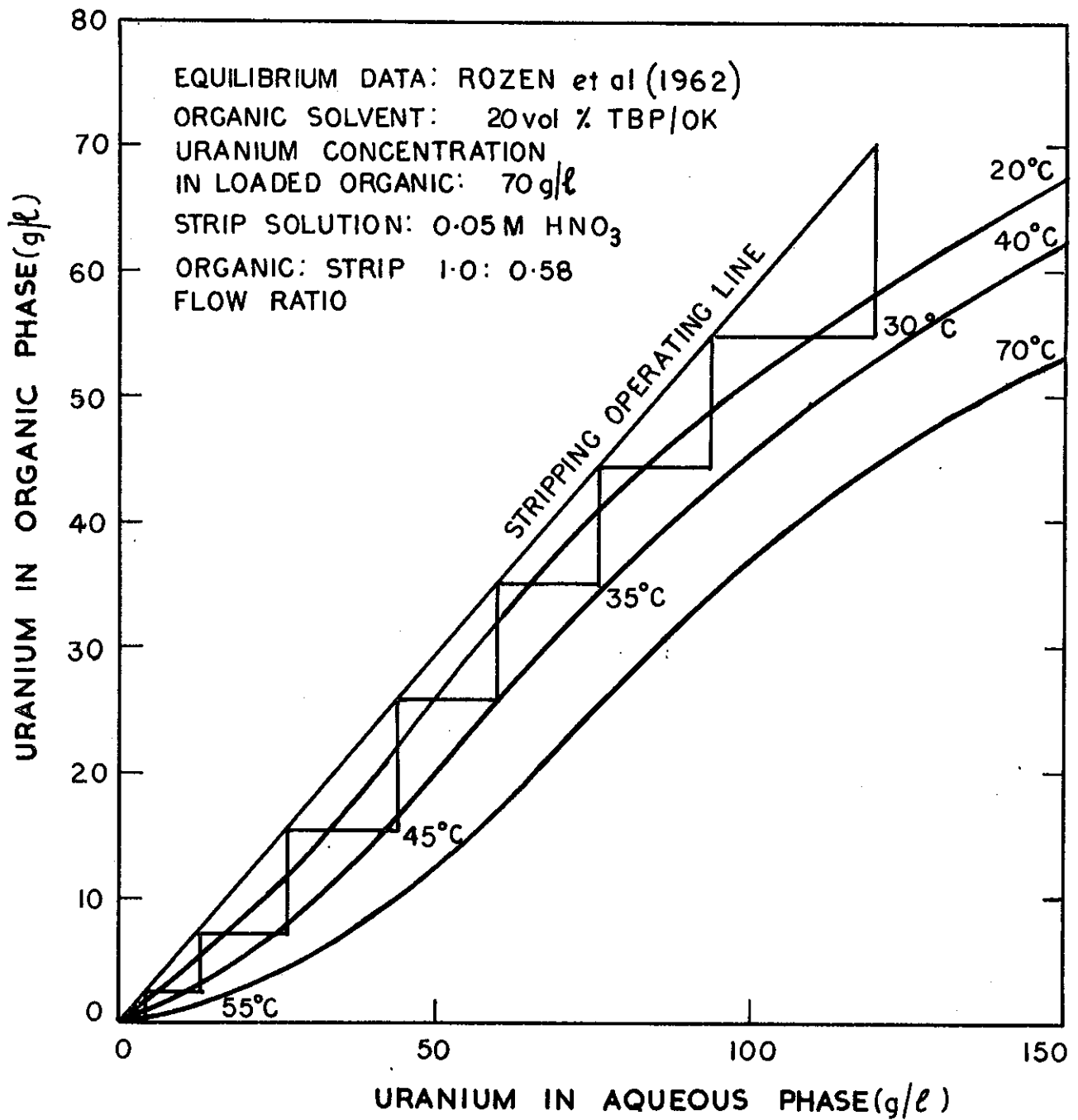


FIGURE 5. EFFECT OF TEMPERATURE ON URANIUM EQUILIBRIUM DATA

