AAEC/E282

AAEC/E282

AUSTRALIAN ATOMIC ENERGY COMMISSION

RESEARCH ESTABLISHMENT

LUCAS HEIGHTS

THE PRODUCTION OF SINTERABLE URANIUM DIOXIDE FROM AMMONIUM DIURANATE

PART I – A REVIEW OF GAS/SOLID CONTACTORS

by

A. G. FANE

April 1974

ISBN 0 642 99628 8

AUSTRALIAN ATOMIC ENERGY COMMISSION
RESEARCH ESTABLISHMENT
LUCAS HEIGHTS

THE PRODUCTION OF SINTERABLE URANIUM DIOXIDE FROM AMMONIUM DIURANATE
PART I - A REVIEW OF GAS/SOLID CONTACTORS

by

A.G. FANE

ABSTRACT

This report reviews the performance characteristics of a variety of contactors used for gas/solid reactions. A critical assessment is made of their suitability for the conversion of ammonium diuranate to sinterable uranium dioxide in terms of their heat transfer and powder handling characteristics, and the capability of obtaining a high conversion efficiency consistent with continuous operation. The pulsed fluidised bed is judged to be particularly promising for future development.

National Library of Australia card number and ISBN 0 642 99628 8

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; CALCINATION; COMPARATIVE EVALUATIONS; FABRICATION; FLUIDIZED BED REACTORS; GASES; HEAT TRANSFER; PERFORMANCE; POWDERS; REDUCTION; SOLIDS; STIRRING; URANIUM DIOXIDE

CONTENTS

(Continued)

CONTENTS (Cont'd.)

1. INTRODUCTION

Uranium dioxide powder for fuel pellet fabrication is usually produced by the precipitation and calcination-reduction of ammonium diuranate (ADU). Both processes have a strong influence on the physical characteristics of the uranium dioxide (UO_2) powder, the ease of the subsequent fabrication stages and the quality of the final product (Alfredson 1969, Alfredson & Janov 1971).

ADU can be converted to UO_2 either by direct reduction or by a two-step procedure involving thermal decomposition (calcination) in an oxidising or inert atmosphere followed by reduction of the intermediate (Huntington 1958, Alfredson & Janov 1971). The conversion reactions can be carried out in a variety of gas/solid contactors; this report assesses some of the alternatives, reviews some of the nuclear applications of the contactors, and surveys their performance characteristics. Included in the assessment is the pulsed fluidised bed which was investigated further at the AAEC Research Establishment. The development of a 0.13 m diameter pulsed fluidised bed reactor will be described in future reports.

2. PRELIMINARY CONSIDERATIONS

There are several factors which are necessary to this assessment:

(i) A readily sintered UO_2 is required, *i.e.* a powder which will sinter to 10.6 g cm^{-3} after 1.5 hours in hydrogen at 1,650°C, following pressing at 279 MPa (K.D. Reeve, AAEC private communication).

(ii) The reduction reaction, which is carried out at approximately 650°C, is exothermic.

(iii) Microsintering within UO_2 particles may occur if high local temperatures prevail during reduction.

(iv) Microuniformity and consistency in physical characteristics of the UO_2 are desirable for the fabrication stage.

(v) ADU is friable and readily produces fines.

(vi) There will be a continuous and growing demand for UO_2 powder.

On the basis of these factors, the desired characteristics of the 'ideal' contactor for the conversion of ADU to ceramic grade UO_2 can be specified as follows:

- Good heat transfer characteristics, with effective means of heat removal from the bulk of the solids to prevent the formation of 'hot spots'; this is discussed more fully below (Section 2.1).
- A high conversion to UO_2 consistent with continuous operation; this aspect is also discussed below (Section 2.2).
- Good powder handling characteristics.
- Amenable to scale up.

In addition, less equipment is necessary if the contactor has the ability to handle direct reduction rather than requiring a precalcined feed. These characteristics provide useful criteria for assessing the various types of gas/solids contactors. Additional insight can be gained by taking a closer look at the heat transfer processes and the effect of continuous solids flow on the degree of conversion in the contactor.

2.1 Heat Transfer

Heat release from a bed of particles in a gas/solids contactor can take place by a variety of mechanisms involving conduction, convection and radiation to the gas phase and to the walls of the vessel. Those mechanisms playing a dominant role will be determined by the equipment design, the flow rates of the phases and their physical properties. It is illustrative to examine the development of the heat transfer processes as the bed of particles undergoes transition from static to well-stirred conditions.

Under static bed conditions, a single particle at elevated temperature will transfer heat to the surrounding particles by a conductive mechanism focused at the points of solid-solid proximity. Radiative heat transfer will occur also, although it is negligible in packed beds below 600°C (Baddour & Yoon 1961). Since radiative transport increases with the fourth power of the absolute temperature, it may assume a significant role at more elevated temperatures.

Botterill & Williams (1963) have demonstrated for spherical particles that negligible heat is transferred by conduction across points of solid contact, and have suggested that the gas phase plays an important role in conducting heat across the narrow gaps between the particles. This agrees with the findings of Deissler & Boegli (1958) who showed that the effective thermal conductivity of powders in various gases is a strong function of the conductivity of the gas. Heat release from the bed to the container walls takes place by a similar conductive mechanism. Under steady-state heat flow, there may be considerable thermal gradients across the bed. Gas, flowing over or through the bed, removes heat by convective transport, although the low heat capacity of gas reduces its effectiveness as a heat transfer medium, *i.e.* large quantities of gas are required to remove relatively small amounts of heat.

Movement of particles by mechanical stirring or by gas agitation will augment the conductive heat transfer process. Single particles or groups of particles at elevated temperature will be brought into contact with many others and unsteady state conduction will take place, tending to reduce thermal gradients within the bed. This transfer of heat from particle to

particle, or group to group, has a time dependent quality which means that the instantaneous heat flux falls rapidly with time (Mickley, Fairbanks & Hawthorn 1961, Botterill & Williams 1963). As a result, the uniformity of temperature in the bed will be related to the local residence times of the particles; the more rapid the mixing the smaller the temperature gradients.

