AAEC/E226

AAEC/E226

AUSTRALIAN ATOMIC ENERGY COMMISSION
RESEARCH ESTABLISHMENT
LUCAS HEIGHTS

SPRAY DRYING OF AMMONIUM DIURANATE SLURRIES

by

D.M. LEVINS
P.G. ALFREDSON
R.C. HIRST
P.R. MACBRIDE

October 1972

ISBN 0 642 99498 6

AUSTRALIAN ATOMIC ENERGY COMMISSION

RESEARCH ESTABLISHMENT

LUCAS HEIGHTS

SPRAY DRYING OF AMMONIUM DIURANATE SLURRIES

by

D.M. LEVINS
P.G. ALFREDSON
R.C. HIRST
P.R. MACBRIDE

ABSTRACT

Slow and fast settling ammonium diuranate (ADU) slurries were dried in a one metre diameter laboratory spray drier using either pneumatic or centrifugal atomisation. Uniform, fine, dry powders were obtained with both atomisation techniques but pneumatic atomisation was preferred. Spray drying did not adversely affect the properties of the subsequent UO_2 powder and pellets. It was not necessary to treat the ADU feed slurry to remove ammonium nitrate in solution.

A theoretical model of droplet evaporation during spray drying is developed, taking into account droplet size distribution, gas-spray hydrodynamics and heat transfer rates. This model satisfactorily accounts for the observed operational characteristics of the drier.

National Library of Australia Card Number and ISBN 0 642 99498 6

The following descriptors have been selected from the INIS Thesaurus to describe the subject content of this report for information retrieval purposes. For further details please refer to IAEA–INIS–12 (INIS: Manual for Indexing) and IAEA–INIS–13 (INIS: Thesaurus) published in Vienna by the International Atomic Energy Agency.

ADU; ATOMIZATION; CENTRIFUGATION; DROPLETS; EVAPORATION; FUEL PELLETS; HYDRODYNAMICS; MATHEMATICAL MODELS; POWDERS; PNEUMATICS; PRESSING; SINTERING; SLURRIES; SPRAY DRYING; URANIUM DIOXIDE

CONTENTS

CONTENTS (Cont'd)

Page

1. INTRODUCTION

Uranium dioxide (UO_2) is the fuel most commonly used in nuclear power reactors. While the method of processing uranium concentrates depends to some extent on whether natural or enriched fuel is required, the ammonium diuranate (ADU) route is most widely used to produce the sinterable uranium dioxide powder required for fuel pellet fabrication. For example, for natural fuel, ADU is precipitated from uranyl nitrate solution with ammonia, then filtered, dried and finally calcined and reduced with hydrogen.

As part of a programme to investigate improved technology for UO_2 production (Alfredson 1970), spray drying of ADU slurries was studied as an alternative to other commonly used methods such as batch tray, rotary kiln and continuous belt drying. The advantages of spray drying are:

(1) The process is continuous and little operator supervision is necessary. This contrasts with the batch tray operations presently used in a number of facilities. As plant capacities grow, there will be an increasing economic incentive to develop continuous and fully automated processes for UO_2 production.

(2) Spray drying is a single operation from slurry feed to dried product. Filtration and washing procedures which normally precede drying can probably be eliminated.

(3) Spray drying typically produces a homogeneous product with characteristics which can be accurately controlled. Quality control is necessary at all stages of UO_2 production to minimise reject rates at the fabrication stage.

(4) The uniformity of the spray dried product contrasts with the 'lumpy' powders produced by other drying methods. Further, most materials can be spray dried in the form of spherical agglomerates. If this shape could be maintained during calcination and reduction, a free-flowing powder might be produced which could be fed to an automatic pellet press without further processing. At present, precompaction, crushing and granulation are generally required to produce a suitable free-flowing powder.

No previous study of the spray drying of ADU has been reported although Berry (1967) indicated that Eldorado Mining and Refining Ltd. has undertaken developmental work on the continuous spray drying of ADU. Seidl (1965) outlined design calculations for a pneumatic 'Micro-Drier' which has some features in common with a spray drier. Some interest has also been expressed in spray drying of uranium dioxide as a means of introducing binder-lubricants and producing a free-flowing powder for automatic pressing (Glatter 1957) and a process to this end has been patented (Wilkinson 1968).

This report describes experiments in a one metre diameter, laboratory spray drier in which both pneumatic and centrifugal atomisation of ADU slurries were studied. The properties of the dried powders are reported and the effect of spray drying on the characteristics of the UO_2 powders and pellets subsequently produced is discussed. A theoretical model of spray drying is presented which accounts for the observed operational characteristics of the drier.

2. THEORY OF SPRAY DRYING

Spray drying is characterised by the creation of a highly dispersed liquid in a high temperature gas followed by rapid evaporation. At least in theory, spray drier performance can be predicted from a knowledge of atomisation, drying and spray-gas hydrodynamics.

2.1 Atomisation

The aim of spray atomisation is to produce a high surface to volume ratio in a liquid phase resulting in high mass and heat transfer rates. Three types of atomisers are commonly employed:

Pressure nozzles: These nozzles convert the energy of a pressurised liquid into a high velocity liquid sheet which collapses into ligaments and ultimately droplets on contacting the gas stream. Pressures employed generally range from 0.7 to 30 MN m^{-2} with the highest pressures required to produce the smallest droplets (Tate 1965). Pressure nozzle atomisation is not suitable for coarse or abrasive slurries because of excessive wear on atomiser internals and because the nozzle orifice can easily be plugged. It was not used in the present experiment, and will not be further discussed.

Pneumatic atomisers: Pneumatic atomisation relies on the shearing forces between a liquid surface and a high velocity air jet for liquid dispersion. Because pneumatic atomisers can produce extremely fine atomisation, they are often used for small-capacity or pilot plant installations. Perhaps the best correlation for droplet size from pneumatic converging nozzle atomisers is due to Gretzinger and Marshall (1961):

$$\bar{d}_m = 2600 \left[\left(\frac{M_l}{M_a} \right) \left(\frac{\mu_a}{G_a d_{wp}} \right) \right]^{0.4} \qquad \ldots(1)$$

where $\bar{d}_m$ is the mass median droplet diameter expressed in micrometres and the other symbols are as defined in Section 10. Gretzinger and Marshall found that droplet size distribution was log-normal with the geometric standard deviation given by

$$\sigma_g = 1.77 \, \bar{d}_m^{\,0.14} \quad . \qquad \ldots(2)$$

The geometric standard deviation (σ_g) is defined as the ratio of the 84.13 per cent diameter to the 50 per cent diameter and for a log-normal distribution is independent of the type of diameter for which it is calculated (Herdan 1960).

Rotary atomisers: These rely on centrifugal force to accelerate a thin film of liquid to the edge of a high speed rotating disk. With peripheral speeds up to several hundred metres per second, the liquid is discharged as a film or as ligaments which subsequently disintegrate into droplets. A wide range of disk designs have been tried from the simple flat and saucer-shapes to the widely used radial vane or slot types. Rotary atomisers are ideal for spraying slurries, particularly where large capacities are required. Droplet size distribution is generally narrower than that obtainable with pneumatic nozzles (Belcher, Smith and Cook 1963). The most widely used correlation for droplet diameter is that of Friedman, Gluckert and Marshall (1952).

$$\frac{\bar{d}_{vs}}{r} = 0.4 \left(\frac{\Gamma}{\rho N r^2} \right)^{0.6} \left(\frac{\mu}{\Gamma} \right)^{0.2} \left(\frac{\sigma \rho L_d}{\Gamma^2} \right)^{0.1} \qquad \ldots(3)$$

where $\bar{d}_{vs}$ is the Sauter (or surface/unit volume) droplet diameter. Masters and Mohtadi (1967) found this correlation reliable for small diameter, high speed atomisers. Friedman, Gluckert and Marshall (1952) found that droplet size distribution was log-normal with the geometric standard deviation given by

$$\sigma_g = 0.93 \, \bar{d}_{vs}^{\,0.1} \qquad \ldots(4)$$

where $\bar{d}_{vs}$ is expressed in micrometres. The Sauter drop diameter can be converted to the mass median diameter by the equation (Herdan 1960),

$$\ell n \, \bar{d}_m = \ell n \, \bar{d}_{vs} + 0.5 \, \ell n^2 \, \sigma_g \qquad \ldots(5)$$

2.2 Drying

Droplet evaporation is a simultaneous heat and mass transfer operation which is a function of temperature, humidity and transport properties of the gas as well as the drop diameter and its velocity relative to the gas stream. The most widely quoted equations for heat and mass transfer are those of Ranz and Marshall (1952),

$$Sh = 2 + 0.60 \, Re^{0.50} \, Sc^{0.33} \qquad \ldots(6)$$

$$Nu = 2 + 0.60\ Re^{0.50}\ Pr^{0.33} \qquad \text{...(7)}$$

For small particles, drag forces predominate over inertial forces so that droplets released into a gas stream quickly attain their terminal velocity. For droplets smaller than 100 µm diameter the terminal velocity can be ignored with little error (Marshall and Seltzer 1950) and Equation 6 and 7 simplify to

$$Sh = d_t k_f / D_v = 2 \qquad \text{...(8)}$$

$$Nu = h d_t / k_f = 2 \quad . \qquad \text{...(9)}$$

With this assumption, the equation for heat transfer can be written,

$$Q = hA\ \Delta T \qquad \text{...(10)}$$

or

$$\frac{\Delta H\ d(\pi \rho d_t^3/6)}{dt} = 2\ k_f\ \pi d_t\ \Delta T \quad . \qquad \text{...(11)}$$

Integration gives the diameter d_t at time t

$$d_t^2 = d_o^2 - \frac{8\ k_f\ \Delta T t}{\rho\ \Delta H} \quad . \qquad \text{...(12)}$$

The time for complete evaporation τ is then

$$\tau = \frac{\rho\ \Delta H d_o^2}{8\ k_f\ \Delta T} \quad . \qquad \text{...(13)}$$

In determining the temperature driving force ΔT, it is usual to assume that the drying air is at the outlet temperature and the droplet temperature is equal to the wet-bulb temperature during evaporation. It should be noted however that when the hot drying air is introduced close to the atomiser, significant deviations from this assumption may occur.

2.3 Gas-Spray Hydrodynamics

This is an extremely complex subject about which little is known. Yet it is an important aspect of spray drier design since the capacity of a drier is a function of its ability to dry the solution or slurry before it impinges on the walls of the drier. If a complete description of the air velocity both inside and outside the atomiser jet were known, it would be possible to follow the trajectory of a droplet as it evaporates. Such an approach is not yet possible. Instead, reliance must be placed on empirical equations of the velocity inside the atomiser jet. Our approach follows the work of Albertson et al. (1948) and Gluckert (1962).