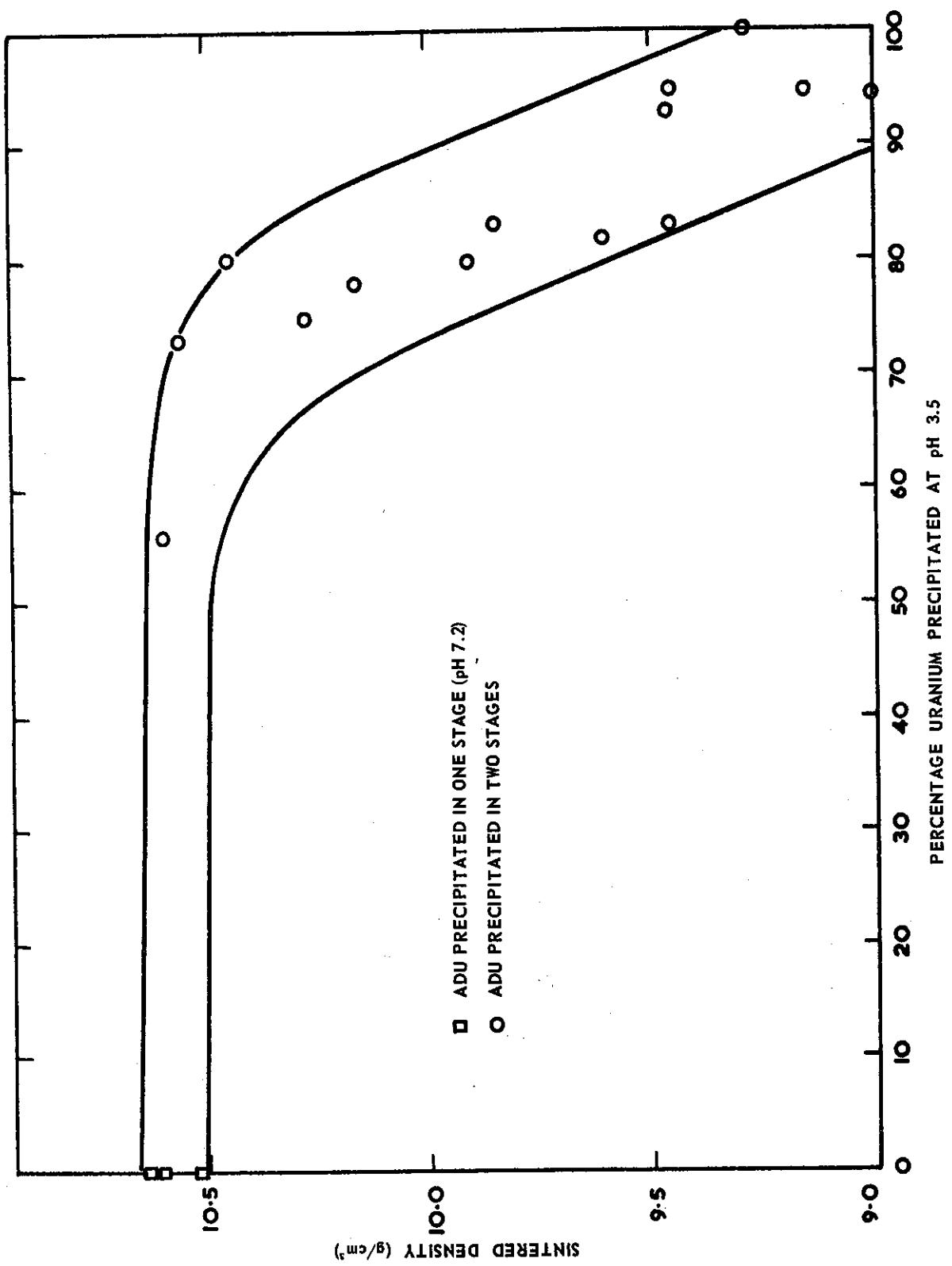


FIGURE 6. PERCENTAGE URANIUM PRECIPITATED AT pH 3.5 v. SINTERED