Applying these arguments to the transfer of heat from the bed to the walls of the vessel, it is evident that the shorter the particle residence time at the walls the higher is the bed-to-surface heat transfer coefficient. This has been verified experimentally by Botterill & Williams (1963) for stirred fluidised beds.

Since the mechanism of heat transfer relies on the rapid replacement of particles adjacent to the surface, it follows that any obstruction to the removal of particles will promote the formation of temperature gradients within the bed. The obstruction may take the form of a relatively stagnant layer of particles adjacent to the walls, which can occur when the general flow pattern encourages classification in a bed of multi-sized particles.

The above discussion serves to emphasise how the solids flow pattern influences the heat transfer processes in a gas/solids contactor.

2.2 Chemical Conversion in Continuous Systems

This section deals with chemical conversion of the solid phase in a continuous flow gas/solids contactor. The conversion of a single solid particle will be dependent on the physicochemical reaction mechanisms and on the time spent in the reactor. Overall conversion of bulk solids will be an integral effect, governed by the distribution of particle residence times.

Residence time distributions are most readily compared in terms of the equivalent number of backmix stages, N. A single backmix stage is characterised by uniform composition throughout the vessel and has a spread of residence times from almost zero to infinity. At the other end of the scale is the plug flow reactor, which is equivalent to an infinite number of backmix stages and has the same residence time for all elements of material. For the majority of gas/solid contactors the particle flow patterns are such that N lies between the two extremes.

The intrinsic reaction rate of a particle is determined by the slowest step in the physicochemical reaction process and is normally time dependent. The calcination and reduction of ADU in hydrogen is a complex process, taking place via a number of intermediates (Huntington 1958, Le Page & Fane 1973). However at temperatures above 600°C, the reduction reaction is very rapid and approximately linear at high hydrogen concentrations (Le Page & Fane 1973).

Combining linear kinetics with the residence time function for N backmix stages, it is possible to calculate the overall conversion ($\bar{X}_B$) for a given value of N and a given ratio of the time for complete conversion (τ) of a single particle to the mean solids residence time ($\bar{t}$) in the reactor systems (Appendix A). Figure 1 is a plot of $\bar{X}_B$ versus $\bar{t}/\tau$ for different values of N and shows the high conversion readily obtainable with multiple backmix stages. However, high (> 99 per cent) conversion can be obtained with a single stage if the mean residence time is sufficiently long and/or the time for complete conversion sufficiently short. These points are discussed more fully in Section 4.

3. TYPES OF GAS/SOLID CONTACTOR

A wide variety of contactors are available for gas/solids reactions (Walas 1959, Smiley 1961, Lloyd 1963, Taylor & Jenkins 1968). This section describes the salient features of some of them, and includes a review of their application to the conversion of ADU and uranium trioxide (UO_3) to UO_2 as well as the hydrofluorination of UO_2 to uranium tetrafluoride (UF_4), which is also an exothermic and temperature-sensitive reaction.

3.1 The Tray Reactor

The solid reactant is placed in shallow trays which are stacked vertically on a support frame and arranged to provide gas space above each bed. This assembly is then housed in a suitable furnace, usually electrically heated. Reactant gas, often mixed with a diluent, flows across the surface of the powder, the gas throughput being limited by the onset of solids transport. Since the reactant gas has to diffuse into the bed of particles, the bed depth is kept at a minimum. Nevertheless, this type of equipment is very susceptible to 'hot spot' formation, a self-aggravating condition caused by the exothermic nature of the reaction. Other disadvantages are that the unit is not suitable for continuous operation and it involves manual loading and unloading.

The simplicity of batch tray operation commended its use in the original large-scale processes adopted for the production of UO_2 and UF_4 in the United Kingdom (Hinton 1955), the United States (Placek & North 1960) and Canada (Berry 1967). These plants have now been superseded by continuous processes using more sophisticated equipment.

3.2 The Moving Bed Reactor

This type of reactor comprises a vertical tube fed at the top with solids and at the bottom with reactant gas; a typical unit is shown in Figure 2. The bulk density of the bed is typically within 3 to 5 per cent of that in the

stationary bed (Taylor & Jenkins 1968).

Distribution data for solid residence time (Morris, Gubbins & Watkins 1964) indicate essentially plug flow conditions with an equivalence of 100 to 300 backmix stages. Negligible axial diffusion is matched by minor radial diffusion which encourages the formation of high temperature gradients.

The moving bed reactor has been used extensively for the reduction of UO_3 to UO_2 and the hydrofluorination to UF_4. Discussing United States experience, Smiley (1961) described a reduction unit 0.35 m diameter and 5 m long with a throughput of 180 to 230 kg(UO_3) h^{-1}. Heated dissociated ammonia was introduced at the bottom of the reactor and passed up through the bed. Some temperature control was achieved by injecting low temperature steam at various levels up the reactor. In spite of this precaution, the formation of 'hot spots' was a characteristic of the operation and Smiley (1961) reported temperature differences within the bed of 300 to 400 K. To maintain a steady flow of solid particles down the reactor it was found necessary to supply a closely sized feed, which was achieved by pelletising.

Reduction and hydrofluorination have been carried out in moving bed reactors in Canada (Melvanin 1958, Hueston 1960). Temperature control was facilitated by the injection of cold nitrogen, and careful feed preparation was found necessary. A throughput of 70 kg (UO_3) h^{-1} was achieved with an 0.2 m diameter reactor.

Delange *et al* (1964) described French practice, which has concentrated on the use of moving bed reactors in series with stirred bed reactors (Section 3.5) for both reduction and hydrofluorination. Feed preparation is achieved by carefully controlling the size of product from the continuous drying/calcination stage. The reduction gas is provided by cracking ammonia within the reactor. It was claimed that this *in-situ* cracking provides some self regulating temperature control since the dissociation reaction is endothermic.