2.3.1 Pneumatic atomisation

The decrease in centre-line velocity in an air stream initially at sonic velocity is given by Albertson et al. (1948) as,

$$U = \frac{dy}{dt} = \frac{6.2\, D_e\, U_M}{y} , \qquad \ldots(14)$$

where U_M is the initial jet velocity which can be determined from a momentum balance between gas and liquid. Since initially the liquid momentum is negligible,

$$U_M = \frac{U_a M_a}{(M_a + M_l)} . \qquad \ldots(15)$$

Integration of Equation 14 gives the distance a droplet in the centre of the jet travels in time t, as:

$$y^2 = 12.4\, D_e\, U_M t . \qquad \ldots(16)$$

2.3.2 Centrifugal atomisation

The decrease in jet centre-line velocity (Gluckert 1962), is given by

$$U = \frac{dy}{dt} = 0.16\, U_M \sqrt{\frac{M_l}{N\rho_a r y (y - r)}} . \qquad \ldots(17)$$

The initial jet velocity is the vector sum of the radial and tangential velocities (Fraser, Eisenklam and Dombrowski 1957).

$$U_M = 2 \sqrt{2}\, \pi r N . \qquad \ldots(18)$$

Integration of Equation 17 gives for $y >> r$,

$$y^2 = 0.32\, U_m t \sqrt{\frac{M_l}{N\rho_a r}} . \qquad \ldots(19)$$

2.4 Spray Drier Capacity

Equations 1 - 19 provide a preliminary basis for spray drier design or selection or, alternatively, a method for the prediction of a particular unit's performance. For satisfactory operation a droplet must dry before it impinges on the spray drier walls. For pneumatic atomisation the limiting case occurs when the spray travels the chamber length L in τ seconds. Then, from Equations

14 to 16

$$\frac{d_o}{L} = 0.80 \sqrt{\frac{k_f \Delta T}{U_a D_e \rho \Delta H} \left(\frac{M_a + M_1}{M_a}\right)} \quad . \qquad \ldots(20)$$

Equation 20 gives the maximum droplet size that can be dried in a chamber length L and implies that the drier diameter is not a limiting factor. This is most certainly the case if

$$D \quad > \quad 2L \tan(\alpha/2)$$

where α is the spray angle, which generally lies in the range 16 - 30° for pneumatic atomisers. In centrifugal atomisation, the spray is discharged in the radial direction and the limiting case occurs when $t = \tau$ and $y = D/2$. Then solving Equations 13, 18 and 19 gives

$$\frac{d_o}{D} = 0.84 \sqrt{\frac{k_f \Delta T}{\rho \Delta H} \left(\frac{\rho_a}{rNM_1}\right)^{\frac{1}{2}}} \quad . \qquad \ldots(22)$$

Equations 20 and 22 can be expressed in terms of the rate of heat transfer to the spray by means of the relation,

$$Q = \Delta H \, M_1 \quad . \qquad \ldots(23)$$

For pneumatic atomisation

$$Q = 0.64 \left(\frac{L}{d_o}\right)^2 \frac{k_f \Delta T}{U_a D_e \rho} \frac{M_1 (M_a + M_1)}{M_a} \qquad \ldots(24)$$

and for centrifugal atomisation

$$Q = 0.70 \left(\frac{D}{d_o}\right)^2 \frac{k_f \Delta T}{\rho} \sqrt{\frac{\rho_a M_1}{rN}} \quad . \qquad \ldots(25)$$

3. EQUIPMENT AND PROCEDURE

ADU slurries were dried in an 'Anhydro' Laboratory Spray Drier (size 1) (see Figure 1). This unit has facilities for either centrifugal or pneumatic nozzle atomisation. Table 1 gives its specifications and Figure 2 is a schematic diagram of the drier and ancillary equipment.

The slurry was pumped from a stirred feed vessel at 2 - 8 litres h^{-1} and passed into the drier via either the rotating disk atomiser or the pneumatic nozzle. The centrifugal atomiser contained four outlets of circular cross-section with a diameter of 1.6 mm on the periphery of a 65 mm disk. The pneumatic atomiser nozzle was supplied by Spraying Systems Co., Illinois, USA (spraying set-up no. 4) and was designed so that contact of air and slurry took place externally to the nozzle (see Figure 2). After atomisation by either method, water was rapidly evaporated from the spray as it contacted the heating air which was blown through the drying chamber at a constant rate. A bank of electrical heaters enabled air inlet temperature to be varied up to a maximum of 280°C. On drying, the powder was conveyed into a small cyclone where it was removed from the air stream. Any ADU dust still remaining in the air was removed by entrainment with water in an ejector scrubber. The ejector design is shown in Figure 3. In practice almost all the ADU was removed by the cyclone separator and little ADU was found in the water scrubber circuit.

Two ADU slurries were prepared which were typical of slow and fast settling suspensions. The 'slow' settling slurry was prepared by single stage precipitation of uranyl nitrate with aqueous ammonia at pH 7.2 while the 'fast' settling slurry was obtained by two stage precipitation (Janov et al. 1971). In most experiments, no attempt was made to filter or wash the ADU before spray drying.

Gravity feed to convey the slurry to the atomiser was found unsuitable because of frequent blockages at the valve leading from the feed vessel. In the final arrangement, slurry was pumped from a feed vessel located below the atomiser level. Little or no throttling of the flow was required and the feed rate was adjusted using a variable speed drive. Except at the lowest flow rates (2 - 3 litres h^{-1}) where accurate control of the slurry feed rate was sometimes difficult, this arrangement was quite satisfactory.

The maximum concentration of slurry that could be spray dried was limited by the final settled density of the ADU and by mechanical problems associated with satisfactory pumping of the suspensions at low flow rates (2 - 8 litres per hour). In the case of the 'slow' settling slurry the final settled concentration was about 300 kg m^{-3} and in practice the maximum feed concentration was limited to about 280 kg m^{-3}. The final concentration of the fast settling ADU was about 800 kg m^{-3}. The maximum feed concentration used in the present series of experiments was 500 kg m^{-3} but more concentrated slurries could be satisfactorily pumped.

The ADU powders were characterised in terms of their moisture content, chemical composition and bulk density. Moisture content of the product powder was determined by drying in an oven at 50°C for 18 hours. Uranium, nitrate and ammonia contents of the powders were measured by conventional chemical methods.

Pour and tap densities were determined according to the following standardised technique. The powder was first sieved to -150 mesh and then poured through a filter funnel into a 17 mm diameter measuring cylinder. The height through which the powder fell varied from 135 mm at the start of pouring to 36 mm at the finish. Pour density was calculated from the weight of ADU occupying 23 cm^3 of poured volume. The powder in the measuring cylinder was then tapped to constant volume by dropping the cylinder onto a cork base from a height of 50 mm. Tap density was calculated from the weight of ADU occupying the tapped volume. Pour and tap bulk densities determined in this way correlated reasonably well (Figure 4).

4. OPERATIONAL RANGE OF THE SPRAY DRIER

4.1 Experimental Results

Preliminary experiments were undertaken with water in place of the slurry in order to determine the operating range of the drier. This range is set by the requirement that complete evaporation should occur before the spray impinges on the walls of the drier. If this requirement is not met, a wall deposit of caked powder will build up with a subsequent deterioration in powder characteristics and recovery. Figures 5 and 6 show the operational limits for both pneumatic and centrifugal atomisation established by observing the spray pattern through the viewing window of the drier. When the capacity was exceeded, droplets of water were visible either on the roof of the drier, in the case of pneumatic atomisation, or as a 'halo' around the drier walls with centrifugal atomisation. Three regions of operation were distinguished; a region of apparent complete evaporation in the drying chamber, a region where only minor wall impingement was noted and a region of gross wall impingement. Completely satisfactory operation is only possible in the first region.

Although the relationships between evaporative capacity and atomiser conditions were determined with water, it was found that they could be applied equally well to ADU slurries. Provided the drier was operated within the limits indicated by Figures 5 and 6, the powder produced was quite dry and typically of a uniformly fine texture. With pneumatic atomisation, maximum evaporative capacity was about 7 kg h^{-1} at 350 kN m^{-2} air gauge pressure but only 4 kg h^{-1} at 100 kN m^{-2}. Evaporative capacity with centrifugal atomisation was about 7 kg h^{-1} at a disk speed of 900 rev s^{-1} and 4 kg h^{-1} at 500 rev s^{-1}.

4.2 Theoretical Predictions

Mean droplet sizes for both atomisers used in the present work have been calculated from Equations 1, 3 and 5 and are shown in Figure 7. Droplet diameter increases with feed rate but decreases as either air pressure or disk speed increases. Pneumatic atomisation produces droplets with the smaller mean diameter but according to Equations 2 and 4, centrifugal atomisation gives the more uniform droplet size distribution.

The operational range of the drier can be predicted from the equations developed in Section 2. From Equations 20 and 22 the maximum droplet size that is completely evaporated can be calculated. All droplets less than this diameter will be dried while the extent of evaporation of drops greater than this diameter can be calculated via Equation 12. Given the droplet size distribution (Equations 1 - 5), the percentage volume of the spray that impinges on the chamber wall can be computed. Results of such calculations are shown in Figures 8 and 9 for both spray drying methods. The curves are of the same general shape as the experimental curves (Figures 5 and 6) though not parallel. In the case of pneumatic atomisation 'gross wall impingement' corresponds to above 13 - 21 per cent by weight of the central portion of the jet hitting the drier roof. 'Complete evaporation' corresponds to below 9 - 16 per cent impingement. The latter figure is higher than expected, probably because the air inlet is located in the centre of the roof and acts to sweep the spray away from the wall. For centrifugal atomisation the figures are lower; 6 - 10 per cent for gross wall impingement and 3 - 7 per cent for complete evaporation. While it is difficult to quantify the terms 'gross wall impingement' and 'complete evaporation', it appears that the capacity of the drier is at least as good as is predicted by the simple models assumed in the theoretical analysis.

5. SPRAY DRYING OF ADU SLURRIES

A series of experiments was undertaken to determine the effect of slurry feed concentration and drier operating conditions on the characteristics of the ADU product.

5.1 Pneumatic Atomisation

5.1.1 Slow settling ADU slurry

The results for the slow settling slurry prepared by single stage precipitation are set out in Table 2. The effect of drier outlet temperature on the pour and tap densities of the product powders is given in Figure 10. As the air inlet temperature was fairly constant at about 275°C, drier outlet temperature was determined mainly by the slurry feed rate. Though there is considerable scatter, a trend towards lower bulk densities as outlet temperature is increased is evident. At the lowest feed rates, the pour density is very low

(~ 350 kg m^{-3}) compared with a true density for ADU of about 4500 - 5200 kg m^{-3} (Woolfrey 1968). A high bulk density is desirable for fuel pellet pressing.

There is general agreement in the literature that increasing drying temperature decreases the bulk density (Marshall 1954). The usual explanation for this effect is as follows. The particle size of the dried powder, and hence the bulk density, depends on the relative rate of drying compared with the rate of shrinkage due to surface tension forces. If the rate of drying is increased (by increasing inlet or outlet temperatures) shrinkage is minimised and particles of greater porosity are produced.

The single run at a lower slurry concentration (219 kg m^{-3}) gave a bulk density significantly above the general trend, suggesting that ADU bulk density increases with decreasing solids content. This is in agreement with most previous studies (Duffie and Marshall 1953, Wallman and Blyth 1951) although at least two workers have reported the reverse effect (Marshall 1954). The abnormally high moisture content of the product powder is another possible reason for the high bulk density.

The free water content of the powders produced was found to vary between negligible amount (< 0.5 per cent) and 5.5 per cent with most results below 1 per cent. Moisture content did not vary consistently with operating conditions but, at the lowest feed rates, a colour change from the yellow slurry to the bright orange powder was noticed, suggesting that some bound water had also been removed.