DENSITY OF DERIVED UO PELLETS

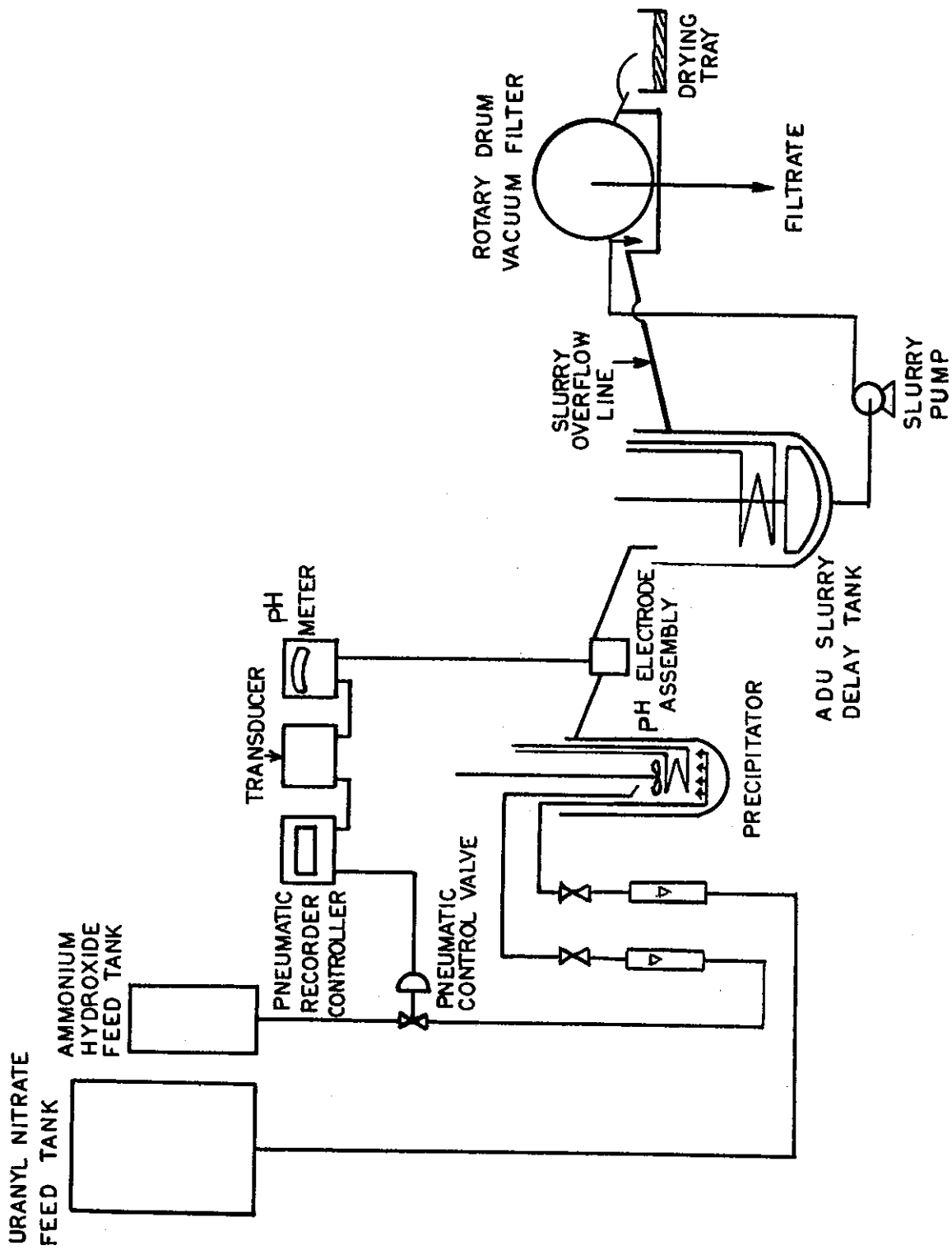


FIGURE 7. PILOT PLANT