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ABSTRACT

Commissioning and operating experience are described for the thermal denitration of uranyl nitrate in a 0.1 m diameter fluidised bed reactor. The effects of operating temperature, uranyl nitrate concentration and feed rate, nozzle air to liquid flow ratio, and the addition of sulphate to the feed, on the characteristics of the product and equipment performance were examined. Particle growth was a predominant feature which was strongly influenced by operating temperature. Changes in the main process variables exerted a minor influence on other properties of the product. The addition of sulphate to the

(continued)

uranyl nitrate feed solution produced an increase in surface area, and a decrease in pour and tap density. The wall-to-bed heat transfer coefficient was in the range 190 to 265 W $m^{-2}K^{-1}$, and shown to be an inverse function of the average particle size.

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DENITRATION; FLUIDISED BED; FLUIDISED BED REACTORS; HEAT TRANSFER; OPERATION; PARTICLE SIZE; PERFORMANCE; PRODUCTION; SULFATES; SURFACE PROPERTIES; URANIUM TRIOXIDE; URANYL NITRATES

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(Continued)

CONTENTS (Cont'd.)

1. INTRODUCTION

The production of uranium trioxide (UO_3) *via* denitration of uranyl nitrate hexahydrate (UNH) is an important step in the production of uranium hexafluoride. Thermal denitration offers savings in chemical costs compared with chemical denitration (by precipitation to produce the diuranate, filtration, drying and calcination to UO_3), since it avoids the use of ammonia and permits the recovery of nitric acid. In addition, thermal denitration in a fluidised bed can produce a UO_3 product which is a free-flowing fluidisable powder, well suited to subsequent processing in fluidised beds (Hawthorn *et al.* 1960a).

The thermal denitration of UNH takes place according to the following endothermic reaction:

$$UO_2(NO_3)_2.6H_2O \rightarrow UO_3 + NO_2 + NO + O_2 + 6H_2O \quad . \qquad \ldots(1)$$

$\Delta H = 595 \pm 20$ kJ(mol U)$^{-1}$ at 300°C (estimated from data of Rand & Kubaschewski 1963).

Thermal denitration in a fluidised bed involves spraying a concentrated uranyl nitrate solution into a bed of UO_3 maintained above approximately 270°C and fluidised with air or steam; the UO_3 produced either deposits on existing particles or forms seed material.

This report serves two purposes. Firstly, it gives a comprehensive review of previous literature on fluidised bed denitration. Secondly, it describes the commissioning and testing of equipment designed to establish the technology for thermal denitration of uranyl nitrate solution produced from Australian yellow cake. This work took the form of a limited experimental study of the effect of the main process variables on the properties of the UO_3 product using a 0.10 m diameter fluidised bed denitrator.

2. LITERATURE REVIEW

The production of UO_3 by thermal denitration of uranyl nitrate was initially carried out batchwise in agitated pot calciners, which gave a reactive product but which was also very fine and not well suited to subsequent powder handling (Harrington & Ruehle 1959). Subsequently, a continuous denitration process was developed using stirred trough calciners (Harrington & Ruehle 1959, Smiley 1961). However,the excellent heat transfer characteristics and mechanical simplicity of fluidised beds were sufficient motivation for the development of a denitration process based on this technology. A related development was the application of fluidised beds to the calcination of highly radioactive nitrate waste solutions from nuclear

fuel reprocessing plants (Grimmett 1964, 1966a, 1966b, Jonke *et al.* 1954, Lee *et al.* 1962, Legler 1967, Loeding *et al.* 1961).

2.1 Equipment Development

Jonke *et al.* (1954) established that uranyl nitrate solution could be denitrated in a controlled manner by spraying it into a hot fluidised bed of UO_3 powder. The best results were obtained by spraying the uranyl nitrate solution through a pneumatic atomising nozzle, with external mixing, mounted flush to the wall below the surface of the bed. This was later shown to be the optimum arrangement (Legler 1967). Spraying onto the top surface of the bed from above, or locating the nozzle too close to the surface, led to the elutriation of large quantities of fines and to caking in the vapour space above the bed, while extension of the nozzle into the bed was shown to contribute to cake formation around the nozzle.

The fluidised bed process was further developed at Weldon Spring from pilot plant scale (Simecek & Trask 1963) to the production scale (Harrell 1964, Robinson & Todd 1966). A few years earlier, a similar process was devised at Springfields and put into production (Hawthorn *et al.* 1960a).

The physical characteristics and operating conditions of the various fluidised bed denitrators reported in the literature are summarised in Table 1. Bed diameters range from 75 mm to 1.17 m, bed depths from 0.3 m to 3.7 m, operating temperatures from 240°C to 450°C and uranium concentrations of the feed solution from 350 to 1,475 g ℓ^{-1}. On the basis of the cross-sectional area of the bed, production rates for UO_3 as high as 1,470 kg h^{-1} m^{-2} have been reported.

2.2 Product Characteristics

Most of the published data is concerned with the particle size of the product and the related topic of particle growth (Section 2.2.1) but some information is presented concerning nitrate and water content (Section 2.2.2) and product reactivity (Section 2.2.3).

2.2.1 Particle growth and particle size

An important operational aspect of denitration in a fluidised bed is the achievement of a steady state particle size distribution. An increase in the average particle size is promoted by the following factors:

(a) coalescence of a drop and an existing particle leading to growth of that particle (Hawthorn *et al.* 1960a);

(b) agglomeration by two or more particles adhering (Hawthorn *et al.* 1960a);

(c) elutriation of fine particles from the bed (Grimmett 1966a, 1966b); and

(d) formation of nozzle and wall cakes which break off and enter the bed (Otero *et al.* 1967, 1970).

Seed material, which is necessary for a steady state particle size distribution, is provided by the following:

(e) drying and decomposition of small discrete drops (Hawthorn *et al.* 1960a);

(f) attrition or fracture of discrete particles (Hawthorn *et al.* 1960a); and

(g) seed addition from external sources (Grimmett 1966a, 1966b).

Factor (a) is judged to be dominant in particle growth (Grimmett 1964, Lee *et al.* 1962), although Simecek & Trask (1963) suggested that agglomeration by particle collision and adhesion (factor (b)) may be the predominant growth factor for high concentrations of feed liquor. Grimmett (1966a, 1966b) assumed elutriation (factor (c)) to be negligible in his calculations, which is valid if the elutriated material is removed from the off-gas stream by filters and returned to the bed, as is common practice.

Otero *et al.* (1967, 1970) examined the formation of cakes in a fluidised bed denitrator and showed that they form only around the nozzle and on the adjacent wall (factor (d)). They were able to relate the rate of cake formation to operating conditions and equipment design. It was noted that large cakes have a tendency to break off and thereby influence the particle size distribution.

The addition of seed from external sources (factor (g)), such as ground product returned to the bed, has been used in the calcination of both aluminium nitrate (Grimmett 1966a, 1966b) and uranyl nitrate (Jonke *et al.* 1954, 1957). Jonke *et al.* (1957) used seed addition rates as high as 20% of the total throughput, until it was shown that particle growth could be controlled by lowering the operating temperature. Jonke *et al.* (1957) suggested that, at lower temperatures, seeds were formed by the fracture of discrete particles (factor (f)). However Lee *et al.* (1962) found that seed formation by attrition was negligible for the calcination of aluminium nitrate. Attrition by jet grinding was used by Nelson (1970) as a means of controlling particle size; it was found that resistance to attrition was higher at lower operating temperatures.

Particle growth is evidently a complex phenomenon and Table 2 summarises the more important effects observed with respect to particle growth and/or

average particle size at steady state.

Under certain conditions, steady state particle size was not readily achieved in the absence of artificial seeding. This behaviour appears to be a greater problem for the smaller diameter fluidised bed reactors. Thus Nelson (1970) was unable to operate his pilot plant (0.10 m diameter) denitration unit without particle growth, in spite of a statistical series of experiments aimed at minimising the phenomenon. However, it was found that particle growth could be controlled in the production unit (0.15 m diameter) by suitably adjusting the operating temperature when using low sulphate feed solutions (Bjorklund & Offutt 1971a).

Similar experience was noted also by Hawthorn *et al.* (1960a, 1960b) who reported that while it was difficult to control the quantity of 'oversize' material (> 350 μm) in a pilot plant denitrator, this problem was completely absent in the production units (~ 1.0 m diameter). Weldon Spring workers may have avoided particle growth problems by choosing a relatively large reactor (0.25 m diameter), and only reported particle growth for unusual operating conditions (Simecek & Trask 1963).

Most workers found that operating temperature was the dominant parameter affecting particle growth and average particle size at steady state; an increase in temperature resulted in an increase in these characteristics. Jonke *et al.* (1957) suggested that, at low temperatures, vaporisation of water and nitrate in the pores caused particles to fracture and produce fines whereas, at high temperatures, the reactions proceeded too rapidly to allow penetration of the feed into the pores and little particle fracture took place. Simecek & Trask (1963) reported a three-fold increase in average particle size at steady state over the temperature range 315°C to 425°C, and Nelson (1970) found temperature to be the only significant factor in his statistical series of experiments. Other operating parameters have markedly less influence on particle growth, although the data tend to be conflicting (Table 2).

Particle size distributions have not been widely reported. Simecek & Trask (1963) presented particle size distributions for products from most of their runs and showed that the distribution was considerably influenced by fluidisation velocity; the narrowest distribution (88 wt.% between 149 and 420 μm) was obtained at a fluidising velocity of 0.5 m s^{-1} (calculated at the operating temperature and pressure below the nozzle region in the bed). Typical data for size distributions were also presented by Jonke *et al.* (1954, 1957) and Levitz *et al.* (1971).

2.2.2 Nitrate and water content

Jonke *et al.* (1954, 1957) showed that, over a temperature range of 240°C to 440°C, the nitrate content of the UO_3 product reduced from 1.2 wt.% to a constant level of about 0.4 wt.%, while the water content reduced from 0.4 to about 0.08 wt.%. Simecek & Trask (1963) reported nitrate contents ranging from about 1.2 to 0.5 wt.%, and water contents ranging from 0.8 to 0.2 wt.%. In a statistical series of experiments, they reported an apparent effect on nitrate content of bed temperature, production rate, nozzle air flowrate and feed concentration. However, the 60% confidence level associated with these effects makes them of very doubtful significance.

2.2.3 Reactivity

The ease of reduction of UO_3 to uranium dioxide (UO_2), and the subsequent ease of hydrofluorination to uranium tetrafluoride (UF_4), are a measure of the 'reactivity' of the UO_3. Initially, product from fluidised bed denitration was considerably less reactive than that produced by pot or trough denitration (Harrington & Ruehle 1959). However, the addition of sulphate ions to the uranyl nitrate feed increased the reactivity of the UO_3 (Cooper & Lloyd 1961, Hawthorn *et al.* 1960a, Morrow *et al.* 1961, Simecek & Trask 1963, Smiley & Brater 1958). The data of Morrow *et al.* (1961) showed that this enhanced reactivity resulted from an increase in surface area. Thus fluid bed UO_3 containing no sulphate had a surface area of 0.08 m^2g^{-1} and UO_3 containing 5,000 $\mu g\ g^{-1}$ sulphate had a surface area of 1.5 m^2g^{-1}. In addition, the rate of reduction was found to be directly related to the surface area of the UO_3. More importantly, from a production point of view, the increased surface area of the UO_2 enhanced the rate of hydrofluorination to UF_4 (Cooper & Lloyd 1961).

Hydration also increased the surface area and the reactivity of fluid bed UO_3 and of the UO_2 derived from it (Cooper & Lloyd 1961). Hydration, which takes place readily at room temperature (Dell & Wheeler 1962), modifies the crystal structure to amorphous UO_3, thus having a permanent effect on the surface area (Landspersky *et al.* 1964).