ADU was prepared by precipitation with ammonia from a uranyl nitrate solution so that the slurry contained ammonium and nitrate ions in addition to the bound ammonia present. No attempt was made to wash the feed slurry. The ammonia and nitrate contents of the dried powder varied substantially with the outlet temperature from the drier as shown in Figure 11, indicating that at the higher outlet temperatures extensive decomposition of the ammonium nitrate took place in the drying chamber.

Ammonium nitrate can decompose in three ways (Thorpe and Whiteley 1947, Feick and Hainer 1954). At low and intermediate temperatures, ammonia is lost endothermically when exposed to air and the residue becomes acidic,

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3 \quad . \qquad \ldots(I)$$

At about 170°C and above, irreversible, exothermic decomposition occurs,

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \quad . \qquad \ldots(II)$$

At very high temperatures nitrogen and oxygen are liberated,

$$2NH_4NO_3 \rightarrow 2N_2 + 4H_2O + O_2 \quad . \qquad \text{...(III)}$$

Under the experimental conditions of this study only reactions (I) and (II) are of interest. The ammonia content of the product decreased more rapidly than the nitrate content as drier outlet temperature increased (see Figure 11) suggesting that at least part of the decomposition occurred via reaction scheme (I). It does not appear likely that any chemically bound ammonia was liberated from the ADU at the temperatures used in these experiments. Woolfrey (1968) indicated that no bound ammonia is liberated below about 250°C with most evolution taking place in the range 350 - 450°C.

No effect of atomising air pressure on particle properties was apparent. However, from visual observation of the spray pattern, a gauge pressure of 250 - 270 kN m^{-2} was found to be most satisfactory for adequate spray dispersion with minimal wall impingement.

Examination of the product powder under an optical microscope revealed that most particles were between 5 - 10 µm in diameter and were of roughly spherical shape. No effect of operating conditions on particle size was apparent.

5.1.2 Fast settling ADU slurry

Table 3 lists results obtained with the fast settling slurry prepared by two stage precipitation. Some of the trends discussed in the previous section are also apparent in these results and will be referred to only briefly.

Product bulk density varied little with operating conditions for the fast settling slurry and no consistent trend was evident. This was in contrast with the effect observed for the slow settling slurry (see Figure 10). The moisture content of all powders was below 1 per cent by weight.

Figure 12 shows the ammonia and nitrate contents of the product powder as a function of drier outlet temperature. The NH_3/U and NO_3^-/U ratios were below those reported for the slurry prepared by single stage precipitation because, in the present case, the mother solution was decanted before the feed slurries were prepared by adding distilled water. The tendency for the ammonia and nitrate contents to decrease with increasing outlet temperature was again apparent. However, because less nitrate and free ammonia was present the effect was not as large.

Powder particle size distribution was determined using a Sharples Micromerograph. The size distribution varied only slightly with drier operating conditions. Figure 13 shows a particle size distribution analysis for a typical dried powder. The mass median diameter of 5.4 μm was consistent with estimates of particle size obtained by optical microscopy.

5.2 Centrifugal Atomisation

Centrifugal atomisation was not as satisfactory as pneumatic atomisation for the ADU slurries studied. Atomisation of slow settling slurries was possible only at relatively low feed concentrations while fast settling slurries quickly blocked the atomiser feed line. These blockages were due to a thick scale of caked ADU which built up at the inlet to the disk feed chamber near the point where the slurry first experienced the high temperatures inside the drier.

Results obtained with the slurry prepared by single stage precipitation are shown in Table 4. The moisture content of the powders, while still acceptable, was generally above that obtained with pneumatic atomisation. The ammonia and nitrate contents of the product which are shown in Figure 14 were found to be a function of drier outlet temperature as observed before. Pour and tap densities did not vary consistently with operating conditions but were in the same range as those obtained by pneumatic atomisation.

A disk speed of 650 - 1000 rev s^{-1} corresponding to peripheral speeds in the range 130 - 200 m s^{-1} and a feed rate of 4 - 5 litres h^{-1} appeared to be the most satisfactory operating conditions for this atomiser. Under these conditions the powders produced were very similar in appearance under the microscope to those obtained by pneumatic atomisation. Mean particle size was about 7 - 10 μm.

5.3 Discussion

The particle size of a spray dried slurry will be smaller than the initial droplet diameter because of shrinkage due to evaporation. A mass balance on a single droplet gives,

$$d_f = \left(\frac{C_f}{\rho_p}\right)^{1/3} d_o \quad , \qquad \ldots(26)$$

where d_f is the diameter of the product particle of density ρ_p. The final particle density ρ_p must be between the tap density (ρ_{tap} = 800 - 1300 kg m^{-3}) and the true density (4500 - 5200 kg m^{-3} (Woolfrey 1968)). If the external void fraction is ε_{ext} then

$$\rho_p = \frac{\rho_{tap}}{(1 - \varepsilon_{ext})} \qquad \ldots(27)$$

These equations can be applied to a typical set of data for pneumatic atomisation. The following values can be extracted from Table 2; feed rate = 4.5 litres h^{-1}, C_f = 243 kg m^{-3}, atomising air pressure = 276 kN m^{-2} and ρ_{tap} = 1170 kg m^{-3}. Substituting these values for C_f and ρ_{tap} in Equations 26 and 27 and assuming $\varepsilon_{ext} = 0.40$, gives $d_f/d_o \sim 0.50$. From Figure 7, $d_o \sim$ 20 μm under these conditions so that $d_f \sim$ 10 μm. This can be compared with an estimated product diameter of 5 - 10 μm.

Taking a typical result using the centrifugal atomiser; feed rate = 4.2 litres h^{-1}, C_f = 153 kg m^{-3}, disk speed 700 rev s^{-1}, ρ_{tap} = 1060 kg m^{-3}; gives $d_f/d_o = 0.42$. Figure 7 predicts $d_o \sim$ 37 μm under these conditions giving $d_f \sim$ 15.5 μm. Product diameter was estimated at 7 - 10 μm. The difference between observed and predicted particle size could be due to a small amount of particle attrition in the drier and in the cyclone collector and to the limitations of the theoretical analysis.

It was hoped that spray drying would result in a free-flowing, spherical ADU powder. This proved to be impossible in this laboratory unit because only relatively fine powders could be produced. Some idea of the particle size that could be produced in a larger drier can be obtained from Equations 20, 22 and 26. If attrition is to be avoided in a larger unit it may be necessary to add a binder to the slurry.

Chemical analysis of the powders produced indicates that ammonium nitrate is decomposed during spray drying at a rate markedly dependent on spray drier chamber temperature. Extrapolation of results of Figures 11, 12 and 14 suggests, that, if chamber temperature were maintained at about 200°C or above, little residual nitrate or free ammonia would be present in the product powder. Any undecomposed ammonium nitrate will, of course, be rapidly lost at the higher temperatures, 600°C or more, required for calcination-reduction. Filtration or washing of the slurry prior to spray drying seems unnecessary.

6. EFFECT OF SPRAY DRYING ADU ON PROPERTIES OF UO_2

Since fuel element performance is related to the properties of the UO_2 powder used in pellet fabrication, it is important to determine if the method of drying has any effect on the properties of uranium dioxide produced after calcination and reduction. Properties of particular interest include the surface area of the UO_2 powder and the density and microstructure of the sintered pellets.

To determine the effect of spray drying on UO_2 surface area, two experiments were conducted. In the first, unwashed ADU slurry was spray dried while, in the control experiment, ADU slurry was treated in the usual manner by washing, filtering and tray drying in an oven (Janov et al. 1971). In both cases, subsequent calcination-reduction to UO_2 was carried out under identical conditions in a batch-tray unit. The surface areas of ADU and UO_2 powders are shown in Table 5. The spray dried ADU powder was of appreciably lower surface area, probably because crystallisation of ammonium nitrate during evaporation greatly reduced the accessible pore area, but, on calcination-reduction, both UO_2 powders gave essentially the same surface area.

Pellet fabrication tests were also carried out for the UO_2 powder prepared from spray dried ADU. Both the powder as received and a -100 mesh fraction were isostatically pressed at 309 MN m^{-2} before sintering at 1600°C. Green and sintered densities are listed in Table 6. Under identical conditions of precipitation, reduction and sintering, a pellet density of 10500 ± 500 kg m^{-3} is normally obtained with UO_2 from tray dried ADU (Janov - AAEC private communication). Within experimental limits, the method of drying appears to have no effect on sintered density.

Examination of the microstructure of UO_2 pellets made from the UO_2 powder as received indicated that agglomerates as large as 150 - 200 μm were present in the unsieved powder. Since the average particle size of the ADU prepared was 5 - 10 μm with few particles above 30 μm, it can only be concluded that some sintering together of particles occurred during batch-tray calcination-reduction. The microstructure of the -100 mesh fraction shown in Figure 15 is quite satisfactory and is at least as good as those obtained with tray dried ADU.

7. CONCLUSIONS

(1) ADU slurries can be spray dried at concentrations up to 80 per cent of the settled density without difficulty. Maximum throughput for the laboratory spray drier investigated was about 7 kg of slurry per hour. The powders produced were quite dry and typically of a uniformly fine texture.

(2) A theoretical analysis of heat transfer rates to droplets dispersed in a jet confirmed the operational limits of the drier established by experiment. It was shown that only relatively fine droplets could be completely evaporated in the one metre drying chamber of the laboratory unit. The particle size of the spray dried ADU product (5 - 10 μm diameter) was consistent with these calculations.

(3) It is not necessary to wash or otherwise treat the slurries before spray drying. Ammonium nitrate, a by-product of ADU precipitation, is partially removed during spray drying at a rate dependent on the drying chamber temperature. The rest will rapidly decompose during calcination-

reduction.

(4) Pneumatic atomisation proved to be the most suitable method of droplet dispersion. Atomisation using a centrifugal disk was satisfactory only at relatively low concentrations because of feed line blockage. It was considered that the performance of this atomiser could probably be improved by minor modifications to feed chamber design.

(5) Spray drying of ADU did not adversely affect the properties of the subsequent, ceramic grade UO_2 powder and pellets.

8. ACKNOWLEDGEMENTS

The authors wish to thank other members of the Chemical Engineering Section, notably Messrs. W.A.F. Layton and R.D. Taylor for their technical assistance and Mr. J. Janov and co-workers who provided the ADU and reduced the product to UO_2 powder. The efforts of Mr. P. Pakalns and co-workers who carried out the chemical analyses of the powders and the Ceramics Fabrication Group in Materials Division who conducted the sintering tests are also gratefully acknowledged.

9. REFERENCES

Alfredson, P.G. (1970) - The production of nuclear grade uranium dioxide from Australian ores. Proc. Aus. I.M. and M. No. 233, 61-66. (Also AAEC/TM514).

Albertson, M.L., Dai, Y.B., Jensen, R.A. and Rouse, H. (1948) - Diffusion of submerged jets. Proc. Am. Soc. Civil Engrs. 49: 1571-96.

Belcher, D.W., Smith, D.A. and Cook, E.M. (1963) - Design and use of spray dryers: Part 2. Design and costs. Chem. Eng. 63 (21): 201-208.

Berry, R.M. (1967) - Ceramic oxide production at Eldorado. Can. Nucl. Tech. 6 (2): 30-33.

Duffie, J.A. and Marshall, W.R. (1953) - Factors influencing the properties of spray dried materials. Chem. Eng. Progr. 49 (9): 480-486.

Feick, G. and Hainer, R.M. (1954) - On the thermal decomposition of ammonium nitrate. Steady-state reaction temperatures and reaction rate. J. Am. Chem. Soc. 76: 5860-63.