3.3 The Vibrating Tray Reactor

In this type of reactor, the horizontal axial flow of solid particles is promoted by mechanical oscillation. The basis of the reactor is a horizontal trough or tube mounted on support arms which transmit a vibratory motion from the drive mechanism (Figure 3). Heat may be supplied by a tunnel furnace designed to allow free movement of the reactor tube. Powder supplied at one end passes through the tube as a result of the vibratory motion. Gas flow can be either co-current or counter-current.

The only reported application of vibrating tray reactors for both reduction and hydrofluorination has been in the United States (Harrington & Ruehle 1959). A production unit 5 m long, 0.6 m wide and 0.15 m deep had a reduction capacity of 230 kg(UO_3) h^{-1}. In this application, vibrations were discontinuous, lasting about 15 seconds every 15 minutes; for the remainder of the time the bed was static. Not surprisingly, the gas/solid contact was poor and similar to that described for the tray reactor (Section 3.1). The equipment was prone to local overheating and temperature gradients of approximately 5 K per mm of bed depth were observed (Harrington & Ruehle 1959). The equipment was designed so that it could operate at its resonant frequency, to minimise stresses in the support members and the drive mechanism, and performed well for eight years without mechanical failure.

Continuous vibration is expected to assist gas/solids contacting, and this can be enhanced further by diverting a proportion of the gas upwards through the bed via a porous distribution plate. For a continuously vibrated tray, without gas assistance and designed to have a reasonably constant solids holdup, it was found that the induced flow rate was proportional to the amplitude at the centre of the bed. The distribution of solids residence times was measured by tracer studies which indicated that the reactor was equivalent to between 20 and 60 backmix stages, *i.e.* essentially plug flow conditions. It was found that the introduction of vertical weirs at evenly spaced intervals along the tray resulted in a deterioration of plug flow owing to the formation of large scale eddies (Taylor & Jenkins 1968).

For the gas-permeated vibrated bed, the gas rate had little effect on the solids residence time distribution until a value approaching the minimum fluidisation velocity, U_{mf}. At 90 per cent U_{mf}, the number of backmix stages (N) was found to be 30, and at 110 per cent U_{mf}, N was 1.2 (Taylor & Jenkins 1968).

3.4 The Rotary Kiln Reactor

This type of reactor consists of an externally heated rotating tube, slightly inclined to the horizontal. In a typical unit (Figure 4a) solid material is fed into one end of the tube and gas into the other.

The mode of solids flow in a rotating tube is largely determined by the speed of rotation of the tube (Rutgers 1965a). In all regimes, the flow is predominantly in a plane normal to the axis of the tube, with a small longitudinal component of transport promoted by the angle of the kiln or sloping surface adopted by the contents. This small longitudinal component contributes to the bulk axial flow of material. The various regimes of

radial solid movement are shown in Figure 4b. The most commonly found regime is 'tumbling', in which the bulk material exhibits a kidney-shaped cross section with a slow moving core. This regime occurs typically below 60 per cent of the critical speed, *i.e.* the speed at which all the particles are just centrifuging. It is common practice to attach flights to the kiln wall to promote the showering of particles through the gas stream, thereby enhancing gas/solid contacting. An additional option is the introduction of an exit baffle which increases the solids holdup and thus increases the average residence time.

The factors influencing mean residence time and solids holdup have been investigated by a number of workers (Sullivan, Maier & Ralston 1927, Saeman 1951, Kramers & Croockewit 1952, and Varentsov & Yufa 1961). For lightly loaded rotary kilns having no internal restrictions and operating in the tumbling regime, the mean residence time is commonly estimated using the empirical relationship of Sullivan *et al* (1927):

$$\bar{t} = 0.19L/nD \sin \alpha \qquad \ldots(1)$$

where n is the rate of rotation of a kiln of diameter D, length L and angle of inclination α. Saeman's model of the tumbling regime indicates that the maximum throughput is obtained when the bed depth is equal to the kiln radius. It is also shown that the mean residence time increases with feed rate to the kiln, the influence being greater for long kilns.

The effect of flights attached to the wall of the kiln on the rate of passage of solids has been reviewed by Friedman & Marshall (1949) and Taylor & Jenkins (1968). Solids transport is partly by 'cascade' action (Figure 4b) which is largely determined by gas flow conditions, and partly by 'kiln' action which takes place when the flights become overloaded.

Residence time distribution studies for rotary kilns indicate a tendency for plugflow behaviour. The data of Rutgers (1965b) correspond to 20 backmix stages in a 0.15 m diameter kiln, approximately 0.6 m long, Akerman, Hoffman & Zablotny (1966) gave results equivalent to 10 stages in an industrial unit, and Luoto & Rotkirch (1958) presented data for a cement kiln, equivalent to 5 stages. Analysis of the cascading behaviour of particles in flighted kilns by Saeman & Mitchell (1954) indicated that a bimodal residence time is to be expected. This is substantiated by the results of Smith (1942).

A further flow characteristic of rotary kilns is the tendency for segregation to occur, with the coarser material migrating to the surface

layer (Perry 1950, Lloyd 1963, Rutgers 1965a). Homogeneous treatment thus requires a close control of particle size distribution.

The transfer of heat to or from the solids in a rotary kiln is by direct contact of the layer of solids adjacent to the shell or in contact with the gas. Temperature gradients within the bed of solids are to be expected if there is a stagnant core or if size segregation occurs. The cascade of solids through the gas stream, which is encouraged by internal flights, would improve the interphase heat transfer.