2.3 Heat Transfer

The thermal denitration of uranyl nitrate is highly endothermic, and therefore equipment with good heat transfer characteristics, such as the fluidised bed reactor, is most suitable. Most systems use external heating through the walls of the reactor and/or internal bayonet heaters immersed in the bed of UO_3 particles. For systems using bayonet heaters, Hawthorn *et al.* (1960b) reported heat transfer coefficients for the heater surface to the

bed of 170 to 285 W $m^{-2}K^{-1}$, and similar values are typical of the figures reported by Simecek & Trask (1963). For a bed heated through the walls, Jonke *et al.* (1954) reported values from 285 to 570 W $m^{-2}K^{-1}$.

Johnson (1958) calculated heat transfer coefficients (wall to bed) based on the equation of Wen & Leva (1956),

$$\frac{h\, d_p}{k_s} = 0.16 \left(\frac{C_s \rho_s\, d_p^{1.5}\, g_c^{0.5}}{k_f} \right)^{0.4} \left(\frac{G_f\, d_p^{2} E}{\mu_f R} \right)^{0.36} . \qquad \ldots(2)$$

This equation, which requires a knowledge of the void fraction of the bed as a function of the fluidisation velocity, was tested by Johnson for typical UO_3 powders produced in a trough calciner, and agreed within 10% with his experimental results. Johnson concluded that a heat transfer coefficient of 170 W $m^{-2}K^{-1}$ could be used as a conservative design figure, and that the heat transfer coefficient was independent of fluidisation velocity when the value of the fluidising velocity was more than seven times the minimum fluidising velocity.

Simecek & Trask (1963) correlated heat transfer coefficients for the heater surface to the bed obtained from their 0.25 m unit, with the following empirical equation:

$$\frac{h}{d_{avg}} = 54{,}000\, V_g - 3{,}340 . \qquad \ldots(3)$$

where $V_g = \dfrac{\text{(total gas flow in nozzle area at STP (ft}^3\text{/min))}}{\text{(reaction zone temperature (°F) - 300)}}$

and $d_{avg} = \sum_{1}^{n} W_i d_i' ,$ $\qquad \ldots(4)$

where W_i = weight fraction retained between screens with apertures d_i and d_{i+1}

and $d_i' = \sqrt{d_i d_{i+1}}$.

For Equation (3), d_{avg} is in inches and h has the dimensions Btu h^{-1} ft^{-2} $°F^{-1}$. The correlation is surprising in that it suggests that the heat transfer coefficient was directly proportional to particle size. This differs from other correlations which have been proposed for wall to bed heat transfer coefficients in fluidised beds, the more important of which have been summarised by Kunii & Levenspiel (1969). These correlations generally suggest

an inverse relationship between the heat transfer coefficient and particle size of the form,

$$h \alpha d_p^{-n} , \qquad \ldots(5)$$

the value of n varying from zero to 0.7.

Simecek & Trask (1963) also reported that the heat transfer coefficient was influenced by both production rate and uranyl nitrate concentration.

3. EQUIPMENT

The equipment used in this work is shown in Figure 1, and as a simplified flowsheet in Figure 2.

3.1 Reactor System

The denitration reactor (Figure 3) was fabricated from AISI 321 stainless steel with a lower (bed) section, 0.10 m inside diameter (4 in. dia. Schedule 40 pipe) and 0.61 m long, and an upper (disengagement) section, 0.20 m inside diameter and 0.41 m long, housing four sintered stainless steel filters, each 50 mm diameter and 0.23 m long. The design pressure of the vessel was 0.35 MPa gauge (50 psig) at 677°C (1,250°F). A carbon bursting disc, 37.5 mm diameter, rated at 70 kPa gauge (10 psig) was provided to protect the reactor from over-pressurisation.

Fluidising air passed through a flowmeter and a preheater before entering the conical base section of the reactor. The base section was an inverted double cone, with the gas inlet through the side of the outer cone, giving a gas passage into the bed *via* a hole in the apex of the inner cone. A guide tube which passed through the hole in the inner cone allowed powder to flow out of the bed leaving an annular space for the fluidising gas to enter the bed. Powder was withdrawn through a 19 mm (¾ in.) ball valve in the pipe attached to the apex of the outer cone into collection vessels of approximately 1.2 ℓ volume. On leaving the reactor, the off-gases passed through the filters, which removed entrained particles from the gas stream. The particles were returned to the bed by the periodic blowback of the filters with a 0.5l to 0.65 MPa pulse of preheated air. The blowback was timed automatically and operated on alternate pairs of filters, typically giving a pulse of 1 second duration every 300 seconds.

The reactor was heated by twenty-eight 500 W calrod heaters bonded to the outer wall of the 0.10 m diameter section with copper and overlayed with flame sprayed stainless steel. A 750 W calrod heater was attached to the outer base cone in the same way. The reactor was insulated with 25 mm thick calcium silicate sections, while gaps were filled with an asbestos paste.

Flanges and pipes were insulated with asbestos tape and rope.

Thermocouple pockets in the lower (bed) section were located so that the reactor wall temperature could be measured at ten levels and the internal (bed) temperature could be measured at four levels.

Heat input could be adjusted by seven 2 kW Variacs, three of which were switched through Cambridge on-off controllers operating on measurements of the bed temperature, the remaining four Variacs providing manual adjustment of the base load.

Pressure drops across the bed and filters were measured penumatically from three pressure tappings located in the outer base cone, the top flange of the reactor and in the off-gas line.

A silica gel drier was provided so that dry air could be used when cooling the bed after a run to prevent hydration of any UO_3 left in the reactor.

3.2 Spray System

Uranyl nitrate was injected into the bed through a pneumatic atomising nozzle with external mixing (Spraying Systems Co. Type 1/4 JCO), using air as the atomising fluid. The spray nozzle was mounted with the spraying face flush with the wall of the bed, 0.23 m above the base cone. A positive displacement piston metering pump was used to control the liquid flow, and a small air-filled chamber of 0.2 ℓ capacity in the feed line acted as a pulsation damper, giving a steady flow to the atomiser. The atomising air flow was controlled by manual adjustment of the pressure at the atomising nozzle and measured by a flowmeter.

3.3 Off-gas Treatment

The off-gases passed through a back-up filter to a venturi scrubber for the recovery of nitrous oxides by contact with dilute nitric acid (initial concentration approximately 0.5 *M*). The venturi had an injection nozzle of 3.6 mm diameter and a throat diameter of 7.9 mm; the acid flowrate was approximately 33 $cm^3 s^{-1}$. Before discharge to the ventilation system, the effluent gases were scrubbed with about 67 $cm^3 s^{-1}$ sodium hydroxide solution (initial concentration approximately 4 *M*) in a glass column 0.2 m diameter and 1.83 m long packed with 9.6 mm (3/8 in.) glass Raschig rings.

4. EXPERIMENTAL

4.1 Feed Materials

The original charge of UO_3 for the experimental work was obtained by the calcination of ammonium diuranate in air at about 400°C, followed by granulation through a 40-mesh screen and sieving to remove the fine particles (-100 BSS).

For the majority of the experimental runs, the uranyl nitrate solutions were produced from Australian yellow cake by solvent extraction purification in pilot plant equipment (Alfredson 1972). These solutions were then concentrated in a thermosyphon evaporator (Levins & Alfredson 1973) to a uranium concentration in the range 450 to 550 g ℓ^{-1}. Higher concentrations were avoided since they would have required heated storage and trace heating of the feed lines to eliminate crystallisation and blockage. Some feed solutions were made by the dissolution in nitric acid of UO_3 product from the denitrator or of UO_2 powder or pellets. In all cases the excess acid was in the range 0.1 to 0.3 *M*.

When required, feed solutions containing sulphate were prepared by stirring ammonium sulphate into warm solution (about 50°C) from the evaporator before charging to the feed tank.

4.2 Typical Operating Procedure

The reactor heaters were switched on with fluidising air flowing and air passing though both ducts of the atomising nozzle. When the wall temperature was above 100°C, approximately 10 kg UO_3 was charged into the reactor through a solids coupling from a hopper, and the bed was heated to the operating temperature in a stream of air with the filter blowback in operation. Water was then pumped to the liquid side of the atomising nozzle at 15 to 25 per cent of the proposed uranyl nitrate flow rate, causing the bed temperature to drop approximately 25 K. When the bed had returned to the desired operating temperature, the water was replaced by uranyl nitrate solution, and the flow gradually increased to the required value over a period of approximately half an hour. The venturi and caustic scrubbing systems were started when uranyl nitrate was first fed to the reactor.

The height of the bed, which was determined from the pressure drop and temperature profile across the bed, was controlled by periodically withdrawing UO_3 product through the base cone and into a glass product collector. The amount removed in each withdrawal was typically 1 to 1.5 kg UO_3 and this maintained a bed height in the range 0.33 to 0.36 m and a submergence of the spray nozzle from 0.10 to 0.13 m.

The venturi scrubber solution (initially about 0.5 *M* nitric acid) increased in concentration during a run to reach a constant (equilibrium) value of approximately 3 *M* nitric acid. The volume of this solution also increased and it was necessary to bleed off and periodically dilute the solution to retain scrubbing efficiency. Similarly the solution in the packed scrubber varied throughout the run, from an initial 4 *M* caustic

solution to approximately neutral at the end of the run.

On completion of the experiment, the spray nozzle was cleaned by flushing with water to remove uranyl nitrate solution and then by blowing with air. The fluidising air flow was reduced and the bed was drained into a product collector. To prevent the caking of any residual UO_3, the inlet air stream was passed through a drier as the reactor was cooled. After each run, the base cone was removed to inspect the interior of the reactor for cakes around the nozzle or the opposite wall and for lumps in the base cone.

4.3 Commissioning Experiments

Approximately 20 experimental runs were carried out initially to establish the general range of operating conditions and to develop a satisfactory operating procedure, which was described in Section 4.2. In addition, the effect of different sized pulsation dampers in the liquid feed line on spray quality was examined visually and photographically in a mockup system. The atomising nozzle was mounted in a perspex box and the liquid (water) and air flowrates were varied to determine the most satisfactory conditions for liquid flows up to 10 $\ell\ h^{-1}$.

Fluidisation tests were also carried out using three UO_3 powders (d_{avg} of 170, 340 and 550 μm) in a 0.10 m diameter glass column with a conical gas inlet/bed support section similar to the denitrator. The quality of fluidisation, bed expansion and minimum fluidisation velocities were observed and compared with published information.

4.4 Statistical Experiments

A statistical series of experiments was carried out to determine the effects of the main process variables on the product characteristics and equipment performance. The factors, chosen on the basis of commissioning experience and with reference to earlier studies, were operating temperature, uranyl nitrate feed concentration, uranyl nitrate feed rate and the nozzle air to liquid ratio; Table 3 gives the levels of these factors. The parameters observed were the particle growth measured as the change in the average particle diameter, the pour density, tap density, nitrate content and surface area of the product, and the wall to bed heat transfer coefficient. These parameters were all measured after a throughput equivalent to about two bed replacements (*i.e.* 18 kg uranium).

The surface area of the UO_3 product was measured by the BET method (Brunauer *et al.* 1938) for which the UO_3 was conditioned at 350°C overnight. Reactivity was also measured for a number of product samples by the method described in Appendix A.

The statistical series of experiments formed a half-replicate design (Davies 1954) and the operating levels and observations from each treatment combination are given in Table 4. Throughout the statistical series, the fluidising gas velocity was 0.5 m s^{-1} (at bed conditions) and the initial bed was UO_3 product from commissioning runs with an average particle size of approximately 200 μm. Appendix B gives a detailed example of the statistical analysis, the complete results of which are given in Table 5.

4.5 Sulphate Addition Experiments

The effect of sulphate addition to the uranyl nitrate feed solution was tested at three concentration levels, 500 mg ℓ^{-1}, 1,000 mg ℓ^{-1} and 2,000 mg ℓ^{-1}. The other operating conditions were similar to treatment combination abcd (Table 4).

5. RESULTS AND DISCUSSION

5.1 Commissioning and Operation Experience

In early runs, nozzle blockages tended to occur at the beginning of a run until the procedures for start up and shut down described in Section 4.2 were adopted. In particular, during the heating state, it was important to have a flow of air through the nozzle to prevent particles from the bed plugging the orifice. At shut down, it was particularly important to flush the nozzle and liquid lines with water to prevent blockages by solidification of residual uranyl nitrate.