Fraser, R.P., Eisenklam, E.P. and Dombrowski, N. (1957) - Liquid atomisation in chemical engineering. Part 2. Rotary atomisers. Brit. Chem. Eng. 2: 496-501.

Friedman, S.J. Gluckert, F.A. and Marshall, W.R. (1952) - Centrifugal disk atomisation. Chem. Eng. Progr. 48 (4): 181-191.

Glatter, J. (1957) - Fabrication of bulk form uranium dioxide for use as nuclear reactor fuel. Nuclear Metallurgy Vol. 4: 131-34. I.M.D. Special Report Series No. 4. The Metallurgical Society, New York.

Gluckert, F.A. (1962) - A theoretical correlation of spray-dryer performance. A.I.Ch.E. Journal. 8 (4): 460-66.

Gretzinger, J. and Marshall, W.R. (1961) - Characteristics of pneumatic atomisation. A.I.Ch.E. Journal. 7 (2): 312-318.

Herdan, G. (1960) - Small Particle Statistics. Butterworths, London.

Janov, J., Alfredson, P.G., Vilkaitis, V.K. (1971) - The influence of precipitation conditions on the properties of ammonium diuranate and uranium dioxide powders. AAEC/E220.

Marshall, W.R. (1954) - Atomisation and spray drying. Chem. Eng. Progr. Monograph series. 50 (2).

Marshall, W.R. and Seltzer, E. (1950) - Principles of spray drying. Part 1. Fundamentals of spray dryer operation. Chem. Eng. Progr. 46 (10): 501-508.

Masters, K. and Mohtadi, M.F. (1957) - A study of centrifugal atomisation and spray drying. Brit. Chem. Eng. 12 (12): 624-626; 13 (1): 26-27; 13 (2): 85-87.

Ranz, W.E. and Marshall, W.R. (1952) - Evaporation from drops. Chem. Eng. Progr. 48 (3): 141-146; 48 (4): 173-180.

Seidl, K. (1965) - Chemical and technological calculations of pneumatic drier. UJV-1172/64.

Tate, W. (1965) - Sprays and spraying for process use. Chem. Eng. 72 (15): 157-162; 72 (16): 111-116.

Thorpe, J.F. and Whiteley, M.A. (1947) - Thorpe's Dictionary of Applied Chemistry. Vol. 1: 335. 4th Edn. Longmans, London.

Wallman, H. and Blyth, H.A. (1951) - Product control in Bowen type spray dryer. Ind. Eng. Chem. 43 (6): 1480-86.

Wilkinson, W.L. (1968) - Improvements in or relating to the production of fuel for nuclear reactors, British Patent 1,105,325.

Woolfrey, J.L. (1968) - The preparation and calcination of ammonium uranates - a literature survey. AAEC/TM476.

10. NOTATION

A = surface area (m^2)
C_f = slurry feed concentration ($kg\ m^{-3}$)
C_p = specific heat ($J\ kg^{-1}\ {}^oC$)
D = drying chamber diameter (m)
D_e = effective diameter of atomiser orifice (m)
D_v = diffusion coefficient ($m^2\ s^{-1}$)
d_t = droplet diameter (μm or m)
d_o = initial droplet diameter (μm or m)
d_f = final particle size (μm or m)
$\bar{d}_m$ = mass median droplet diameter (μm or m)
$\bar{d}_{vs}$ = Sauter (surface/unit volume) droplet diameter (μm or m)
d_{wp} = diameter of wetted periphery between air and liquid (μm or m)
G_a = mass velocity of air at nozzle outlet ($kg\ m^{-2} s^{-1}$)
h = heat transfer coefficient ($W\ m^{-2}\ {}^oC$)
k = mass transfer coefficient ($m\ s^{-1}$)
k_f = thermal conductivity at mean film temperature ($W\ m^{-1}\ {}^oC$)
L = drying chamber length (m)
L_d = wetted periphery of disk/stream (m)
M_a = mass rate of air from nozzle ($kg\ s^{-1}$)
M_l = mass rate of liquid flow ($kg\ s^{-1}$)
N = centrifugal disk atomiser speed ($rev\ s^{-1}$)
Q = heat transfer rate (W)
r = centrifugal disk atomiser radius (m)
T = temperature (${}^oC$)
t = time (s)
U = fluid-spray velocity ($m\ s^{-1}$)
U_R = fluid-drop relative velocity ($m\ s^{-1}$)
U_a = velocity of air through nozzle ($m\ s^{-1}$)
U_M = initial jet velocity ($m\ s^{-1}$)
y = distance in direction of jet flow (m)
α = spray angle (rad)
Γ = feed rate of liquid/unit of surface periphery ($kg\ ms^{-1}$)
ΔH = enthalpy change from liquid at feed conditions to vapour ($J\ kg^{-1}$)
ΔT = temperature driving force (${}^oC$)
ε_{ext} = external void fraction -
μ = viscosity of feed solution ($kg\ ms^{-1}$)

NOTATION (Cont'd.)

μ_a = viscosity of drying air (kg ms^{-1})
ρ = density of feed solution (kg m^{-3})
ρ_a = density of drying air (kg m^{-3})
ρ_p = product particle density (kg m^{-3})
ρ_{tap} = tap density (kg m^{-3})
σ = surface tension (N m^{-1})
σ_g = droplet diameter geometric standard deviation -
τ = time required for droplet to evaporate completely (s)

Dimensionless Groups

Nu = Nusselt number = hd_t/k_f
Pr = Prandtl number = $C_p\mu_a/k_f$
Re = Reynolds number = $d_tU_R\rho_a/\mu_a$
Sc = Schmidt number = μ_a/ρ_aD_v
Sh = Sherwood number = d_tk_f/D_v

TABLE 1

SPRAY DRIER SPECIFICATIONS

Dimensions	
Chamber diameter	1.0 m
Chamber height, cylindrical section	0.75 m
conical section	1.0 m
Air Flow Rate (constant)	0.035 kg s^{-1}
Electrical Heating	
Maximum heater output	9 kW
Maximum inlet air temperature	280°C
Maximum Evaporative Capacity	7 kg h^{-1}
Pneumatic nozzle air consumption (max.)	7.2 m^3 h^{-1}
Air gauge pressure (max.)	400 kN m^{-2}
Centrifugal Atomiser	
Disk diameter	65 mm
Maximum rotational speed	1000 rev s^{-1}

TABLE 2

PNEUMATIC ATOMISER EXPERIMENTS - ADU PREPARED BY SINGLE STAGE PRECIPITATION

Feed Conc. (kg m^{-3})	Feed Rate (litre h^{-1})	Atomising Air Gauge Pressure (kN m^{-2})	Inlet Temp. °C	Outlet Temp. °C	Pour Density (kg m^{-3})	Tap Density (kg m^{-3})	$\frac{NH_3}{U}$ Molar Ratio	$\frac{NO_3^-}{U}$ Molar Ratio	Moisture Per Cent
243	8.0	138	275	108	750	1270	1.03	0.80	< 0.5
243	8.5	276	280	104	600	1110	1.15	0.86	1.2
243	8.0	474	273	92	670	1150	1.27	0.96	1.3
243	4.5	138	275	130	580	1060	0.76	0.67	2.1
243	4.5	276	275	122	620	1170	0.94	0.72	< 0.5
243	4.0	474	275	114	580	1080	0.96	0.79	1.0
243	2.0	138	283	150	370	800	0.58	0.45	< 0.5
243	2.5	474	275	144	320	740	0.62	0.47	< 0.5
219	4.5	276	275	115	860	1370	0.92	0.80	5.5
279	5.0	276	275	118	570	1160	0.83	0.59	2.2

TABLE 3

PNEUMATIC ATOMISER EXPERIMENTS - ADU PREPARED BY TWO STAGE PRECIPITATION

Feed Conc. (kg m^{-3})	Feed Rate (litre h^{-1})	Atomising Air Gauge Pressure (kN m^{-2})	Inlet Temp. °C	Outlet Temp °C	Pour Density (kg m^{-3})	Tap Density (kg m^{-3})	$\frac{NH_3}{U}$ Molar Ratio	$\frac{NO_3^-}{U}$ Molar Ratio	Moisture Per Cent
211	3.3	177	290	128	770	1290	0.54	0.159	0.7
211	8.0	270	273	110	N.A.	N.A.	0.62	0.226	0.6
211	6.0	270	275	130	650	1170	0.56	0.203	0.3
211	4.5	270	280	133	640	1140	0.50	0.141	0.4
211	5.5	270	200	95	680	1150	0.62	0.200	0.3
350	6.0	270	270	130	670	1120	0.55	0.186	0.2
350	4.0	270	270	118	630	1130	0.58	0.201	0.2
350	2.5	270	280	155	640	1120	0.45	0.136	0.3
507	5.0	270	275	120	650	1110	0.58	0.172	0.2

N.A. = Not Available

TABLE 4

CENTRIFUGAL ATOMISER EXPERIMENTS - ADU PREPARED BY SINGLE STAGE PRECIPITATION

Feed Conc. (kg m^{-3})	Feed Rate (litre h^{-1})	Atomiser Disk Speed (rev s^{-1})	Inlet Temp. °C	Outlet Temp. °C	Pour Density (kg m^{-3})	Tap Density (kg m^{-3})	$\frac{NH_3}{U}$ Molar Ratio	$\frac{NO_3^-}{U}$ Molar Ratio	Moisture Per Cent
153	1.5	830	270	150	560	1070	0.54	0.39	0.9
153	3.1	330	270	140	770	1230	0.67	0.59	1.5
153	2.5	950	283	148	570	1100	0.60	0.52	1.0
153	1.2	350	275	160	N.A.	1250	0.47	0.44	0.5
153	4.2	700	275	120	N.A.	1060	0.82	0.65	1.3

N.A. = Not Available

TABLE 5

EFFECT OF DRYING METHOD ON SURFACE AREAS OF ADU AND UO_2

(BOTH POWDERS WERE PRECIPITATED IN A SINGLE STAGE AT pH 7.2)

Drying Method	$\frac{NH_3}{U}$ Molar Ratio	$\frac{NO_3^-}{U}$ Molar Ratio	ADU Surface Area ($m^2\ kg^{-1}$)	UO_2 Surface Area ($m^2\ kg^{-1}$)
Spray dried	0.65	0.50	2800	5100
Tray dried	0.53	0.03	14300	5000

TABLE 6

PRESSING AND SINTERING TESTS ON UO_2 PRODUCED FROM SPRAY DRIED ADU

Preparation	Green Density ($kg\ m^{-3}$)	Sintered Density ($kg\ m^{-3}$)
As received	5340	10490
- 100 mesh fraction	5640	10450

Precipitation Conditions: pH 7.2, residence time = 8 minutes.

Spray Drying Conditions: Air inlet temperature = 275°C
Atomising Air Gauge Pressure = 270 kN m^{-2},
Feed Rate = 4 litre h^{-1}.

Reduction Temperature: 670°C, Isostatically pressed at 309 MN m^{-2}.

Sintering Temperature: 1600°C.