In spite of the limited powder handling and heat transfer characteristics of rotary kilns, they are popular for the conversion of calcined ADU to UO_2. Countries which use or have used rotary kilns include Canada (Berry 1967), France (Delmas & Holder 1963), Germany (Wirths & Ziehl 1958), India (Fareeduddin *et al* 1964), Sweden (Gelin, Mogard & Nelson 1958), and the United States (Caputo & Perry 1961). Typical of these units was that used in France (Delmas & Holder 1963) which had a throughput of 10 kg(UO_2) h^{-1}, and was 0.15 m diameter and 4 m long with a heated length of 1.5 m. Feed to the kiln was ADU calcined at 400°C on a continuous belt drier designed to give a controlled size product. Material produced in the kiln could be sintered to greater than 10.7 g cm^{-3} after 6 hours at 1,650°C, although densities averaged 10.55 g cm^{-3} in a large scale test. Wirths & Ziehl (1958) reported densities of 10.5 g cm^{-3} for ADU derived UO_2, even though green densities of 6.2 g cm^{-3} were obtained and sintering temperatures of 1,750°C were used.

Caputo & Perry (1961) and Fareeduddin *et al* (1964) gave results which indicated that densities greater than 10.6 g cm^{-3} were not readily achieved with their product.

3.5 The Stirred Bed Reactor

This type of contactor comprises a fixed horizontal tube through which solids pass as a result of the rotation of a specially designed stirrer (Figure 5). Solids motion is predominantly radial, with axial transport promoted either by pusher blades or by the helical nature of the stirrer ribbons. Gas/solid contacting is enhanced by the showering of particles through the gas space.

According to Taylor & Jenkins (1968) who reported data for a 50 mm diameter reactor 1.25 m long, the holdup of solids is directly related to the imposed feed rate and strongly influenced by stirrer speed. They also claimed for their equipment that changing from a lifting rotor to a screw-type rotor had little influence on the holdup. For a 0.4 m diameter unit (Smiley 1961), the residence time at a given rotational speed was largely

fixed by the number of pusher blades, although feed rate and powder flow characteristics were also found to have some effect. Unlike the results for the 50 mm reactor, those for the 0.4 m unit showed only a small effect of stirrer speed on residence time.

Taylor & Jenkins (1968) measured the residence time distribution in their equipment and found that it was equivalent to 20 backmix stages. It was independent of rotor speed, fractional solids holdup and gas flow rate.

In a similar sized reactor used for the reduction of UO_3 to UO_2 and the hydrofluorination of UO_2 to UF_4, Taylor & Dell (1966a,b) found that conversion was independent of rotor speed and flow rates up to a critical gas velocity, at which point the conversion deteriorated drastically. This effect was thought to be due to the onset of solids entrainment in the gas stream.

Stirred beds have been criticised for their poor heat transfer characteristics (Lloyd 1963). Experience with the 0.4 m diameter production unit used for the reduction of UO_3 and the hydrofluorination of UO_2 indicated local temperature excursions of approximately 150 K and bed to wall temperature differences of 250 K (Smiley 1961). Reaction rates were found to be six to eight times lower than those found in thermobalance measurements (Briggs 1958). By contrast, Taylor & Dell (1966a) reported results for their 50 mm diameter reactor which showed negligible 'hot spot' formation, and bed to wall temperature differences of 15 to 20 K. Moreover, the reaction rates derived from the stirred bed data were very similar to the thermobalance data. The different performance of the two reactors may be attributed to a number of factors. Firstly, scale of operation militates against the larger unit since the heat transfer surface to volume ratio is lower. In addition, the larger unit employed stirrer speeds of 0.17 rev s^{-1} compared with speeds up to 2 rev s^{-1} for the smaller unit. On the basis of the heat transfer mechanism of Botterill & Williams (1963), discussed in Section 2.1, the heat transfer coefficient would be expected to be significantly higher for higher stirrer speeds.

According to Taylor & Dell (1966b), the bed to wall heat transfer coefficient in the 50 mm reactor was estimated at 230 to 970 W m^{-2} K^{-1} depending on stirrer speed. These figures are somewhat higher than the 30 to 200 W m^{-2} K^{-1} suggested for vacuum-rotary driers (Perry 1950).

An important feature of the stirred bed reactor is that no feed preparation, other than size reduction, is necessary. Stirrer action does not promote classification, as in rotary kilns. However, if friable materials

are to be handled, stirring action may have to be limited to prevent the formation of an excessive amount of fines.

3.6 Fluidised Bed Reactors

Fluidised bed techniques have been widely applied in the petroleum, chemical and nuclear industries. In the conventional form, fluidisation involves the passage of a steady flow of gas up through a bed of particles, at such a rate that the bed expands and bubbles of gas rise through it. A number of refinements of this basic approach have been employed, particularly in the nuclear industry, the most important of which are the tapered bed, the stirred bed and the pulsed bed. Nuclear applications of fluidisation have been reviewed by Alfredson (1967), Lloyd (1963) and Smiley (1961).

3.6.1 The conventional fluidised bed

This method of gas/solid contacting has been the most extensively researched and analysed, and is the subject of a number of text books (Leva 1959, Zenz & Othmer 1960, Davidson & Harrison 1963, 1971, Zabrodsky 1966, Kunii & Levenspiel 1969). The most widely accepted concept is the two-phase theory of fluidisation (Davidson & Harrison 1963) which has been used by Kunii & Levenspiel (1969) as the basis for their bubbling bed model. This model assumes that the gas flow comprises two components, that which passes through the bed at the minimum fluidisation velocity and the remainder which passes through in the form of well defined bubbles. As each bubble rises, it carries with it a wake of solids. Particles close to the bubble path may be drawn into the wake and then discarded. The overall effect is that the axial and lateral dispersion of solids within the bed is high.

The bubbling bed model explains the general properties of conventionally fluidised beds, which are as follows :

- good heat transfer characteristics;
- effective gas/solid contacting; and
- the behaviour of the bed as a well-mixed system.