The other early difficulty with the spray system related to the size of the pulsation damper. Without a damper, the spray was visibly pulsed, and with a damper of 1 ℓ capacity the shut down procedure was made more difficult due to the large holdup of uranyl nitrate. A pulsation damper of 0.2 ℓ capacity was found to be the most suitable for liquid flow rates up to 10 ℓ h^{-1}.

Spray quality was examined for various values of the air to liquid (water) volumetric flowrate ratio. Figure 4a shows a poor dispersion obtained with an air/liquid ratio of 195 and Figure 4b shows a satisfactory dispersion obtained with a ratio of 485. As a result of these tests, the levels of the ratio chosen for the statistical series of experiments were 250 and 500.

Bed blockages occurred when particles agglomerated and finally bridged across the reactor in the spray region. The first indication that a blockage was building up was an uneven temperature distribution in the bed, and this was used as a sign to shut down. In the early runs, blockages resulted when too much product was withdrawn and the nozzle was no longer submerged. This

difficulty was overcome by improved diagnosis of bed level, using both bed pressure drop and temperature profile as indicators. In addition, tests in the 0.1 m diameter glass mockup column with various UO_3 powders demonstrated that the observed bed expansion was in reasonable agreement with values calculated from the correlation reported by Leva (1959a), as shown in Figure 5. Thus, it was possible to use the Leva correlation with confidence to predict values of submergence of the spray nozzle. Tests were carried out at the same time to assess the quality of fluidisation and the minimum fluidising velocity (U_{mf}). Whereas satisfactory fluidisation was obtained with fluidising velocities two to five times the observed U_{mf}, the values of U_{mf} calculated from the correlation due to Leva (1959b) were two to three times the observed values (Table 6). This difference was due possibly to the presence of fine particles in the bed.

A more intractable problem, which resulted in bed blockage, was the tendency for the average particle size to steadily increase; this difficulty appears to be a feature of small scale fluidised bed denitrators (Section 2.2.1). The large particle sizes encountered (d_{avg} up to 700 μm) tended to lead to uneven fluidisation and the rapid formation of large agglomerates. With an initial bed having an average particle size of about 200 μm, operation was found to be trouble free over a period of at least 10 hours. A production rate of 380 kgU $h^{-1}m^{-2}$ was sustained without difficulty for this period, and a maximum rate of 570 kgU $h^{-1}m^{-2}$ was demonstrated. These production rates compare favourably with those for similar sized reactors (Table 1).

It was necessary to increase the packed length of the sodium hydroxide scrubber column from 1.22 to 1.83 m because traces of brown nitrous fumes were visible at the top of the column. Following this modification, the scrubber system performed efficiently with 55 to 60% of the nitric oxides being removed in the venturi scrubber and the remainder in the packed column scrubber.

The off-gas filter system performed satisfactorily with intermittent blowback (Section 3.1) and had a pressure drop typically ranging from 20 to 35 kPa between blowback operations. Typical operating pressures in the reactor were 28 to 45 kPa (gauge) above the bed and 40 to 57 kPa (gauge) below the bed.

5.2 Particle Size Characteristics

Particle size analyses were carried out on the UO_3 product collected throughout the experimental runs. The results are presented either as cumulative particle size distributions (some typical data are shown in

Figures 6 and 7), or as the average particle size, d_{avg} (see Equation 4).

Whereas steady state values of d_{avg} were achieved in some experiments, most runs were characterised by particle growth (Figure 8). Since particle growth appears to be a problem in small scale denitration equipment, and in view of the difficulty in obtaining steady state particle sizes, the growth rate for a given throughput of material was the most suitable means of characterising particle size behaviour.

The particle growth data for the statistical series of experiments are given in Table 4. Analysis of the results (Table 5) showed that the only significant factor (with a confidence of > 99%) was the operating temperature; an increase in temperature produced an increase in particle growth. This result agrees with most other workers who found that temperature had a strong influence on particle growth or equilibrium particle size (Section 2.2.1 and Table 2). The particle size distributions were generally similar to those presented by other workers.

The measured pour and tap densities which are shown in Table 4 compare with the pour densities of 3.6 to 4.1 g cm^{-3} and the tap densities of 4.0 to 4.3 g cm^{-3} quoted by Hawthorn *et al.* (1960a). Analysis of the results suggests that pour density may have been influenced by all the factors considered although the low confidence levels ($\leqslant$ 85%) limit the significance of this observation. Similarly, tap density may have been influenced by the feed concentration.

5.3 Nitrate Content

None of the chosen process variables was found to influence strongly the nitrate content of the product. The only factor of significance was feed concentration; increasing concentration caused an apparent decrease in the nitrate content, but only at the low confidence level of 75% (Table 5). There was no evidence of a relationship between operating temperature and nitrate content as reported by Jonke *et al.* (1954, 1957). The results are closer to those of Simecek & Trask (1963) who reported a low confidence level of 60% (*i.e.* probably not significant) for the effects of the four process variables, feed concentration, operating temperature, production rate and nozzle air flowrate.

5.4 Surface Area and Reactivity

At the 80% confidence level (*i.e.* possibly significant), the surface area increased with an increase in both feed concentration and nozzle air to liquid ratio (Table 5). The addition of sulphate to the uranyl nitrate feed solution increased the surface area of the product (Section 5.5).

The product reactivity was measured in terms of the apparent maximum rate of reduction at 600°C with 30 vol.% hydrogen in nitrogen (Appendix A). The rate increased with surface area, and was generally greater than the values derived from the data of Morrow *et al.* (1961) for the initial reaction rate at 550°C of UO_3 produced in a fluidised bed denitrator (Figure 9). The data of Morrow *et al.* have been corrected for temperature with their activation energy of 105 kJ mol^{-1}, and for hydrogen concentration with their partial pressure exponent of 0.8. The difference between the two curves probably results from comparing maximum rates with initial rates. Morrow *et al.* (1961) reported rate curves with a sigmoidal shape, particularly at lower surface areas, which would give an initial rate less than the maximum rate.

5.5 Effect of Sulphate Addition

The major effect of sulphate addition to the feed was an increase in the surface area of the product. The data are presented in Figure 10 and are in general agreement with the results of Cooper & Lloyd (1961).

The particle size distributions in Figure 7 show a minor effect of sulphate addition in that the narrowest distribution was obtained without sulphate and the widest with the highest concentration of sulphate (2,000 mg ℓ^{-1}). This contrasts with the data of Simecek & Trask (1963) which showed a considerable variation of size distribution with sulphate concentration, with the narrowest distribution obtained at about 2,500 mg ℓ^{-1} sulphate. There was no evidence that the addition of sulphate affected the particle growth rate.

Pour and tap densities decreased with increasing addition of sulphate (Figure 11). This corresponds to an increased porosity with sulphate addition (Morrow *et al.* 1961) which manifests itself most noticeably as an increase in the effective surface area.

5.6 Heat Transfer

Heat transfer coefficients were calculated from the measured temperature gradients in the denitrator. The average wall temperature was obtained by taking a mean value weighted with respect to the surface area of the walls of the reactor. Both bed and wall temperatures were averaged over about 1,000 seconds. The heat transfer surface was calculated using an estimate of the expanded bed height obtained from the correlation of Leva (1959a) which was shown to be applicable (Section 5.1). Heat input was based on the enthalpy requirements to heat, vaporise and decompose the uranyl nitrate feed solution using the data of Rand & Kubaschewski (1963). The heat transfer coefficient calculated from the above information (Table 4) approximates the

wall to bed film coefficient (h) if it is assumed that there was negligible resistance to heat transfer in the reactor wall.

Analysis of the data (Table 5) suggests that the heat transfer coefficient decreased with an increase in both feed concentration and feed rate. These results have a 90% confidence level and are possibly significant. A similar effect was reported by Simecek & Trask (1963). The mechanism whereby the heat transfer coefficient was influenced is not at all clear. Equation (2) suggests that particle size should have an important influence on the heat transfer coefficient, yet operating temperature, the only significant factor with respect to particle size, is probably not significant having a confidence level of only 70%.

If the heat transfer coefficients are plotted against average particle size (Figure 12), an inverse relationship is obtained of the form,

$$h \propto (d_{avg})^{-0.33} \qquad \ldots(6)$$

The points all lie within ± 20% of the line of least squares. Equation (6) is in agreement with Equation (5), which summarises most of the literature correlations.

There is no evidence that a relationship of the form of Equation (3) (Simecek & Trask 1963) will correlate the results, particularly as it implies a direct relationship between h and d_{avg}.

The heat transfer coefficients, which ranged from 190 to 265 W $m^{-2}K^{-1}$ compare with typical values ranging from 170 to 570 W $m^{-2}K^{-1}$ reported previously (Section 2.3).

6. CONCLUSIONS

The results of studies with the 0.1 m diameter fluidised bed denitrator are in general agreement with those of other workers.

Particle growth, which was a predominant feature, was significantly influenced by operating temperature and increased with increasing temperature. Minimum growth required an operating temperature of about 300°C, and a production capacity of 380 kgU $h^{-1}m^{-2}$ was sustained for an extended period at this temperature.

Changes in the main process variables exerted a minor influence on other properties of the UO_3 product. An increase in the feed concentration produced a decrease in nitrate content and pour density, and an increase in surface area. An increase in the feed rate produced an increase in the pour density, and an increase in the nozzle air/liquid ratio produced a decrease in the surface area.

The addition of sulphate to the uranyl nitrate feed solution produced an increase in surface area, and a decrease in the pour and tap density of the UO_3 product. Reactivity, measured in terms of the rate of reduction in hydrogen, was found to increase with an increase in surface area.

The wall to bed heat transfer coefficient, h, was in the range 190 to 265 W $m^{-2}K^{-1}$, and was a function of the average particle diameter (d_{avg}) represented by,

$$h \propto (d_{avg})^{-0.33} \quad .$$

The coefficient was also moderately decreased by an increase in either the feed concentration or the feed rate.

Further work is required to clarify the mechanisms which relate to the product and equipment characteristics to the main process variables and to extend the range of conditions giving a steady state particle size.

7. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the contributions of Mr. R. Hubery for the initial design of the equipment, Mr. W. Layton for construction of the equipment, Messrs. C. Stone, P. Stewart and G. Jackson for assistance in operation, Messrs. V. Vilkaitis, H. Romyn and co-workers for the supply of uranium solutions, Messrs. J. Sarbutt and A. Berzins for surface area measurements, Mr. P. Pakalns for chemical analyses, and Mr. N. Adamson (University of Auckland vacation student) and Mr. V. Vilkaitis for reactivity measurements.

8. NOMENCLATURE

C	heat capacity
d_{avg}	average particle diameter (Equation (4))
d_i	aperture of sieve i
d_{i+1}	aperture of sieve i+1
d'_i	$= \sqrt{d_i d_{i+1}}$
d_p	characteristic particle diameter
E	efficiency factor
g_c	conversion factor 32.2 ft $lb_m/lb_f s^2$
G	mass flowrate of fluidising medium
h	heat transfer coefficient
k	thermal conductivity
R	bed expansion
U	superficial gas velocity
V_g	gas velocity in region of spray nozzle (Equation (3))

W_i weight fraction retained between screens with apertures d_i and d_{i+1}

μ viscosity

ρ density

Subscripts

f fluid

mf minimum fluidisation

s solid.