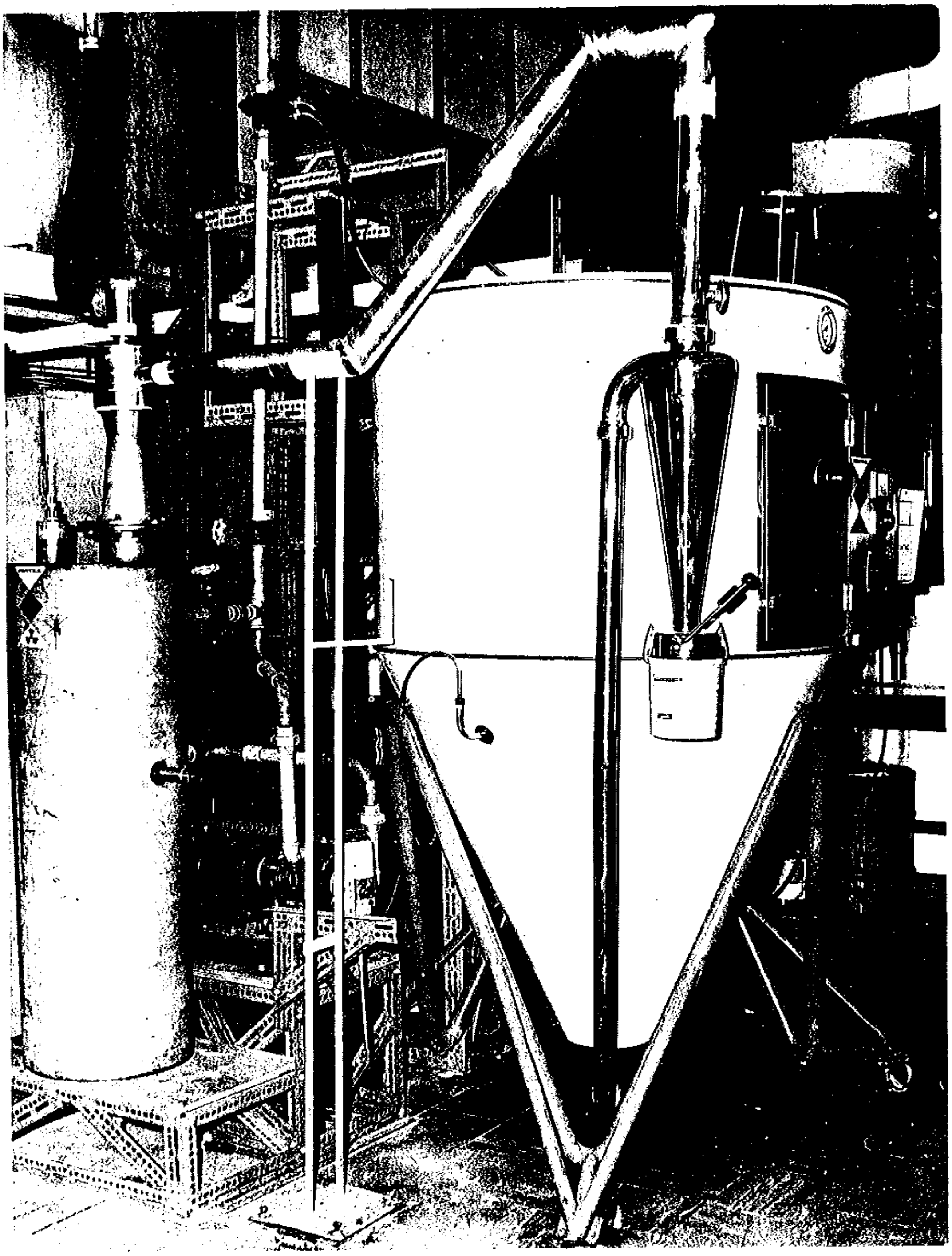

FIGURE 1. LABORATORY SPRAY DRYING UNIT

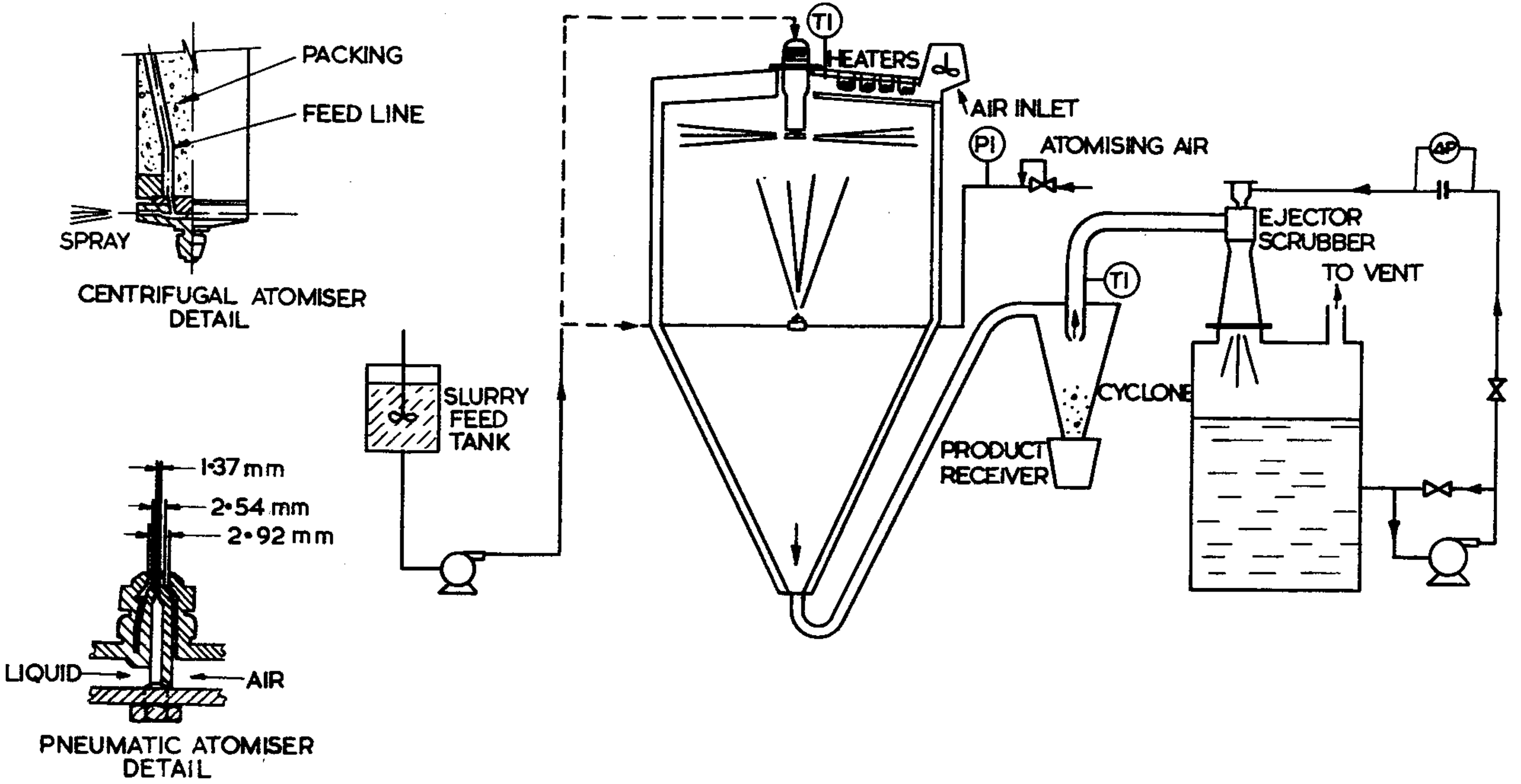

FIGURE 2. SCHEMATIC DIAGRAM OF SPRAY DRIER AND ANCILLARY EQUIPMENT

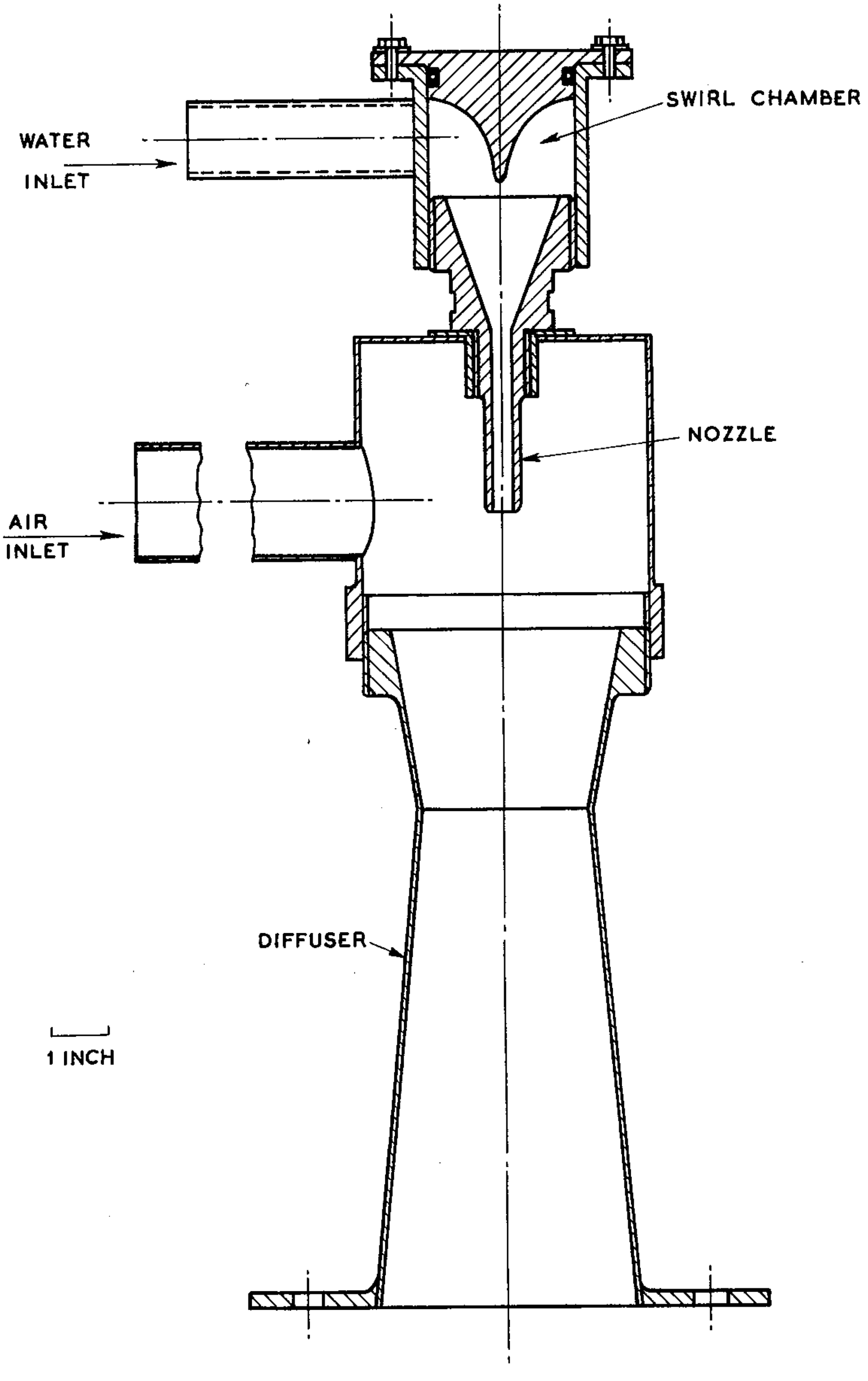

FIGURE 3. EJECTOR DESIGN FOR OFF-GAS SCRUBBING

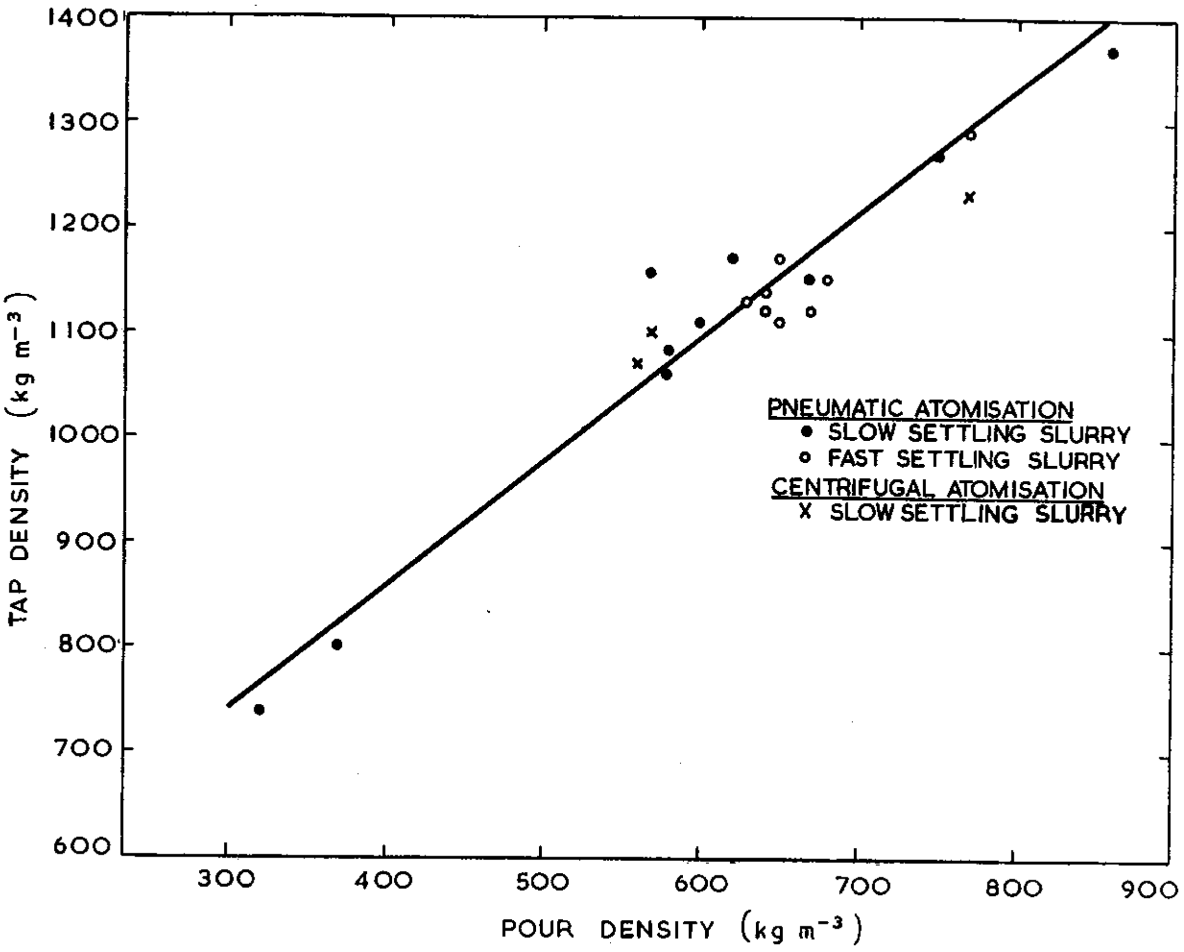

FIGURE 4. CORRELATION BETWEEN POUR AND TAP DENSITIES

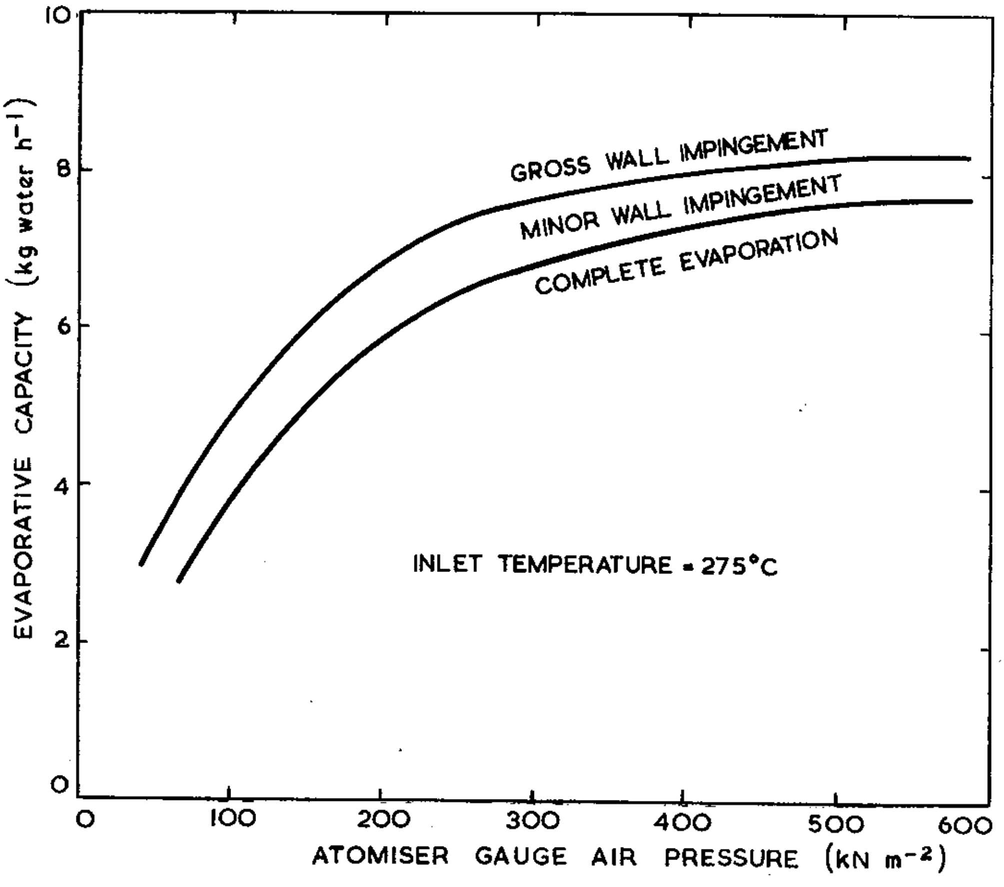

FIGURE 5. EVAPORATIVE CAPACITY OF SPRAY DRIER - PNEUMATIC ATOMISATION