PRECIPITATOR AND FILTER

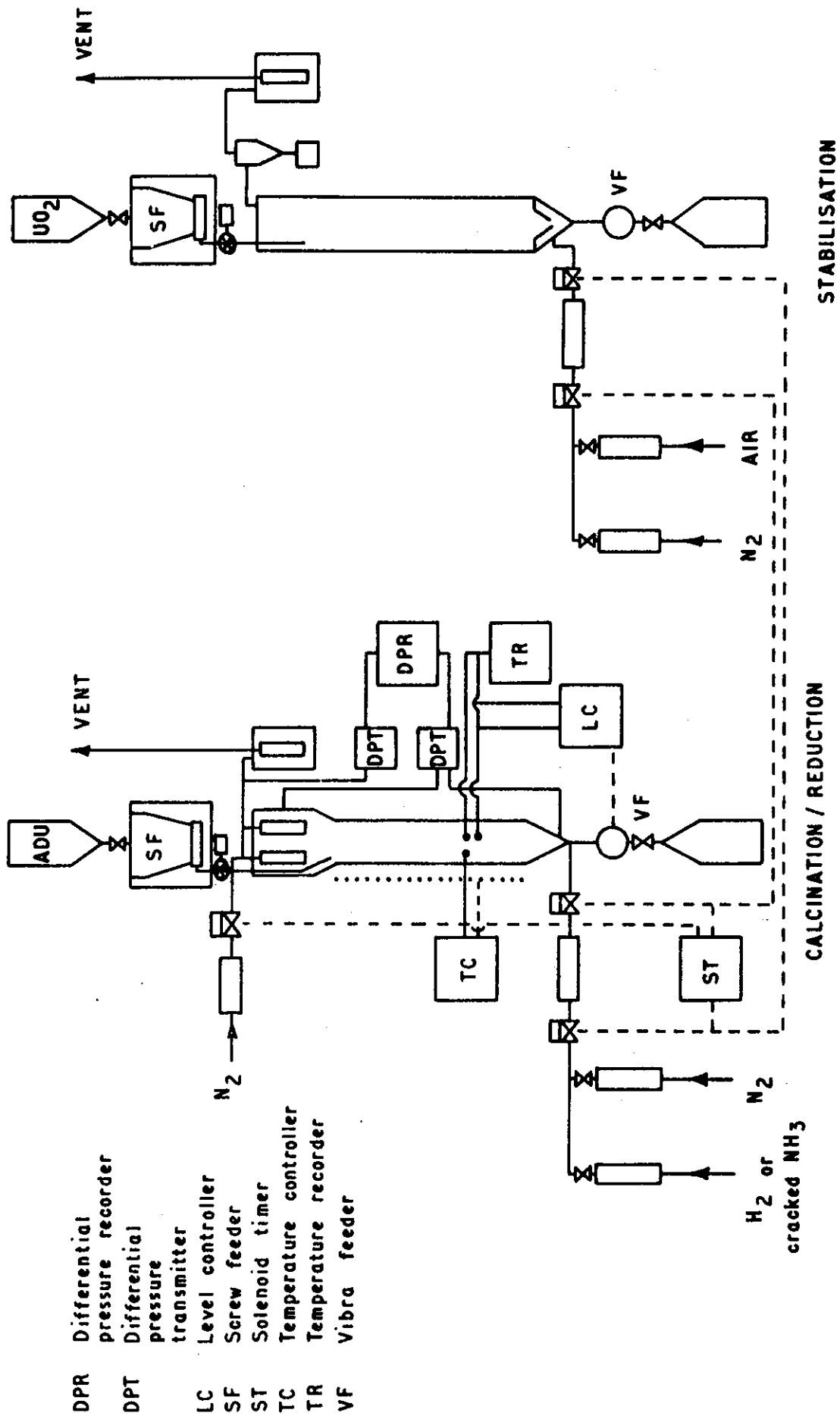


FIGURE 9. PULSED FLUIDISED BED REACTOR SYSTEMS