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TABLE 1

SUMMARY OF FLUIDISED BED THERMAL DENITRATION EQUIPMENT

Application	Diameter (m)	Bed Depth (i) (m)	Location of Nozzle above the Support Plate (m)	Fluidising Velocity ($m\ s^{-1}$)	Uranium Conc. in Feed ($g\ \ell^{-1}$)	Bed Temperature (°C)	Production Rate ($kg\ h^{-1}m^{-2}$)	Reference
UO_3 - Pilot plant	0.15	0.38 (static)	0.15	0.4-0.55	780-1,120	240-450	420-730	Jonke *et al.* (1954, 1957)
UO_3 - Pilot plant	0.23	0.92	not stated	not stated	1,120	350	not stated	Hawthorn *et al.* (1960a)
UO_3 - Pilot plant	0.25	1.52	1.07	0.3-2.8	up to 1,475	315-430	up to 1,470	Simecek & Trask (1963)
UO_3 - Pilot plant	0.14/0.2	not stated	0.60	not stated	1,120	300	not stated	Otero (1967)
UO_3/PuO_2 - Pilot plant	0.075	0.31	0.23	0.9-1.5	570	300	not stated	Levitz (1970, 1971)
UO_3 (enriched) - Pilot plant	0.10	0.25	not stated	1.2-1.8	350	300-400	up to 240	Nelson (1969, 1970)
UO_3 (enriched) - Production plant	0.15	0.31 (static) 0.46	0.18	1.2	350	300-400	up to 240	Bjorklund & Offutt (1970, 1971a, 1971b)
UO_3 - Production plant	~1.0	not stated	not stated	not stated	1,120	350	not stated	Hawthorn *et al.* (1960b)
UO_3 - Production plant	1.17	3.70	3.25	2.0	1,320 ± 26	288	1,420	Robinson & Todd (1966)

(*i*) *Operating bed depth unless otherwise stated.*

TABLE 2

SUMMARY OF REPORTED EFFECTS OF OPERATING PARAMETERS ON PARTICLE SIZE CHARACTERISTICS IN FLUIDISED BED DENITRATION

Bed Diameter (m)	Range of Conditions Giving Equilibrium Particle Size	Reported Effect of Increasing Parameters on Equilibrium Particle Size (d) or Particle Growth ($\dot{d}$)								Reference
		Temperature		Feed Rate		Feed Concentration		Nozzle/Air Liquid Ratio		
		d	$\dot{d}$	d	$\dot{d}$	d	$\dot{d}$	d	$\dot{d}$	
0.15	(i) Temperature < 350°C (ii) Feed Conc. < 70% UNH (iii) With Seed Addition	+		+			-	0		Jonke *et al.* (1954, 1957)
0.25	Temperature < 425°C	+		0		+ (315°C) 0 (370°C)		-		Simecek & Trask (1963)
0.10	Equilibrium not achieved (300-350°C)		+		-		-		0	Nelson (1970)
0.15	(i) Temperature < 400°C (ii) With Thermal Shocking and Jet Grinding	+								Bjorklund & Offutt (1970, 1971a, 1971b)

\+ *Increase in characteristic;*

0 No effect;

\- *Decrease in characteristic.*

TABLE 3

LEVELS OF FACTORS IN THE STATISTICAL EXPERIMENTS

Factor	Level	
	+	-
A = Feed Concentration g(U) ℓ^{-1}	550	450
B = Operating Temperature (°C)	340	295
C = Feed Rate (ℓ h^{-1})	5.4	4.0
D = Nozzle Air/Liquid(i)	500	250

(i) Nozzle air/liquid is the ratio of the air to liquid volumetric flowrates (at STP) supplied to the atomising nozzle.

TABLE 4

EXPERIMENTAL DESIGN AND OBSERVATIONS

Treatment Combination	Level of Factor				Observation					
	A	B	C	D	Particle Growth (μm)	Pour Density (g cm^{-3})	Tap Density (g cm^{-3})	Nitrate Content (wt.%)	Surface Area (m^2 g^{-1})	Heat Transfer Coefficient (W $m^{-2}K^{-1}$)
(1)	-	-	-	-	57	3.86	4.31	0.45	0.23	250
ad	+	-	-	+	41	3.96	4.30	0.58	0.28	216
bd	-	+	-	+	100	4.00	4.34	0.71	0.15	235
ab	+	+	-	-	89	3.94	4.31	0.44	0.38	186
cd	-	-	+	+	27	4.09	4.35	0.58	0.06	203
ac	+	-	+	-	0	3.93	4.22	0.52	1.00	196
bc	-	+	+	-	100	4.08	4.32	0.64	0.16	205
abcd	+	+	+	+	122	3.97	4.26	0.37	0.12	182
Repeat abcd	+	+	+	+	105	4.01	4.47	0.46	(i)	222
Mean value					71	3.98	4.32	0.53	0.30	211

(i) Surface area not measured .

TABLE 5

EFFECTS AND CONFIDENCE LEVELS FOR THE STATISTICAL EXPERIMENTS

Factor		Dependent Variable					
		Particle Growth (a)	Pour Density (a)	Tap Density (a)	Nitrate Content (a)	Surface Area (b)	Heat Transfer Coefficient (b)
A = Feed Concentration	Effect	- 8	- 0.06	- 0.06	- 0.12	+ 0.30	- 28
	Confidence Level	None (c)	75%	65%	75%	80%	90%
B = Operating Temperature	Effect	+ 71.5	+ 0.04	+ 0.01	+ 0.01	- 0.20	- 14
	Confidence Level	99%	60%	None	None	60%	70%
C = Feed Rate	Effect	- 9.5	+ 0.08	- 0.03	- 0.02	+ 0.10	- 25
	Confidence Level	None	85%	None	None	None	90%
D = Nozzle Air/Liquid	Effect	+ 11	+ 0.05	+ 0.02	+ 0.05	- 0.30	0
	Confidence Level	None	70%	None	None	80%	None

(a) Estimate of error obtained from the repeat experiment and by assuming no 2-factor interactions.

(b) Estimate of error obtained by assuming no 2-factor interactions.

(c) 'None' is a confidence level ⩽ 50%.

TABLE 6

MINIMUM FLUIDISING VELOCITIES FOR UO_3 POWDERS

Average Particle Size (μm)	550	343	170
Observed U_{mf} (m s^{-1})	0.2	0.075	0.04
Calculated U_{mf} (m s^{-1})	0.6	0.25	0.07