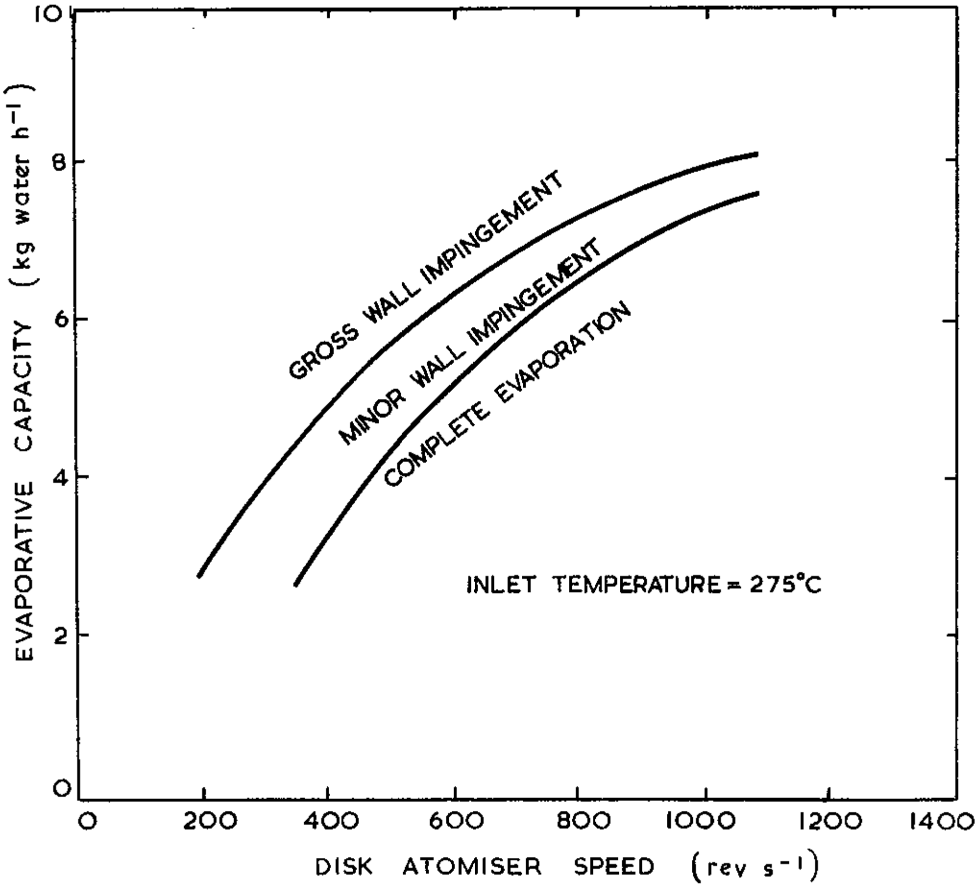

FIGURE 6. EVAPORATIVE CAPACITY OF SPRAY DRIER - CENTRIFUGAL ATOMISATION

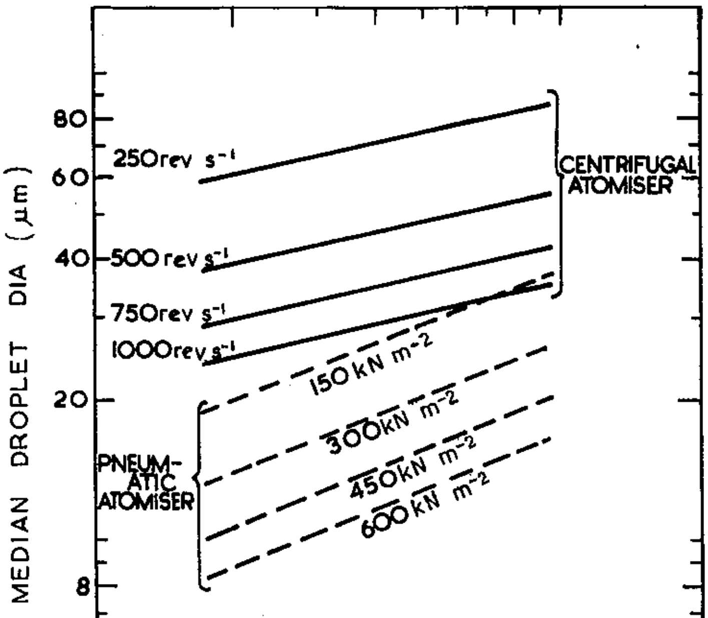

FIGURE 7. CALCULATED MEDIAN INITIAL DROPLET SIZE FOR PNEUMATIC AND CENTRIFUGAL ATOMISERS

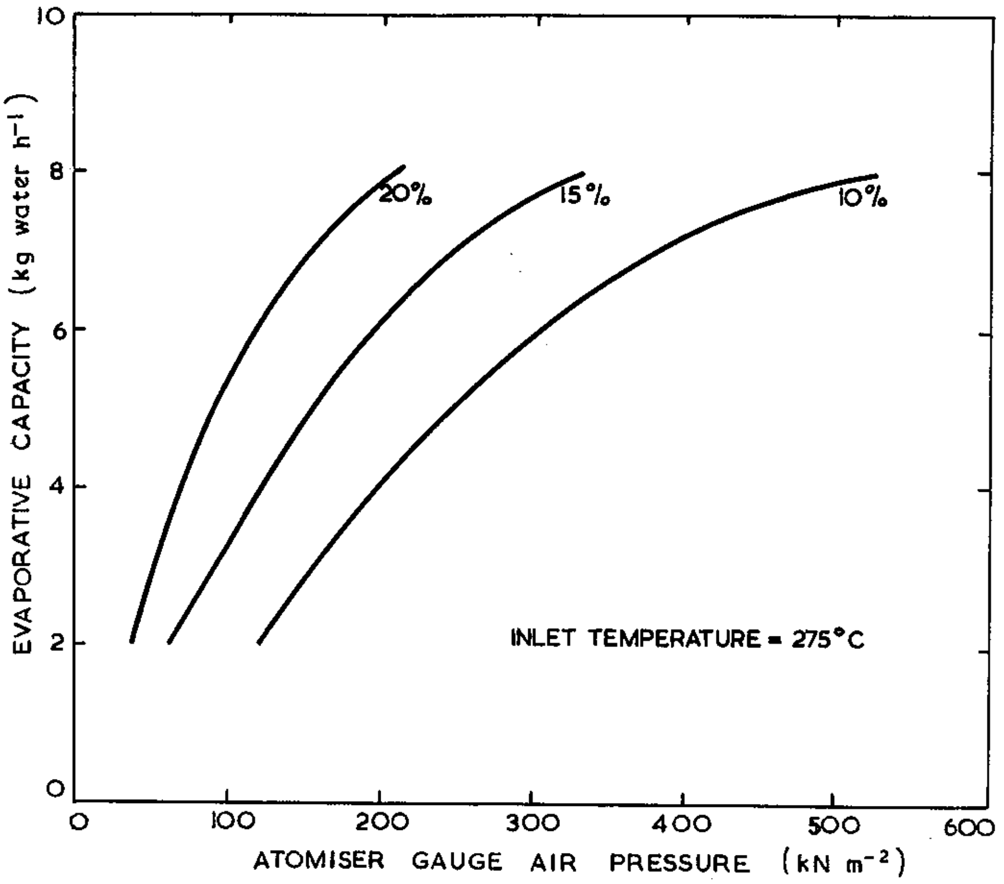

FIGURE 8. THEORETICAL SPRAY DRIER CAPACITY - PER CENT CENTRE-LINE JET IMPINGEMENT FOR PNEUMATIC ATOMISATION

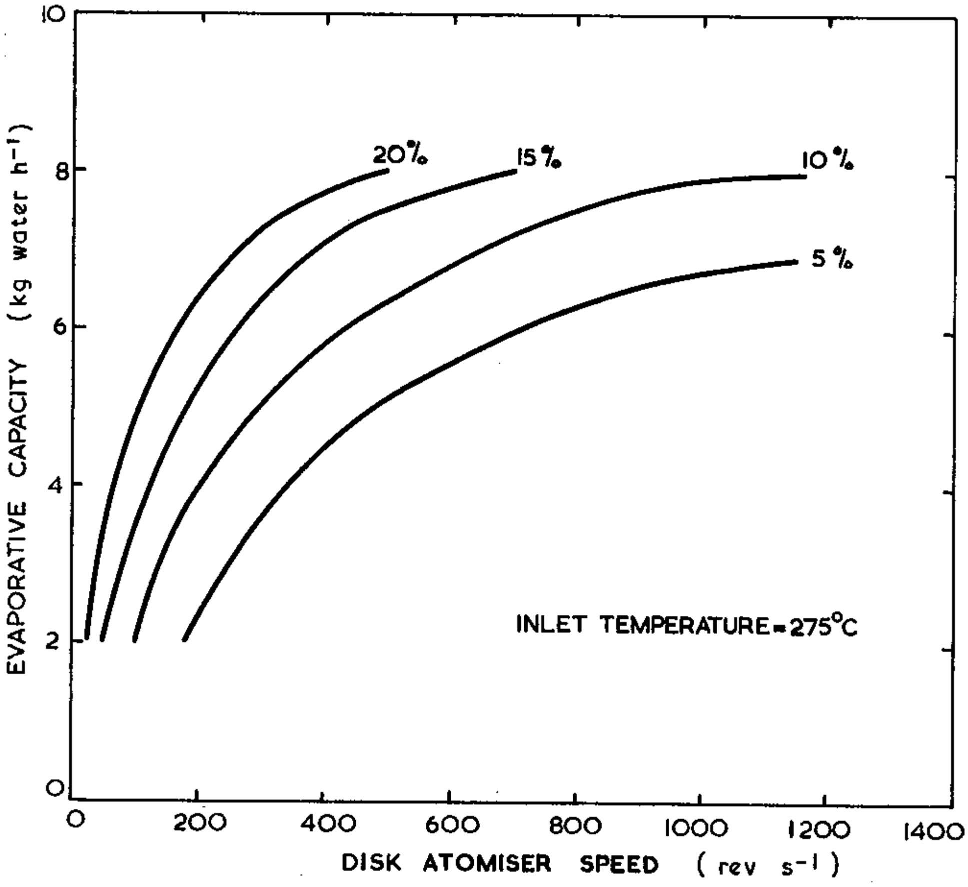