Residence time studies show that, for the particles fed into a fluidised bed, the body of powder is approximately equivalent to a single backmix reactor (Yagi & Kunii 1961). Accordingly, it would be expected that a continuously operated fluidised bed would not give complete conversion as discussed in Section 2.2. However, tests by Overcashier, Todd & Olney (1959) and Morina *et al* (1970) showed that the introduction of horizontal grid baffles in the bed increased the number of backmix stages, presumably as a result of bubble collapse and consequent dispersal of the upward-moving wake. Other ways of overcoming the well-mixed situation are to use multistage beds

or to minimise bubbling action as in the tapered bed described below. In addition, recent work (Rowe, Nienow & Agbim 1972) indicated that deviations from the well mixed condition readily occur for mixtures of particles of different density. This characteristic is particularly relevant to the direct reduction of ADU to UO_2 which is accompanied by a significant increase in particle density (discussed further in Section 4).

Conventional fluidised beds are used in a number of major commercial uranium hexafluoride (UF_6) production facilities such as the Springfields 'Dryway' process (Rogan 1972) and the Allied Chemical process (Sutton *et al* 1966). In both of these processes, conventional fluidised beds are used for the reduction, hydrofluorination and fluorination steps. At Springfields, the first two steps are carried out on a batch-continuous basis which involves the continuous feeding and conversion of solid material until a specified level is obtained, followed by bulk discharge of most of the bed, leaving a small 'heel' as a basis for the next cycle. Batch-continuous processing, which is readily carried out in fluidised beds, has the advantage that complete conversion of the solid can be obtained, and that a number of consecutive steps can be carried out in the same piece of equipment if desired (an example of this is given in Section 3.6.3). It should be noted that, for both the Springfields and Allied Chemical processes, the feed input to the fluidised bed system is a readily fluidised material, being in the first case UO_3 ex fluid-bed denitration and in the second case pelletised and granulated ore concentrate. Attempts to fluidise ADU powder with a wide range of particle size were not successful (Hawthorn, Shortis & Lloyd 1960). The stirred and pulsed fluidised beds described below were developed to overcome this difficulty.

3.6.2 The tapered fluidised bed

With conventional fluidisation and a deep bed (height to diameter ratio, L/D>4) of dense particles such as uranium compounds, the magnitude of the pressure drop across the bed may result in a significant gradient in superficial velocity. In many cases, the top of the bed may be vigorously fluidised and the bottom quiescent. This can be overcome if the cross section of the bed increases with height, either by tapering the walls of the reactor (Levey *et al* 1960) or more simply by inserting a tapered mandrel into the reactor (Simecek & Trask 1963) - see Figure 6a. Levey *et al* (1960) showed that satisfactory fluidisation can be obtained with an L/D of 14, although a closely sized feed is required. Residence time studies showed that the tapered bed was equivalent to at least 10 backmix stages, the reduction in

axial mixing presumably resulting from the absence of vigorous bubbling.

The Mallinckrodt Co. used tapered-mandrel fluid-bed reactors for pilot plant studies of the continuous production of UO_2 and UF_4 from UO_3 (Simecek & Trask 1963). The reduction reactor was 0.13 m diameter by 1.75 m long with a mandrel 1.35 m long tapering from 73 mm at the bottom to 16 mm at the top. It was found that the fluctuation of bed pressure drop, $\Delta(\Delta P)$, was a useful indication of bed mixing. A $\Delta(\Delta P)$ of 0.6 kPa indicated a low degree of back mixing whereas 3.5 to 7.0 kPa corresponded to a well mixed bed. The feed material was UO_3 ex fluidised bed denitration with a relatively narrow size distribution, more than 60 per cent of the particles being in the -40 +70 mesh range.

3.6.3 The stirred fluidised bed

The stirred fluidised bed (Figure 6b) is suitable for finely divided powders with poor flow properties and also has a greater practical operating range of fluidising velocities than a conventional fluidised bed, since the larger bubbles are broken up by the stirrer. It was developed at the Oak Ridge Gaseous Diffusion Plant to handle a variety of UO_3 and UO_2 powders, some of which tended to cake in a conventional fluidised bed (Brater *et al* 1966).

Agitator design does not appear to be critical as long as the structure is rugged enough to stir the bed and as long as the blade to wall clearances are small. Satisfactory stirring was achieved with a 4-armed agitator rotating at 0.08 rev s^{-1} in a 0.15 m diameter reactor with a 0.75 m bed depth, and a 2-armed agitator rotating at 0.33 rev s^{-1} in a 0.75 m diameter reactor with a 1.83 m bed depth.

In addition to preventing caking, stirrers have been shown to enhance the bed to wall heat transfer coefficients (Botterill & Williams 1963). The effect is caused by the reduced residence time of the particles at the wall brought about by the passage of the stirrer blades. Botterill & Williams (1963) showed that, in a small air-fluidised bed of 200 μm glass ballotini, particle residence time (at the wall) of 0.2 s gave a coefficient of 970 W m^{-2} K^{-1} whilst a 1.0 s residence time gave 285 W m^{-2} K^{-1}. However a time of 0.2 s corresponds to a four-armed stirrer rotating at 1.25 rev s^{-1}, which is considerably greater than that required to prevent caking.

An additional example of the stirred fluidised bed is that described by Hackstein & Pirk (1967) for the production of sinterable UO_2 from ammonium uranyl carbonate. This 0.3 m diameter unit was operated batch-continuously for a number of steps, including calcination, reduction, steam stripping and

high temperature stabilisation.

A disadvantage of mechanical stirring is the difficulty of sealing the agitator shaft; the equipment described by Brater *et al* (1966) required a rather elaborate gland design. A further disadvantage of stirring is that friable materials tend to break up and produce an excessive amount of fines.