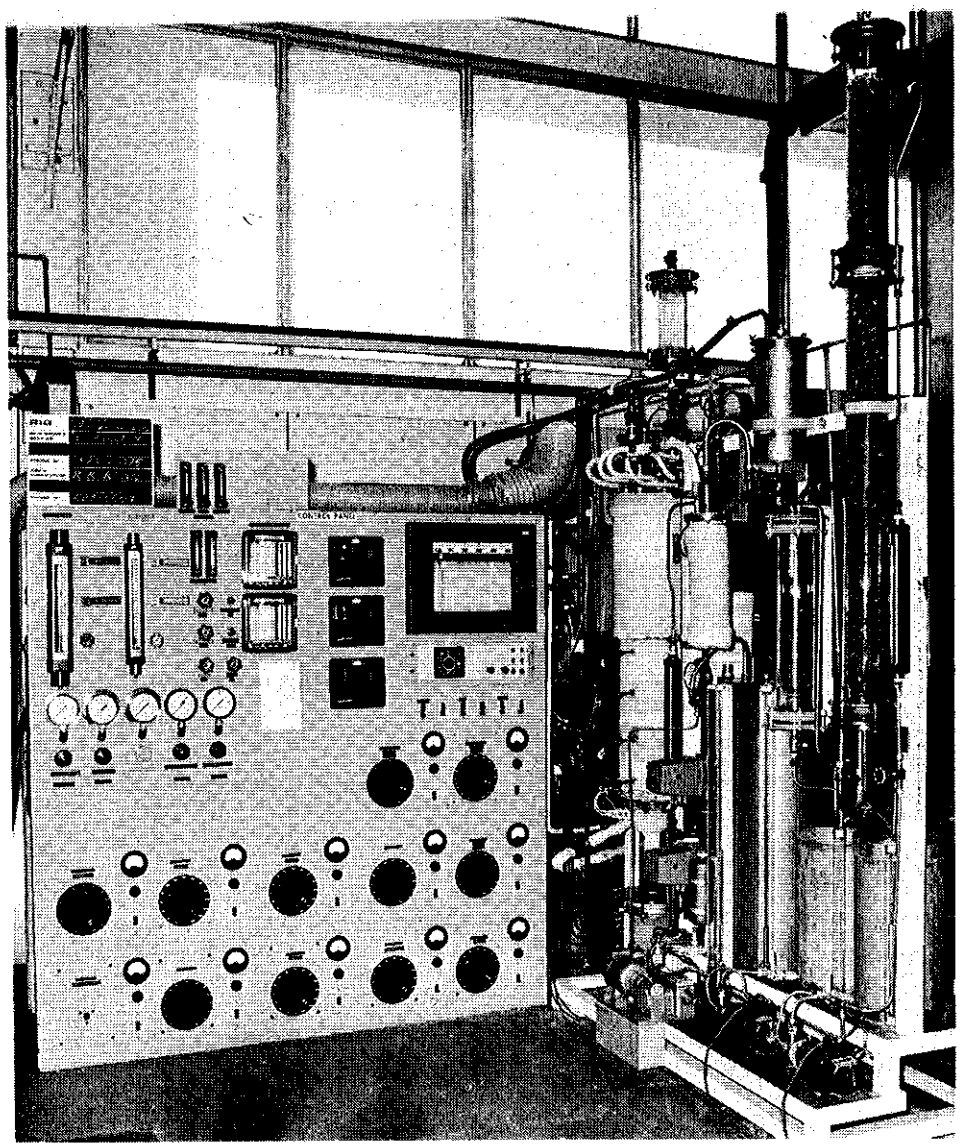

FIGURE 1. FLUIDISED BED THERMAL DENITRATION EQUIPMENT

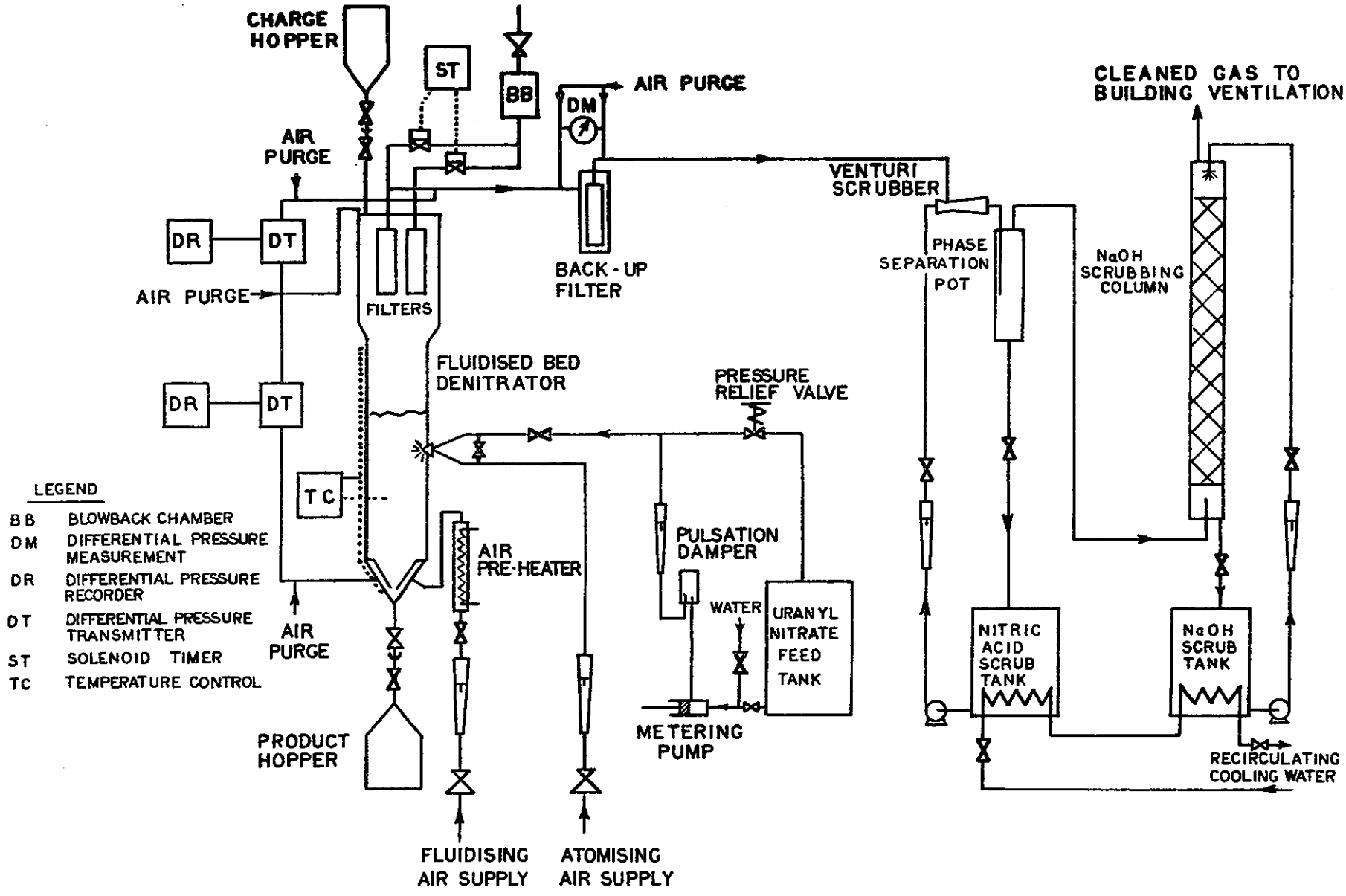

FIGURE 2. FLOWSHEET FOR FLUIDISED BED THERMAL DENITRATION EQUIPMENT

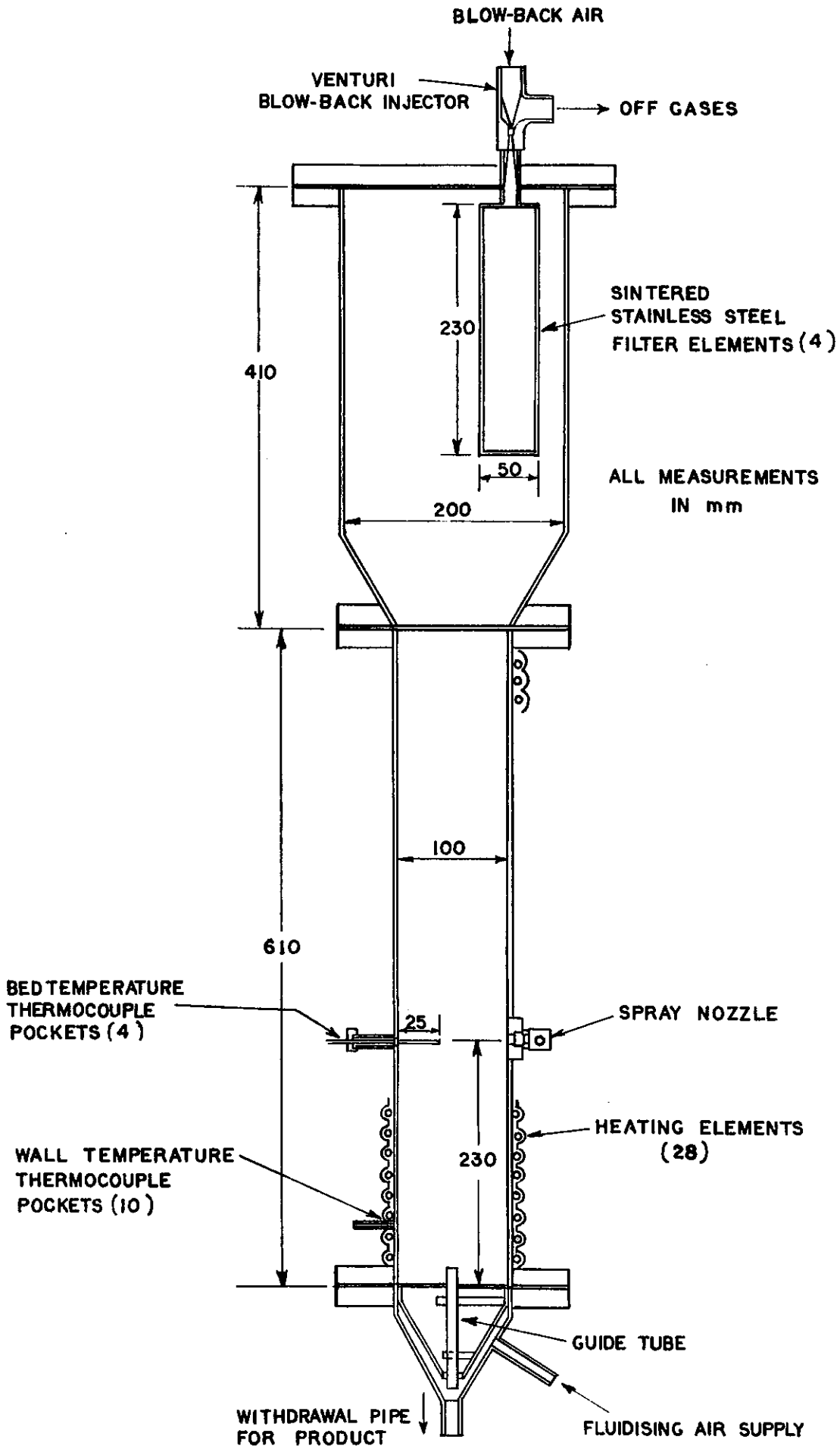

FIGURE 3. FLUIDISED BED DENITRATOR

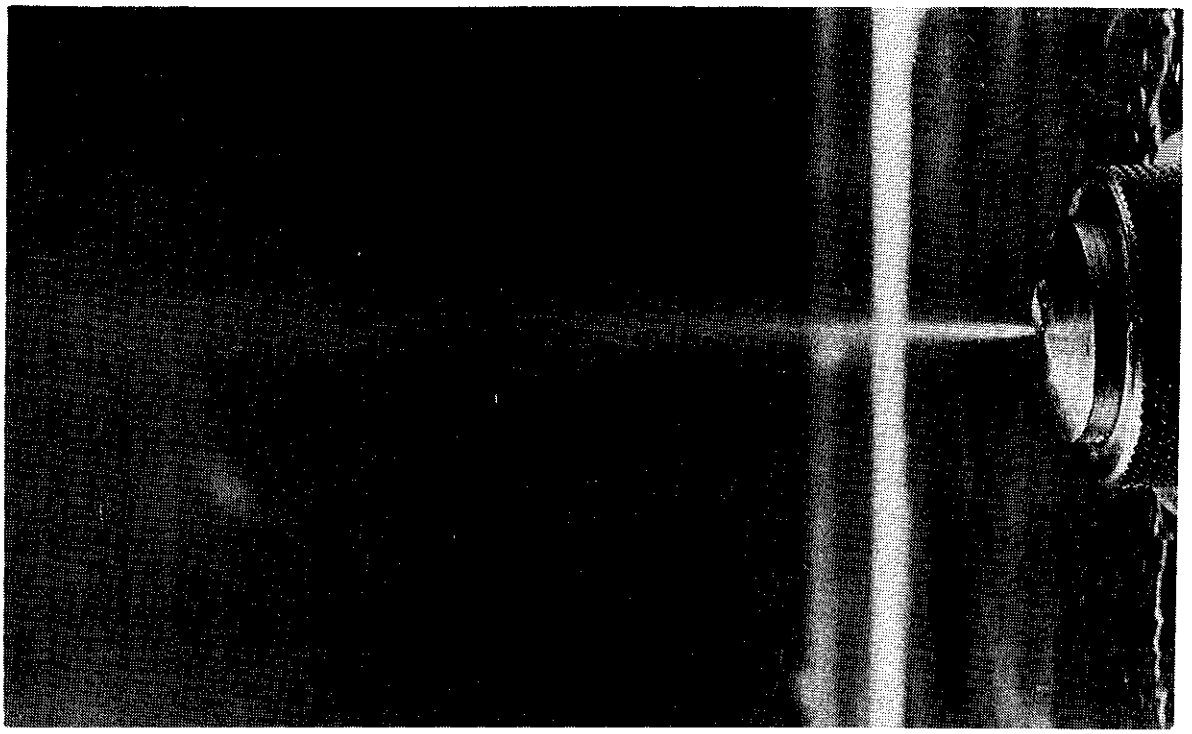

FIGURE 4a. UNSATISFACTORY SPRAY DISPERSION (WATER 1.5 $cm^3 s^{-1}$, AIR 293 $cm^3 s^{-1}$, FLOW RATIO 195)

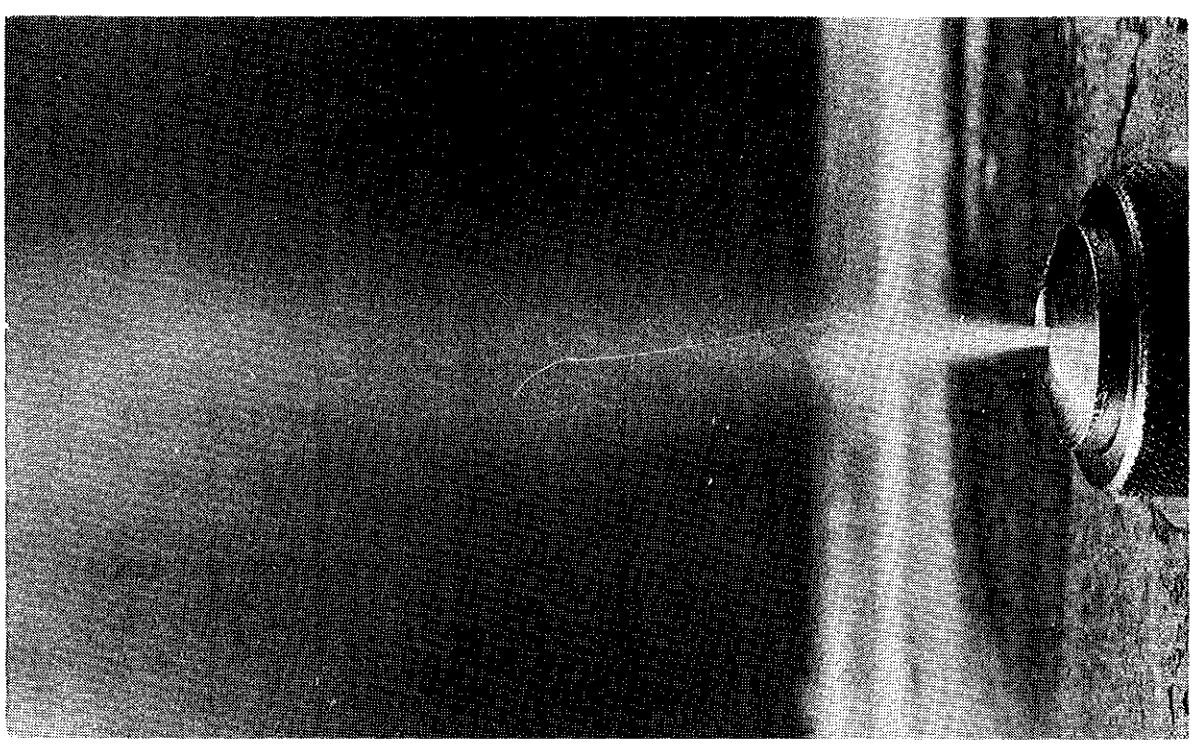

FIGURE 4b SATISFACTORY SPRAY DISPERSION (WATER 1.5 $cm^3 s^{-1}$, AIR 725 $cm^3 s^{-1}$, FLOW RATIO 485)