FIGURE 9. THEORETICAL SPRAY DRIER CAPACITY - PER CENT CENTRE-LINE JET IMPINGEMENT FOR CENTRIFUGAL ATOMISATION

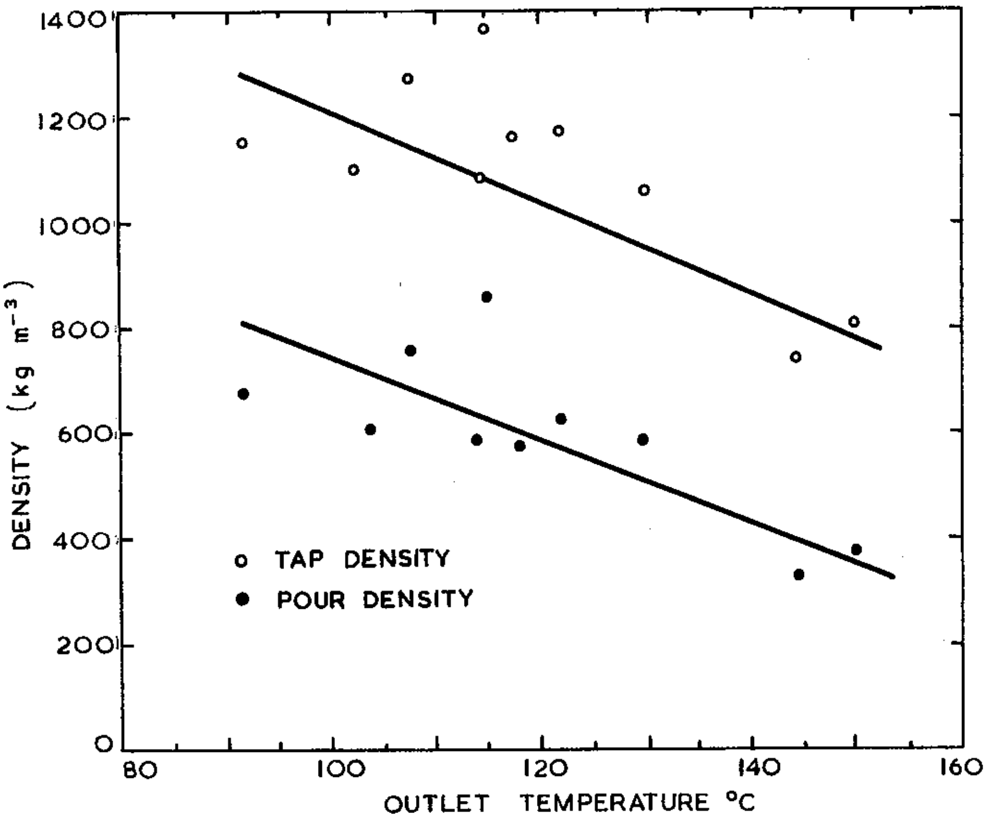

FIGURE 10. EFFECT OF DRIER OUTLET TEMPERATURE ON POUR AND TAP DENSITIES OF PRODUCT - PNEUMATIC ATOMISATION OF SLURRY PREPARED BY SINGLE STAGE PRECIPITATION

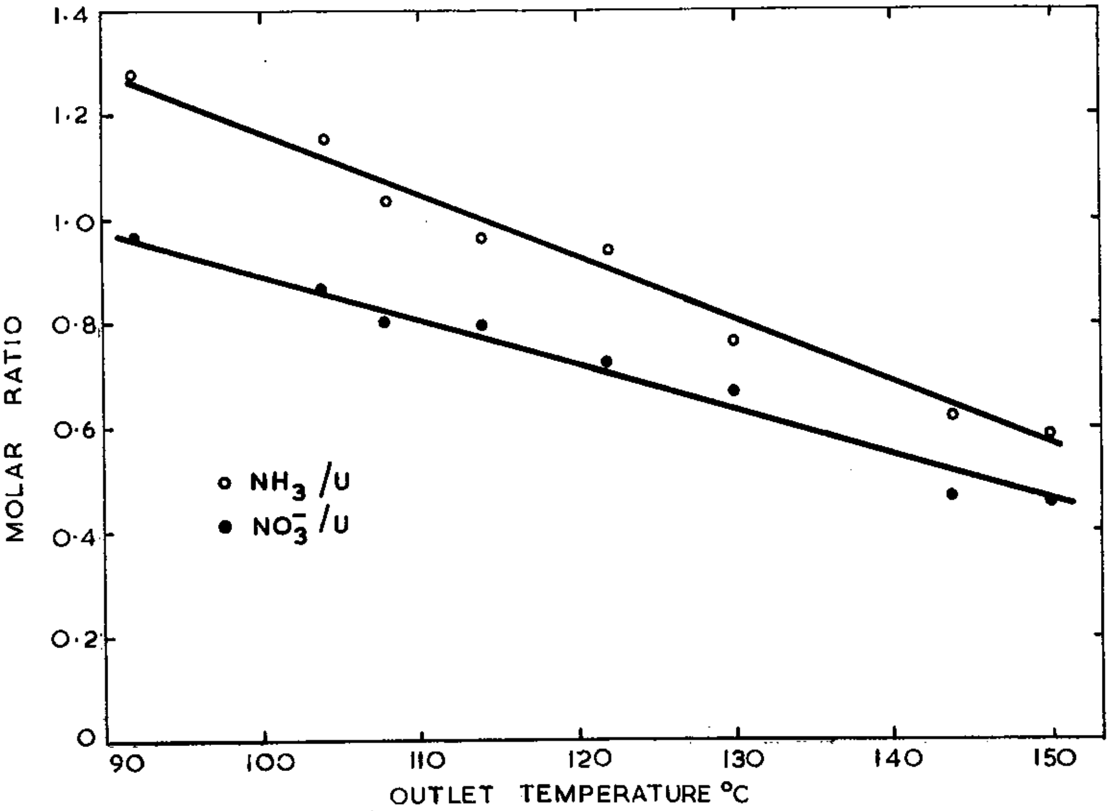

FIGURE 11. AMMONIA AND NITRATE CONTENTS OF PRODUCT POWDER - PNEUMATIC ATOMISATION OF SLURRY PREPARED BY SINGLE STAGE PRECIPITATION