3.6.4 The pulsed fluidised bed

Considerable difficulties are encountered in fluidised beds containing a significant portion of very fine particles (less than 50 μm) or when the range of sizes is large (maximum to minimum diameter ratio of 10 to 1). Under these conditions, the gas tends to 'channel' through the bed and the gas/solid contacting is poor. Moreover, since fluidisation velocity is roughly proportional to particle size, the supply of reactant gas to a bed of fine particles may be unfavourably limited. These problems can be overcome by introducing the fluidising medium in a series of pulses, rather than in a continuous stream (Figure 6c).

Pulsing can be achieved by passing the fluidising gas into a pulse chamber through a quick-acting solenoid valve which is activated by a timer. This valve is then closed and an outlet solenoid valve opened allowing the gas to surge through the bed of solids. Under typical conditions (Alfredson & Doig 1970), the pulse produces a slug of gas which lifts the bed as a piston before rising through the bed, followed by a trail of smaller bubbles which tend to produce conventional fluidisation. The bed then collapses to a nearly static condition before the next pulse is introduced.

Bed behaviour is largely determined by pulse frequency and pulsed gas velocity. The latter is a function of the properties of the system such as pulse chamber volume and pressure, design of the gas distributor, and bed height. Bed expansion and pressure fluctuations during pulsed fluidisation have been investigated by Alfredson (1972), Alfredson & Doig (1970), Kobayashi, Ramaswami & Brazelton (1970) and Massimilla, Volpicelli & Raso (1966). Alfredson (1972), Alfredson & Doig (1973a) and Kobayashi *et al* (1970) presented models to predict bed expansion for intermittent pulsed fluidisation based on the two-phase theory of fluidisation. This general approach has also been extended to describe the contraction of the bed when the gas flow is shut off (Alfredson 1972, Alfredson & Doig 1973b).

No residence time studies have been reported for pulsed fluidised beds, although conflicting data are available concerning particle mixing. Kobayashi *et al* (1970) showed that an initially segregated bed of differently sized particles mixed rapidly with a pulsed gas flow but remained partially

segregated with a steady gas flow. On the other hand, Eveson & Richards (1966) claimed that a pulsed gas flow gave improved separation of materials of different density. It is significant that the mixture used by Kobayashi *et al* (1970) had a particle size range of 20 to 1, which would not be expected to give satisfactory conventional fluidisation but could be handled by pulsed fluidisation (Levey 1965). However, in the absence of specific residence time distribution data, it should be assumed that the pulsed bed is equivalent to a single backmix stage.

Heat transfer from a heater immersed in a pulsed fluidised bed has been shown to be higher under a variety of pulsing conditions than for conventional fluidisation (Bokun & Zabrodsky 1966, Zabrodsky & Bokun 1966, Alfredson & Doig 1970, Kobayashi *et al* 1970, Alfredson 1972). For example, in a 0.15 m diameter reactor with a bed of fine iron powder pulsed at a frequency of 1 Hz, pulsed fluidisation gave approximately 20 per cent improvement in heat transfer compared with conventional fluidisation for the same time-averaged gas flow rate (Alfredson & Doig 1970).

The applications of pulsed fluidisation have been summarised by Alfredson (1972), Alfredson & Doig (1970) and Kobayashi (1969). Examples include the batch reduction of ADU and hydrofluorination of UO_2 in a 0.13 m diameter reactor, with particle sizes in the range 1 to 500 μm (Levey 1965, Heidt, Levey & Hamrin 1966). Canadian workers have developed a 0.15 m diameter reactor for the continuous calcination and reduction of ADU (Alfredson & Doig 1970, Alfredson 1972).

4. DISCUSSION

The selection of the most suitable type of gas/solid contactor for the calcination and reduction of ADU involves the comparison of a number of qualitative characteristics. As discussed in Section 2, the most important factors are the heat transfer characteristics, the degree of solids conversion and the powder handling properties of the equipment. Table 1 lists these characteristics and includes a comment on the mechanical complexity of the contactors described earlier, excluding the tray reactor which is suitable only for batch operation.

No contactor represents the 'ideal' reactor. Firstly, the requirement for good heat transfer characteristics, which calls for effective radial diffusion, conflicts with the need for a high degree of solids conversion, which is promoted by low axial diffusion. The stirred bed reactor appears to offer a means of overcoming the conflict, at least at small diameters, and the tapered fluidised bed also represents a compromise, maintaining some of

the heat transfer characteristics of the conventional fluidised bed, whilst reducing the solids backmixing which may lead to incomplete conversion.

Secondly, the majority of contactors are limited in the type and condition of solid they can handle, whereas ADU is a difficult material which is friable and readily produces fines. The only contactors suited to accepting a feed of ADU powder and not requiring a separate calcination stage and/or varying degrees of particle size control are the stirred fluidised bed and the pulsed fluidised bed. Of these two, the stirred fluidised bed is less suitable since the stirring action must be restricted to minimise the production of an excessive amount of fines.

The rotary kiln, stirred bed and stirred fluidised bed all require elaborate bearing or gland designs when handling flammable, toxic or corrosive gases. The vibrating tray is mechanically complex and must be designed to operate at the system frequency. The moving bed, conventional, tapered and pulsed fluidised beds are all relatively simple, although the pulse generator for the latter will probably require regular maintenance.

The only apparent limitation of the various fluidised bed systems, apart from the tapered bed, is that with continuous operation complete conversion of the solids may not be achieved, because the bed may only be equivalent to a single backmix stage.

The conservative nature of this assumption in the context of ADU calcination and reduction can be appreciated by considering the effect of density changes which occur during the process. Thus the ratio of tap densities, ADU to UO_2, is about 1 to 1.5, and a similar ratio is expected for the effective particle densities. From the data of Rowe *et al* (1972), a density ratio of this magnitude would be expected to lead to segregation within the bed, the lighter component concentrating at the top. Density increases resulting from calcination and reduction would gradually encourage the material to enter the well-mixed bulk of the bed. An overhead feed and bottom withdrawal system would take advantage of this situation.