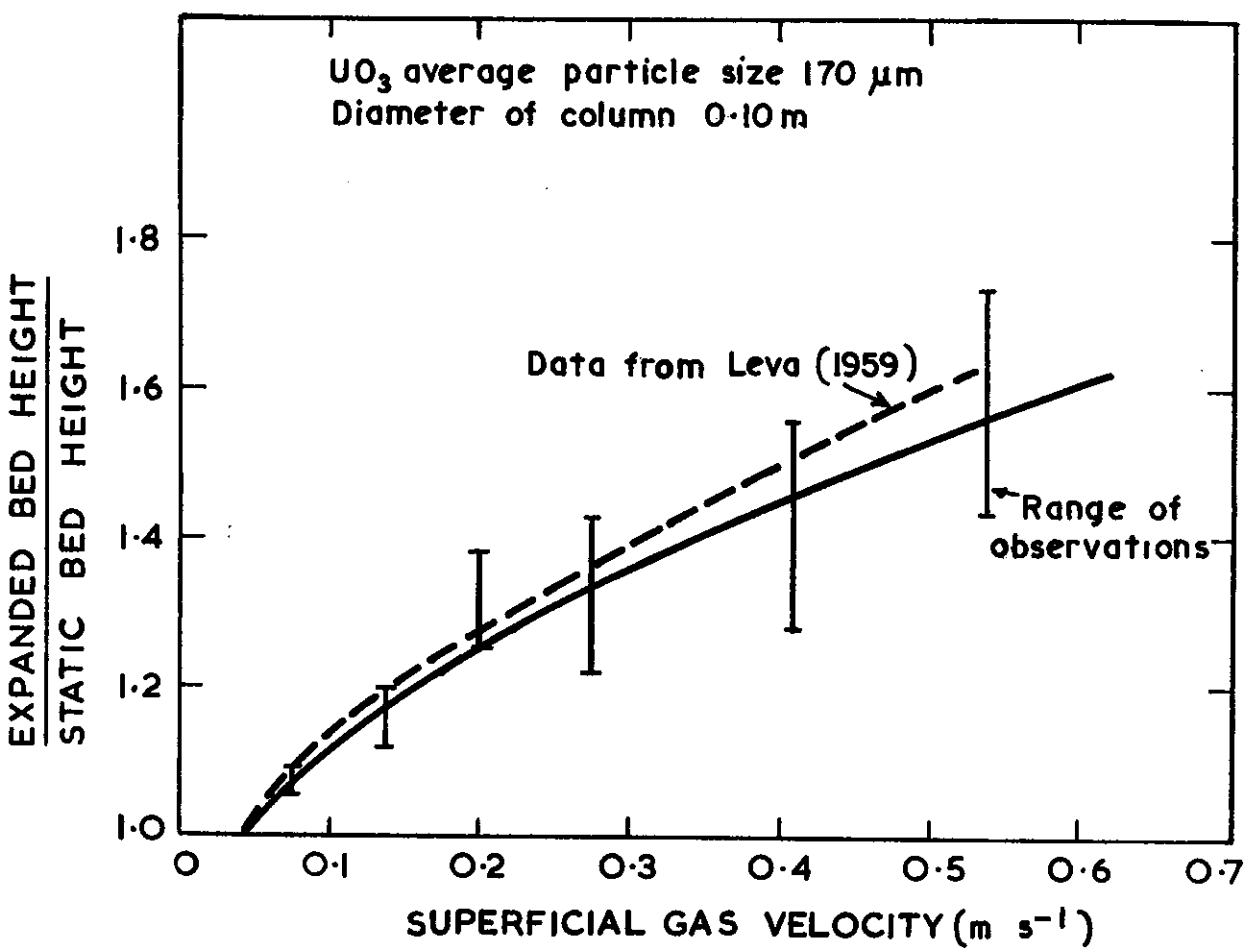

FIGURE 5. BED EXPANSION AS A FUNCTION OF SUPERFICIAL GAS VELOCITY

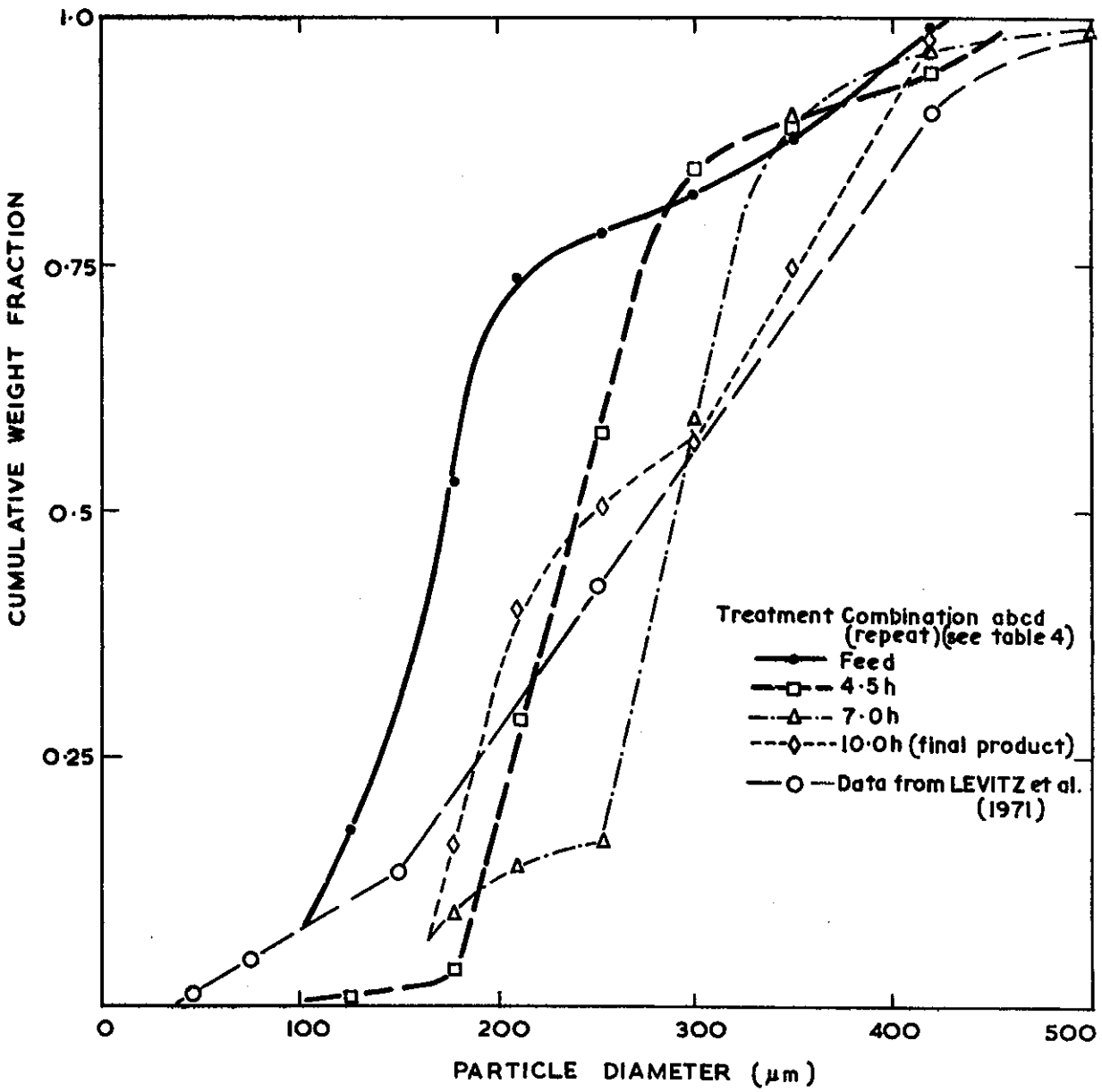

FIGURE 6. VARIATION OF PARTICLE SIZE DISTRIBUTION WITH TIME

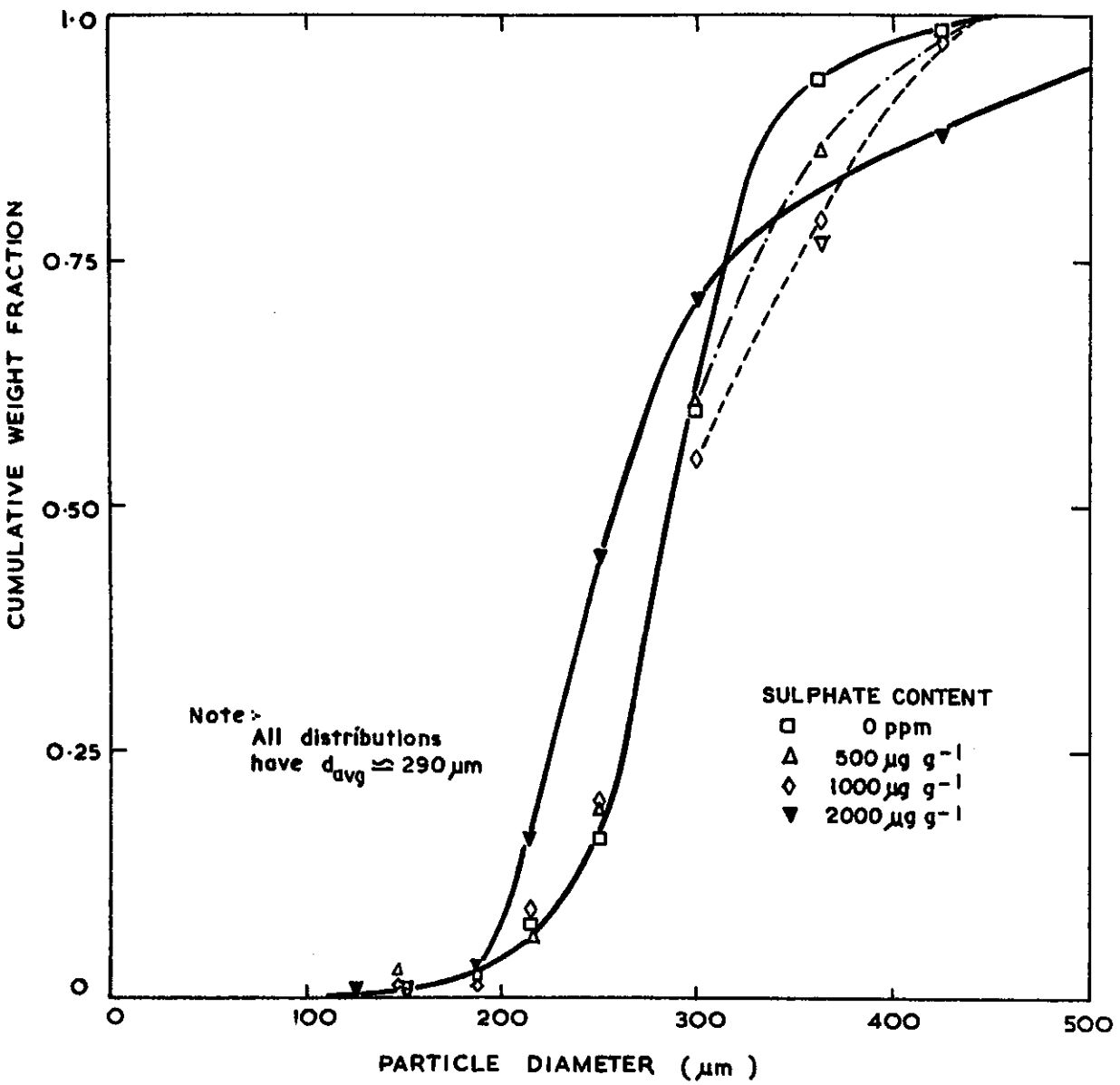

FIGURE 7. EFFECT OF SULPHATE CONCENTRATION ON PARTICLE SIZE DISTRIBUTION

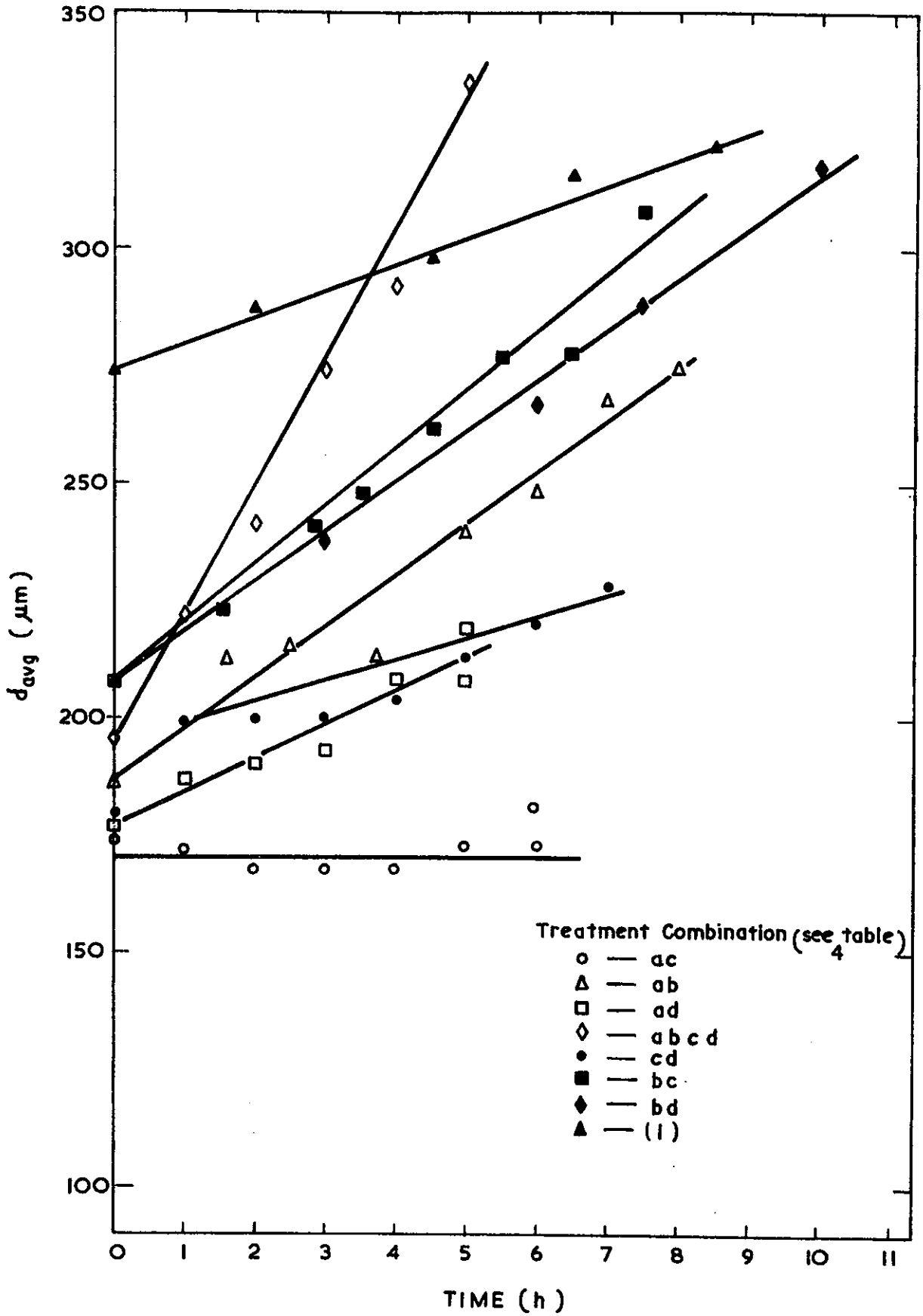

FIGURE 8. VARIATION OF AVERAGE PARTICLE DIAMETER WITH TIME (STATISTICAL EXPERIMENTS)