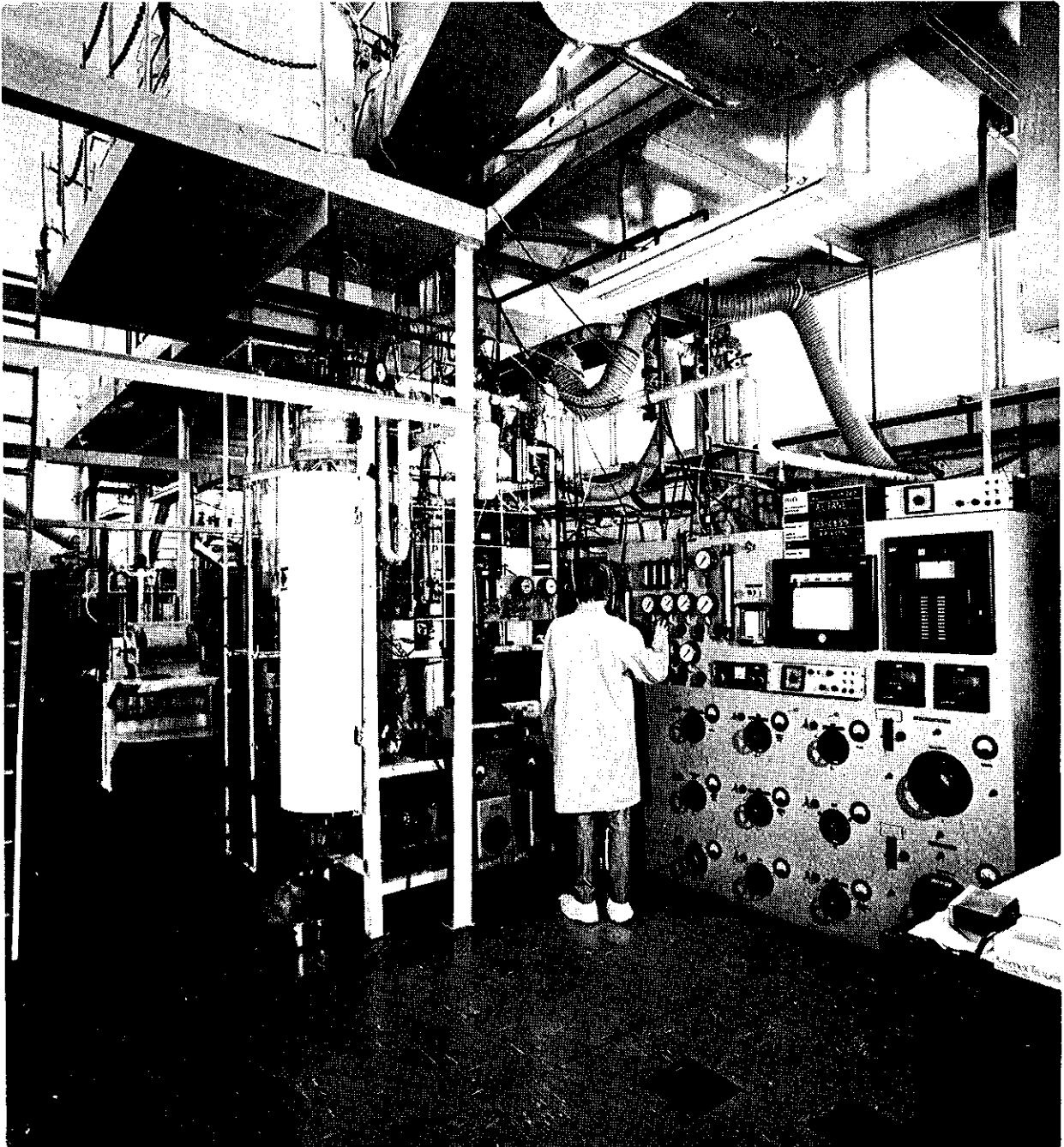


FIGURE 10. PULSED FLUIDISED BED REACTOR EQUIPMENT