However it can be readily shown that for a relatively fast reaction the limitation of a single backmix stage is not severe. Thus in a thermobalance the reduction of calcined ADU (that is, U_3O_8) at about 650°C with 100 per cent hydrogen is completed in approximately 10 s (Le Page & Fane 1973). With 20 to 25 per cent hydrogen, a conversion time of 40 to 50 s would be expected, on the assumption that the reaction rate is proportional to hydrogen concentration (Le Page & Fane 1973). Calculations (Le Page, AAEC unpublished work) indicate that a typical particle would heat up in about 10 s from introduction

into the bed and that the time for calcination would be of the same order as the time for reduction. Thus the total conversion time, τ, for a single particle would be in the range 60 to 120 s. On the assumption that a particle mean residence time, $\bar{t}$, of 1 h is practicable and that linear kinetics prevail, the overall conversion can be estimated from Figure 1 and is found to be in the range 98.4 to 99.2 per cent. A mean residence time of 1 h would correspond to a throughput of 10 to 12 kg(UO_2) h^{-1} in a 0.13 m diameter reactor, or approximately 150 kg(UO_2) h^{-1} (1,000 t y^{-1}) in a 0.3 m diameter reactor.

The foregoing analysis shows that a pulsed fluidised bed reactor has good heat transfer and powder handling characteristics, is relatively simple mechanically and can be expected to give high conversions of ADU to UO_2 with a reasonable throughput.

Table 2 compares estimated performance data for the pulsed fluidised bed with data for some other types of contactor used for the production of UO_2.

The moving bed reactor has a high capacity, presumably because its effective volume is 100 per cent, and makes efficient use of the gaseous reactant. However it has the disadvantage that feed preparation is required and that radial temperature gradients would be expected. It is claimed (Delange *et al* 1964) that by cracking the reductant NH_3 *in situ* some temperature regulation is possible.

In spite of its popularity, the rotary kiln reactor is not particularly suited to the production of ceramic grade UO_2 from ADU. In general, separate reactors are required for calcination and reduction, and these operate with a rather large ΔT within the reactor and a relatively low capacity.

The stirred bed reactor developed by Taylor & Dell (1966a,b) has promising performance characteristics although it is not clear how it would handle a friable material like ADU. A similar piece of equipment seems to have been used by Smith *et al* (1964) for the production of $(Pu,U)O_2$ powders suitable for sintering. However the larger diameter stirred bed described by Smiley (1961) suffered from excessive temperature gradients, which may be a result of the scale of operation.

The data for the conventional fluidised bed, with a UO_3 feed, show the effect of using two stages and of scaleup. Reactor capacities compare well with those for other reactors, and temperature effects are small.

The pulsed fluidised bed compares favourably with other types of contactor with regard to capacity, temperature uniformity and hydrogen usage.

Coupled with an ability to handle difficult powders, this suggests that the pulsed fluidised bed reactor is particularly well suited for the production of UO_2 from ADU.

5. CONCLUSIONS

The calcination and reduction of ADU to give sinterable UO_2 ideally requires a gas/solid contactor with good heat transfer characteristics, the ability to handle a friable powder with a wide particle size distribution, and a high conversion consistent with continuous operation. A pulsed fluidised bed reactor would satisfy these requirements, and should give a conversion typically in the range 98.4 to 99.2 per cent for a throughput of 10 to 12 kg(UO_2) h^{-1} in a 0.13 m diameter reactor.

6. ACKNOWLEDGEMENTS

The author wishes to thank Dr. P.G. Alfredson, who initiated the AAEC investigation of the pulsed fluidised bed reactor for the conversion of ADU to UO_2, for useful discussions during the preparation of this report. He would also like to thanks Messrs. H. Salvador and B. Vertucia (Manila Electric Co.Phillippines) who assisted in the preparation of a preliminary report.

7. REFERENCES

Alfredson, P.G. (1967) - The Applications of Fluidised Bed Processes in Nuclear Chemical Engineering, paper presented at Fluidisation Symposium, 16-18 Sept. 1967, Monash University.

Alfredson, P.G. (1969) - AAEC/TM514.

Alfredson, P.G. (1972) - Ph.D. thesis, University of New South Wales.

Alfredson, P.G. & Doig, I.D. (1970) - I. Chem. E. Symp. Series, No.33, Chemeca '70, Session I, p 117.

Alfredson, P.G. & Doig, I.D. (1973a) - Trans. Instn. Chem. Engrs. 51, Part I, p 232.

Alfredson P.G. & Doig, I.D. (1973b) - Trans. Instn. Chem. Engrs. 51, Part II, p 242.

Alfredson, P.G. & Janov, J. (1971) - AAEC/TM599.

Akerman, K., Hoffman, P. & Zablotny, W. (1966) - Brit. Chem. Eng. 11 (1), 26.

Baddour, R.F. & Yoon, C.Y. (1961) - Chem. Eng. Prog. Symp. Series, 57 (32), 35.

Berry, R.M. (1967) - Can. Nucl. Tech. 6 (2), 30.

Bokun, I.A. & Zabrodsky, S.S. (1966) - Investigation of Heat and Mass Transfer in Technological Processes and Apparatus, Minsk : Nauka : Tekhnika, p 27. (Translation USAEC Report ANL-TRANS-592, tr. E.K. Wilip.)

Botterill, J.S.M. & Williams, J.R. (1963) - Trans. Instn. Chem. Engrs. 41, 217.

Brater, D.C., Castro, D.L., Dean, L.A., Pashley, J.H. & Smiley, S.H. (1966) - Chem. Eng. Prog. Symp. Series, 62 (65), 1.

Briggs, G.G. (1958) - USAEC Report NLCO-720.

Caputo, A.J. & Perry, J.E. (1961) - USAEC Report Y-1301.

Davidson, J.F. & Harrison, D. (1963) - Fluidised Particles. Cambridge University Press, Cambridge.