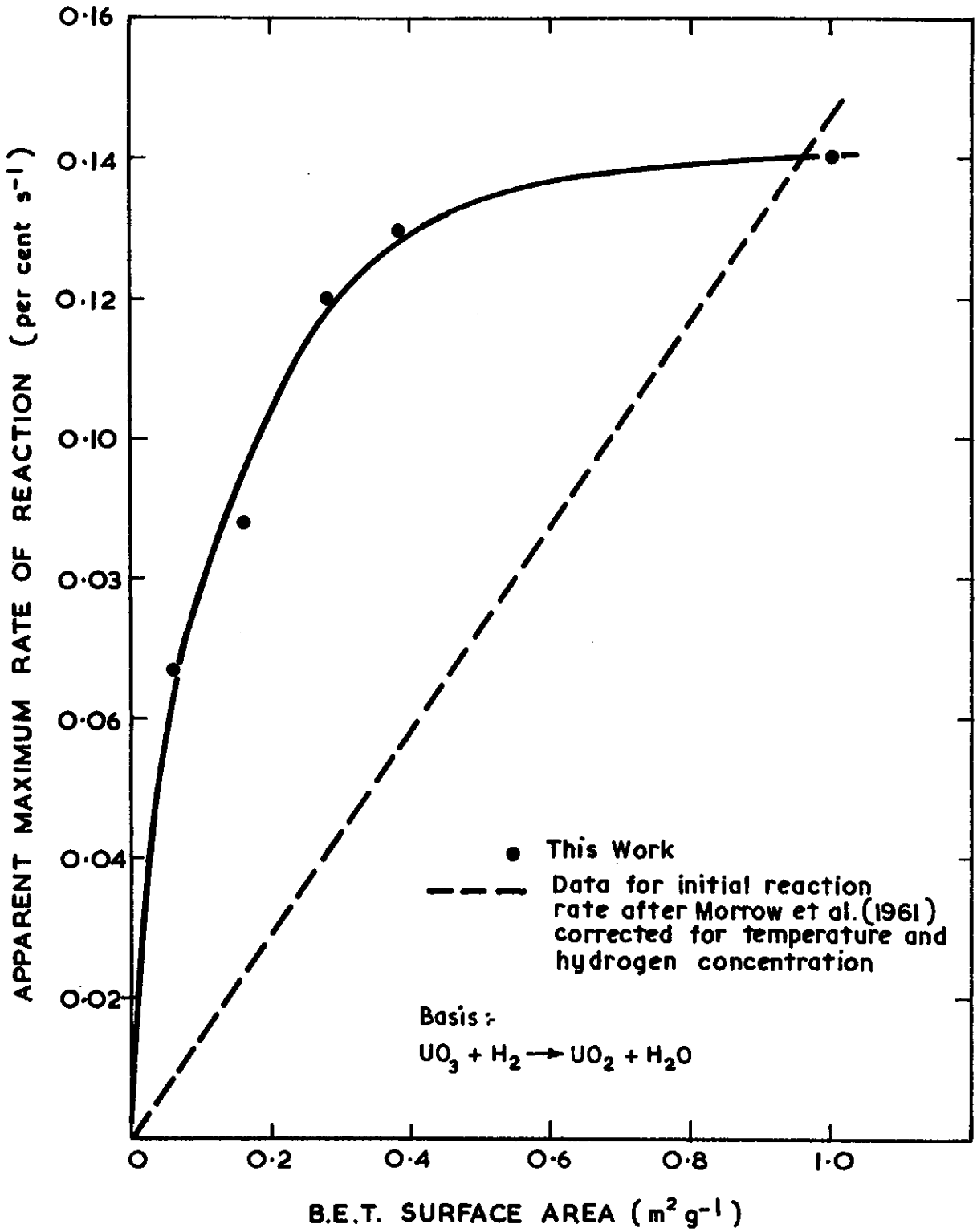

FIGURE 9. EFFECT OF SURFACE AREA ON APPARENT MAXIMUM RATE OF REACTION OF UO_3 WITH 30% HYDROGEN AT 600°C

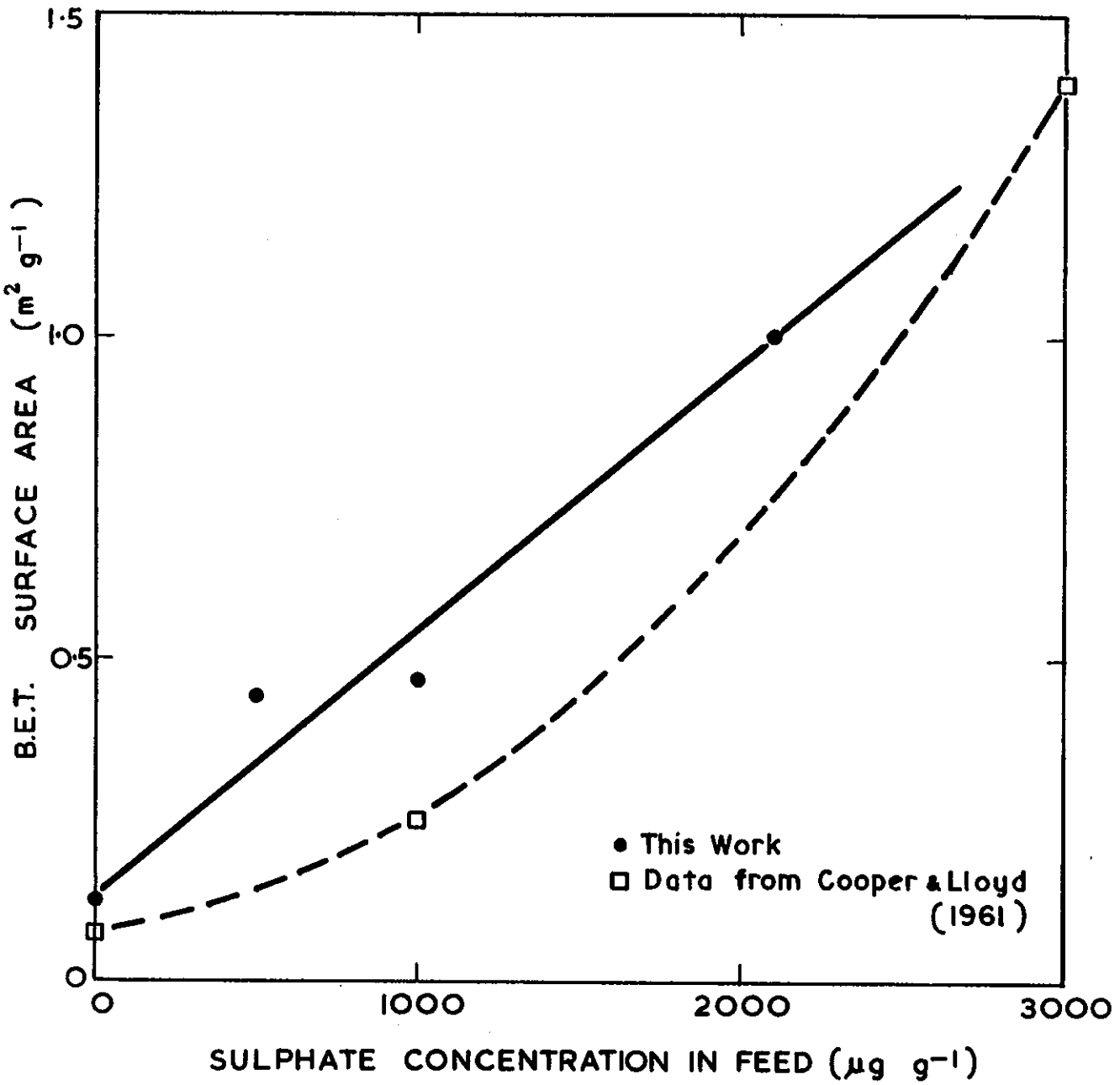

FIGURE 10. EFFECT OF SULPHATE CONCENTRATION IN THE FEED SOLUTION ON THE SURFACE AREA OF THE UO_3 PRODUCT

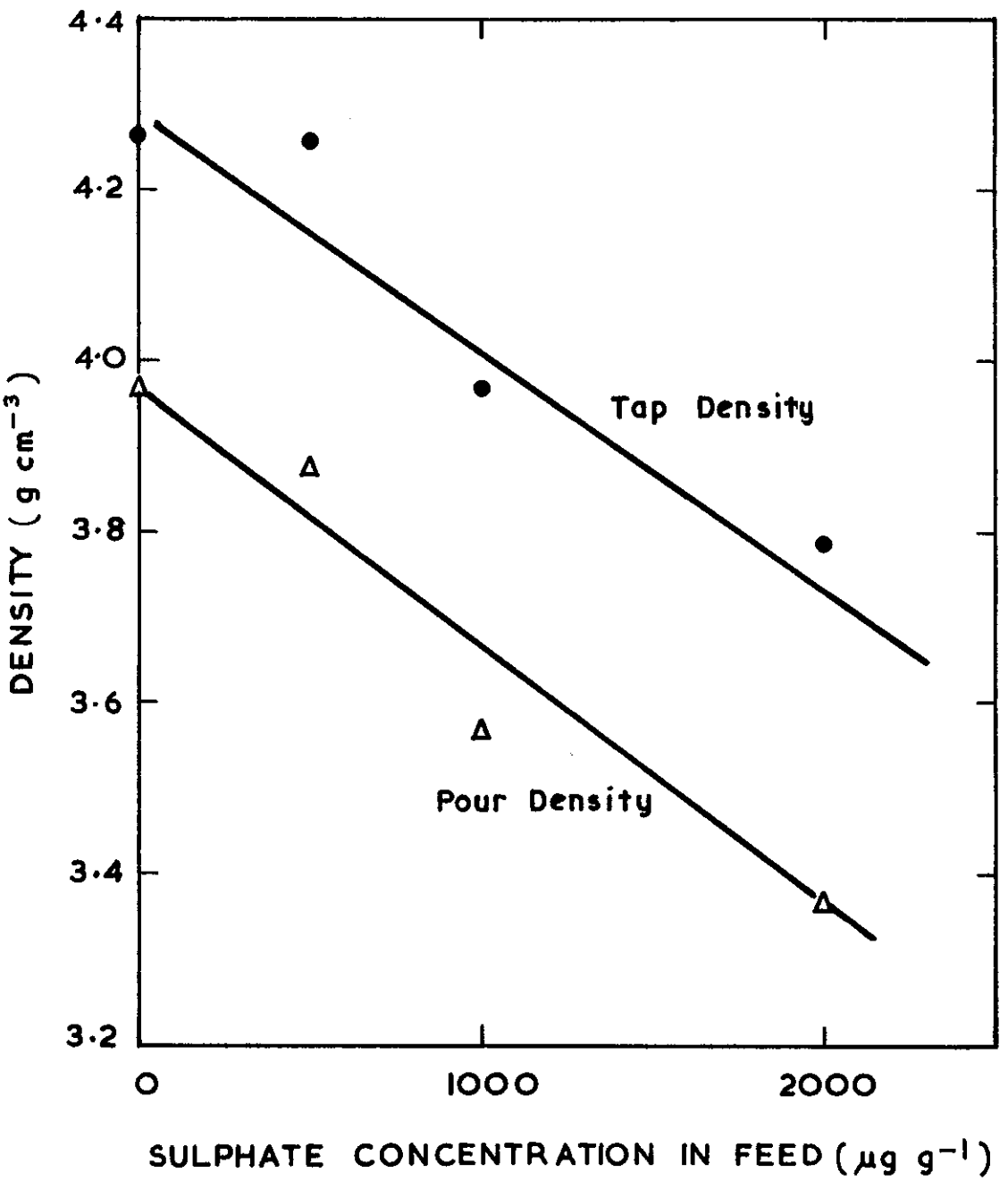

FIGURE 11. EFFECT OF SULPHATE CONCENTRATION IN THE FEED SOLUTION ON THE POUR AND TAP DENSITY OF THE UO_3 PRODUCT

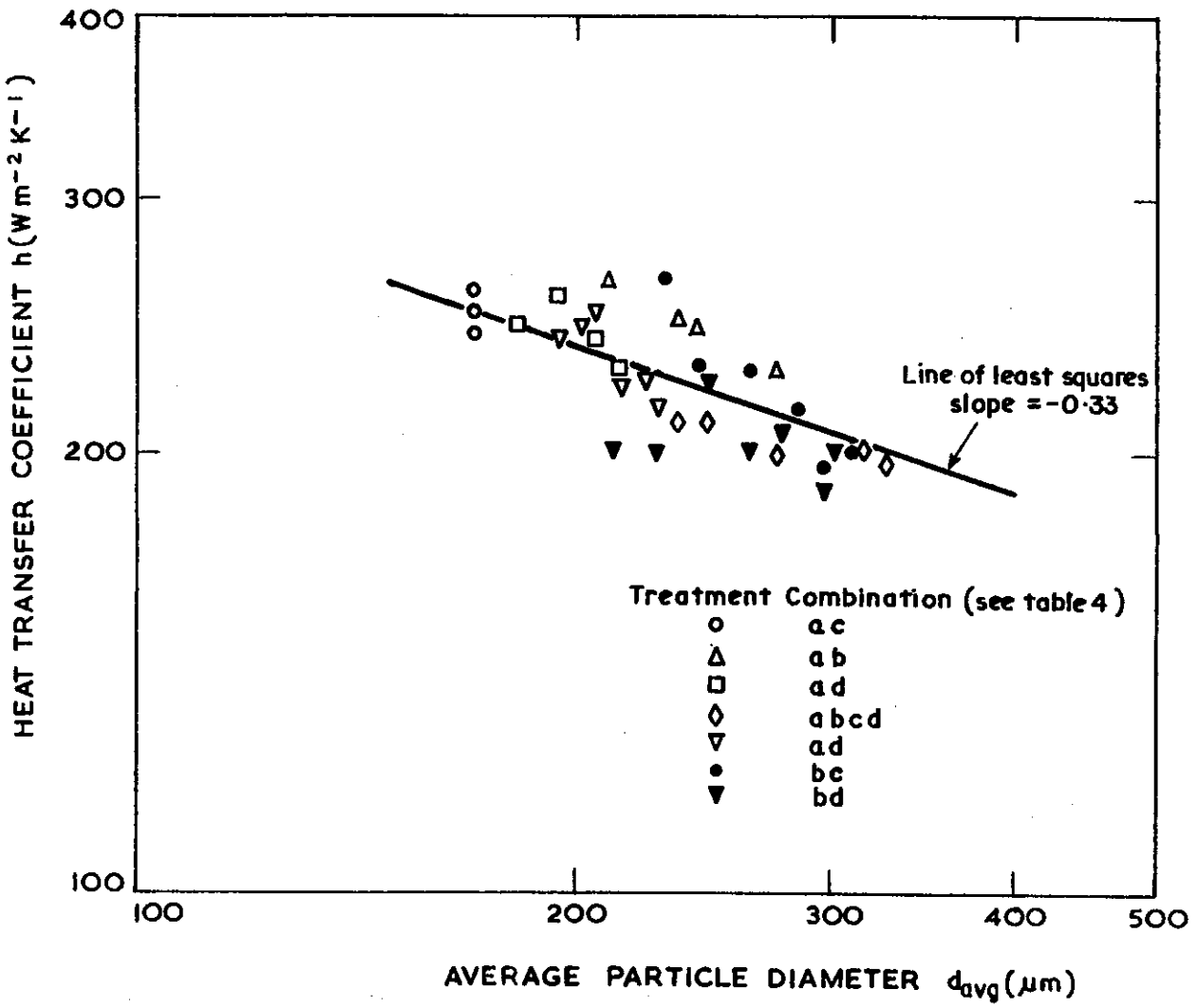

FIGURE 12. VARIATION OF HEAT TRANSFER COEFFICIENT WITH PARTICLE DIAMETER

APPENDIX A

MEASUREMENT OF PRODUCT REACTIVITY

The reactivity of the UO_3 product was assessed by measuring the rate of reduction to UO_2 in a hydrogenous atmosphere at 600°C.

Reductions were carried out in a silica boat located in a 25.4 mm diameter silica tube mounted horizontally in a furnace. The progress of the reaction was followed by monitoring the moisture content of the off-gas using an electrolytic moisture meter.

Typical operating procedure involved placing a 40 mg sample of as-received UO_3 in the silica boat, which was then positioned in the centre (hot zone) of the tube. The equipment was thoroughly purged with dried nitrogen as the hot zone temperature was raised to 600°C over a period of about 2,400 seconds. The reaction was commenced by introducing dry hydrogen, giving a 30 vol.% mixture in nitrogen with a total flowrate of about 29 cm^3s^{-1}. The water produced in the reduction was detected by the moisture meter, and recorded on a Heath flat-bed recorder.

The recorder trace showed a maximum moisture content within 200 to 300 seconds of the introduction of hydrogen and this was taken as a measure of the apparent maximum reaction rate of the sample. The data obtained were used to produce the curve shown in Figure 9.

In calculating the apparent reaction rate, it was assumed that the starting material for the reduction was UO_3 and that no significant decomposition to U_3O_8 occurred during the heating period. If some decomposition had occurred, the calculated rates are under-estimated. However, according to Dell & Wheeler (1962), the product from fluidised bed thermal denitration is the relatively stable γUO_3 which does not exhibit significant thermal decomposition below about 600°C.

APPENDIX B

STATISTICAL ANALYSIS

Analysis of the results of the statistical experiments was carried out using the general procedures outlined by Davies (1954). The following example is the analysis carried out on the measured values for the heat transfer coefficient (see Table 4).

B1 Calculation of Effects and Mean Sum of Squares

The calculations were carried out in tabular form (Table B1). The top half of column (1) was obtained by adding successive pairs of figures from the observation column, and the lower half by taking the differences of the same pairs, the first from the second in each case. Column (2) is derived from column (1) in the same way, likewise column (3) is derived from column (2). The total effects calculated are, in fact, the algebraic sum of the responses at the high (+) level and the low (-) level of each factor. The final column gives the factors which were varied to produce the effects calculated. It should be noted that each main factor (A,B,C or D) was confused with a three-factor interaction, which was assumed negligble. Thus the mean effect of factor A (feed concentration) on the heat transfer coefficient is -28.3, of factor B (operating temperature) is -14.3, and so on.