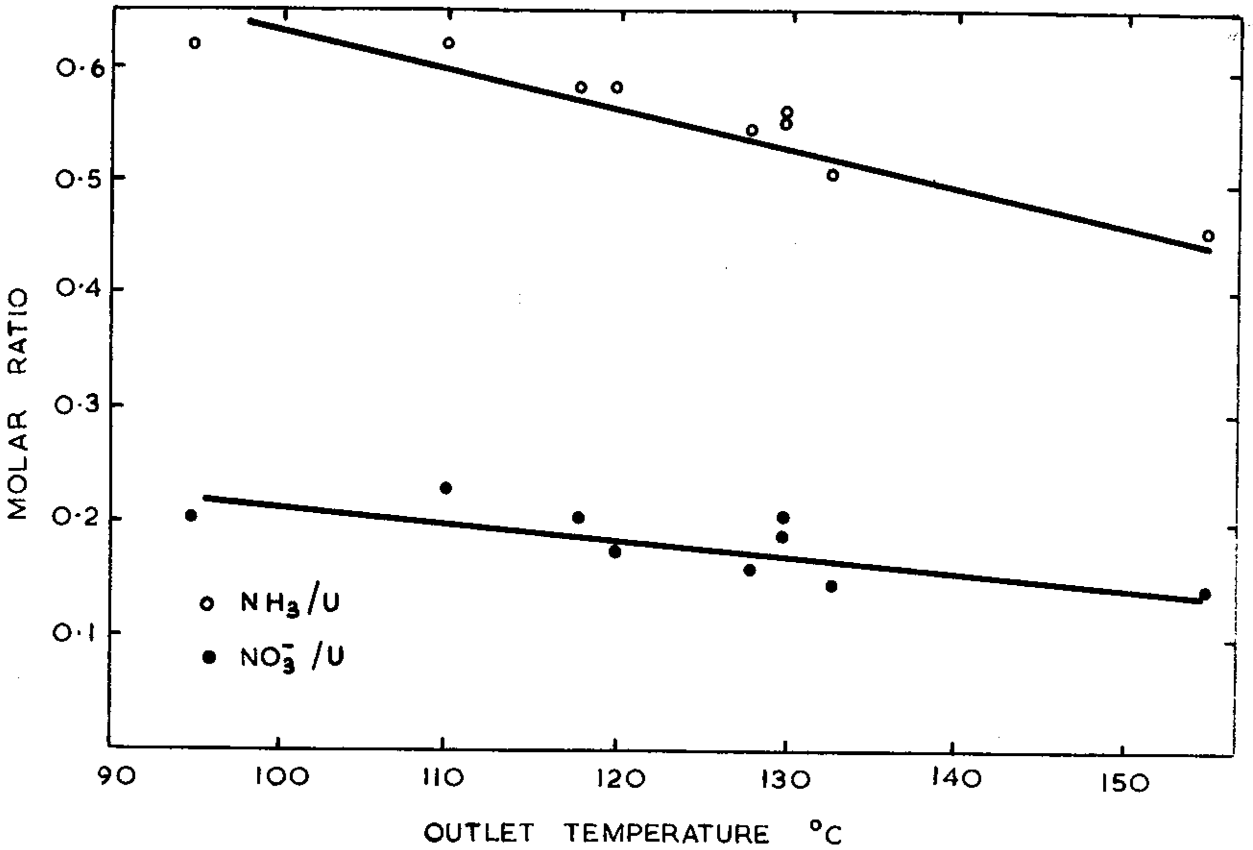

FIGURE 12. AMMONIA AND NITRATE CONTENTS OF PRODUCT POWDER - PNEUMATIC ATOMISATION OF SLURRY PREPARED BY TWO STAGE PRECIPITATION

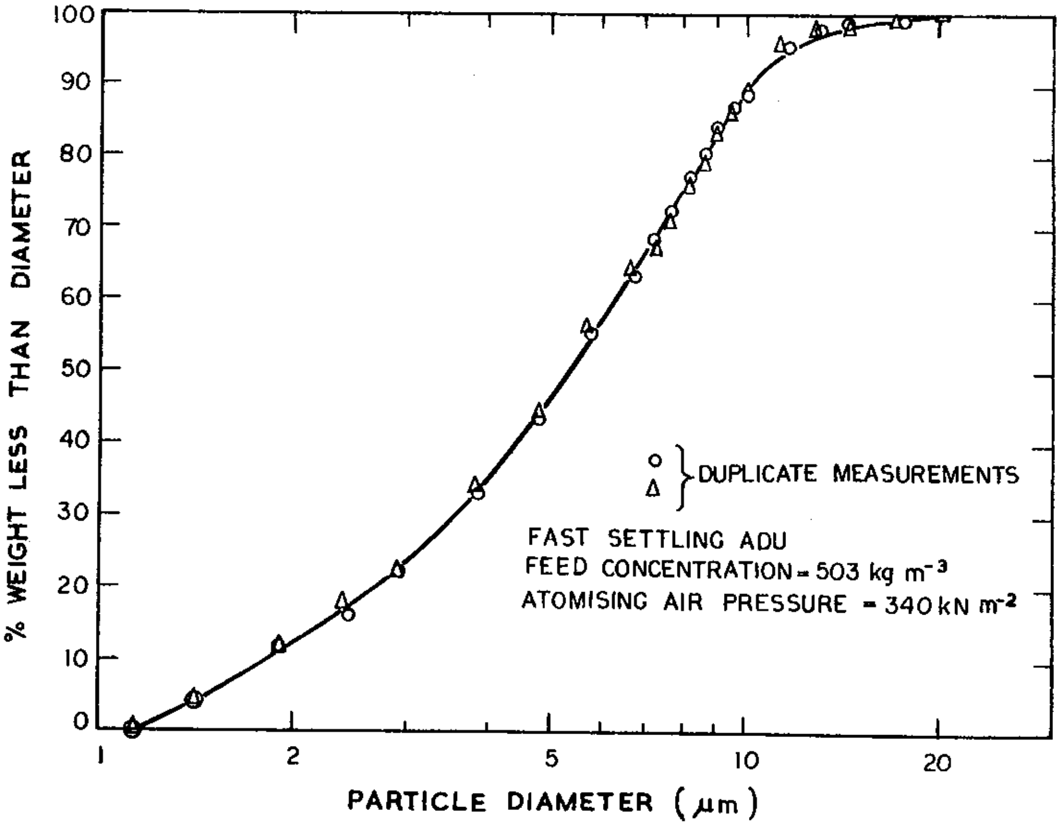

FIGURE 13. PARTICLE SIZE DISTRIBUTION ANALYSIS BY SHARPLES MICROMEROGRAPH

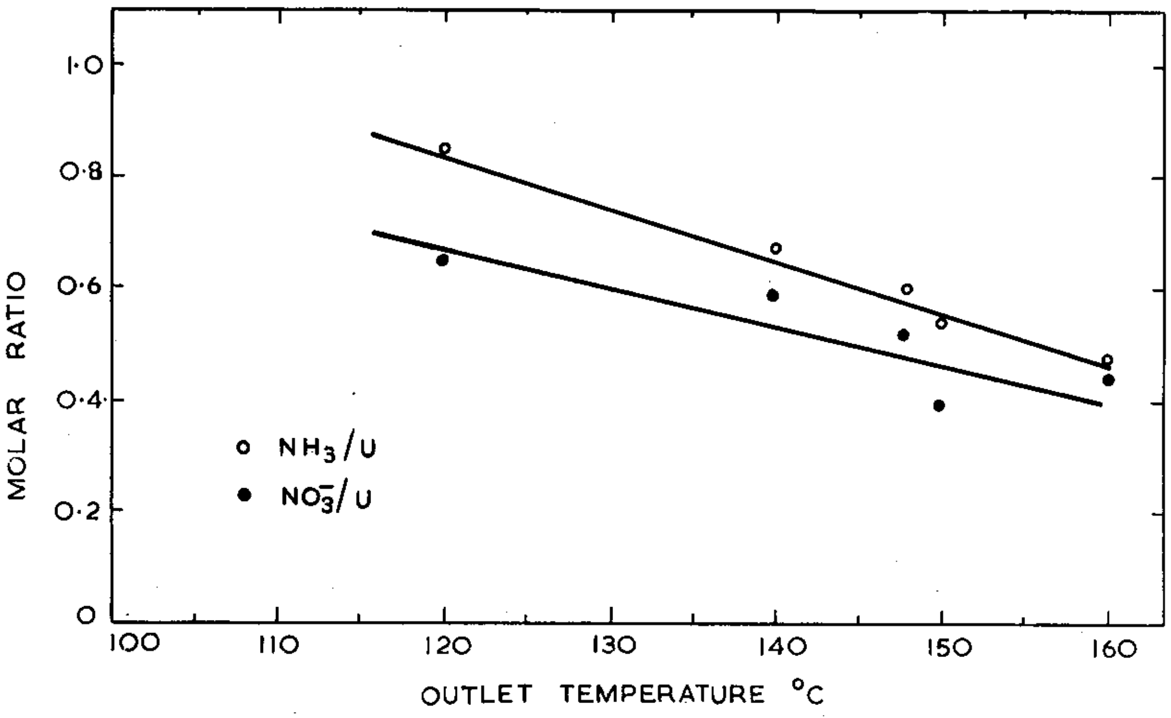

FIGURE 14. AMMONIA AND NITRATE CONTENTS OF PRODUCT POWDER - CENTRIFUGAL ATOMISATION

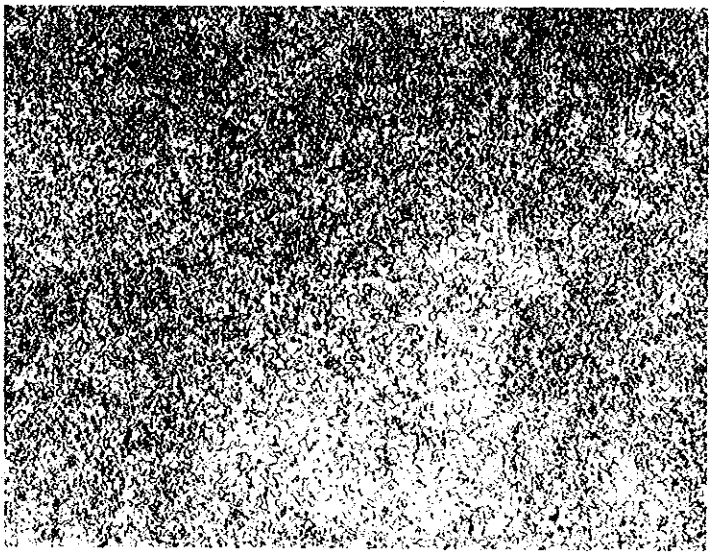

FIGURE 15. MICROSTRUCTURE OF URANIUM DIOXIDE PELLET PREPARED VIA SPRAY DRIED ADU (Table 6) MAGNIFICATION X100