B2 Estimate of Error Variance

An estimate of the error variance was obtained from the repeat experiment thus:

Observation I	186
Observation II	222
Mean of I and II	204
Sum of Squares	648

With one degree of freedom the mean square of the error (the error variance) obtained from the repeat experiment was 648.

An estimate of the error based on a single repeat experiment has obvious limitations, and to improve on this it was assumed that the two-factor interactions were negligible, and that their sums of squares were additional estimates of the error variance. This procedure is recommended by Davies (1954) and gave three more degrees of freedom for the estimate of error variance which was required for the subsequent analysis.

B3 Analysis of Variance

The analysis of variance (Table B2) was interpreted as follows:

(i) An increase in feed concentration (factor A) produced a decrease in the heat transfer coefficient; the degree of confidence in this result is about 90%, *i.e.* it is possibly significant.

(ii) An increase in operating temperature (factor B) produced a decrease in the heat transfer coefficient; the degree of confidence in this result is about 70%, *i.e.* it is probably not significant.

(iii) An increase in feed rate (factor C) produced a decrease in the heat transfer coefficient; the degree of confidence in this result is about 90%, *i.e.* it is possibly significant.

Similar analyses were carried out for the particle growth, pour density, tap density and nitrate content of the product UO_3. Analysis of the surface area data, for which there was no repeat value, was carried out with an estimate of the error variance based solely on the sums of squares for the two-factor interactions; the degrees of freedom for the error were reduced to 3. The results of the statistical analyses are given in Table 5.

TABLE B1

CALCULATION OF EFFECTS AND MEAN SUM OF SQUARES

Treatment Combination (See Table 4)	Observation (Heat Transfer Coefficient)	Total Effect (1)	(2)	(3)	Mean Effect (col 3)/4	Sum of Squares (col 3)^2/8	Factors Causing the Effect
(1)	250	466	887	1,673	-	-	-
ad	216	421	786	- 113	- 28.3	1,596	A,BCD
bd	235	399	- 83	- 57	- 14.3	406	B,ACD
ab	186	387	- 30	- 31	- 7.8	120	AB,CD
cd	203	- 34	- 45	- 101	- 25.3	1,275	C,ABD
ac	196	- 49	- 12	53	13.3	351	AC,BD
bc	205	- 7	- 15	33	8.3	136	BC,AD
abcd	182	- 23	- 16	- 1	- 0.3	0.13	ABC,D

TABLE B2

ANALYSIS OF VARIANCE

Source of Variation	Sum of Squares	Degrees of Freedom (ϕ)	Mean Square (V)	V_1/V_2	Confidence Level* (%)
Main effects		ϕ_1	V_1		
A	1,596	1	1,596	5.09	91.3
B	406	1	406	1.29	68.5
C	1,275	1	1,275	4.06	88.5
D	0.1	1	0.1	3×10^{-3}	- 0
Interactions		ϕ_2	V_2		
AB,CD	120	1			
AC,BD	351	1			
BC,AD	136	1			
Repeat	648	1			
	1,255	4	314	-	-

* *Confidence levels were interpolated from tables of the F-distribution in Bennett & Franklin (1954) for degrees of freedom $\phi_1 = 1$ and $\phi_2 = 4$.*

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