Davidson, J.F. & Harrison, D. (1971) - Fluidisation. Academic Press, London and N.Y.

Deissler, R.G. & Boegli, J.S. (1958) - Trans. ASME. 80, 1417.

Delange, M., Falcoz-vigne, R., LeRoy, C. & Tachon, O. (1964) - Bulletin d'Informations Scientifiques et Techniques. 80, 11. (Translation AAEC LIB/TRANS 176, tr. Mary Ritchie.)

Delmas, R. & Holder, J. (1963) - New Nuclear Materials, including Non-Metallic Fuels. 1, 95. IAEA Vienna (Translation AAEC LIB/TRANS 189, tr. M.A. Hinze.)

Eveson, G.F. & Richards, G.T. (1966) - US Patent 3,288,282.

Fareeduddin, S., Garg, R.K., Gupta, U.C., Kantan, S.K., Rajendran, R., Rao, N.K., Sinha, K.K., Somayajulu, G.V.S.R.K. & Subramanian, K. (1964) - Proc. 3rd Int. Conf. on Peaceful Uses of Atomic Energy. 11, 345.

Friedman, S.J. & Marshall, W.R. (1949) - Chem. Eng. Prog. 45 (8), 482.

Gelin, R., Mogard, H. & Nelson, B. (1958) - Proc. 2nd Int. Conf. on Peaceful Uses of Atomic Energy. 4, 36.

Hackstein, K.G. & Pirk, H. (1967) - Kerntechnik. 9, 261. (Translation UKAEA report, Risley Trans. 1540).

Harrington, C.O. & Ruehle, A.E. (1959) - Uranium Production Technology. D. Van Nostrand Company, Inc., Princeton, N.J.

Hawthorn, E., Shortis, L.P. & Lloyd, J.E. (1960) - Trans. Inst. Chem. Engrs. 38 (4), 197.

Heidt, H.M., Levey, R.P. & Hamrin, C.E. (1966) - Chem. Eng. Prog. Symp. Series, 62 (65), 43.

Hinton, C. (1955) - Trans. Instn. Chem. Engrs. 33, 45.

Hueston, F.H. (1960)- Can. J. Chem. Eng. 38, 29.

Huntington, C.W. (1958) - USAEC Report NLCO 775.

Kobayashi, M. (1969) - USAEC Report ANL-7592

Kobayashi, M., Ramaswami, D. & Brazelton, W.T. (1970) - Chem. Eng. Prog. Symp. Series, 66 (105), 47.

Kramers, H. & Croockewit, P. (1952) - Chem. Eng. Sci. 1 (6), 259.

Kunii, D. & Levenspiel, O. (1969) - J. Wiley & Sons, Inc. New York.

Le Page, A.H. & Fane, A.G. (1974) - J. Inorg. Nucl. Chem. 36, 87.

Leva, M. (1959) - Fluidization. McGraw-Hill Book Co., New York.

Levey, R.P. (1965) - US Patent 3,164,440.

Levey, R.P., De La Garza, A., Jacobs, S.C. Heidt, H.M. & Trent, P.E. (1960) - Chem. Eng. Prog. 56 (3), 43.

Lloyd, J.E. (1963) - Progress in Nuclear Energy, Series IV, vol.5, 371.

Luoto, U.A. & Rotkirch, E.G. (1958) - Proc. 2nd Int. Conf. on Peaceful Uses of Atomic Energy. 19, 31.

Massimilla, L., Volpicelli, G. & Raso, G. (1966) - Chem. Eng. Prog. Symp. Series, 62 (62), 63.

Melvanin, F.W. (1958) - Proc. 2nd Int. Conf. On Peaceful Uses of Atomic Energy. 4, 133.

Mickley, H.S., Fairbanks, D.F. & Hawthorn, R.D. (1961) - Chem. Eng. Prog. Symp. Series. 57 (32), 51.

Morina, I.M., Chernysheva, R.K., Gazanchiyants, M.G. & Martyushin, I.G. (1970) - Int. Chem. Eng. 10 (1), 27.

Morris, D.R., Gubbins, K.E. & Watkins, S.B. (1964) - Trans. Instn. Chem. Engrs. 42, 328.

Overcashier, R.H., Todd, D.B. & Olney, R.B. (1959) - A.I.Ch.E. Journal 5 (1), 54.

Perry, J.H. (1950) - Chemical Engineers Handbook, 3rd ed. McGraw-Hill Book Co., New York.

Placek, G. & North, E.D. (1960) - Ind. Eng. Chem. 52 (6), 458.

Rogan, H. (1972) - Production Scale Processes and Plants in the United Kingdom - The Conversion of Uranium Ore Concentrates to Nuclear Grade Uranium Hexafluoride and to Enriched Uranium Dioxide. Paper presented to IAEA Study Group Meeting on the Facilities and Technology needed for Nuclear Fuel Manufacture, 4-15 Sept., Grenoble.

Rowe, P.N., Nienow, A.W. & Agbim, A.J. (1972) - Trans. Instn. Chem. Engrs. 50, 324.

Rutgers, R. (1965a)- Chem. Eng. Sci. 20, 1079.

Rutgers, R. (1965b) - Chem. Eng. Sci. 20, 1089.

Saeman, W.C. (1951) - Chem. Eng. Prog. 47 (10), 508.

Saeman, W.C. & Mitchell, T.R. (1954) - Chem. Eng. Prog. 50 (9), 467.

Simecek, S. & Trask, W.T. (1963) - USAEC Report MCW-1478.

Smiley, S. H. (1961) - Progress in Nuclear Energy, Series IV, vol.4. 191.

Smiley, S.H. & Brater, D.C. (1958a) - Proc. 2nd Int. Conf. on Peaceful Uses of Atomic Energy. 4, 153.

Smiley, S.H. & Brater, D.C. (1958b) - Progress in Nuclear Energy, Series III, vol.2, p 114.

Smith, B.A. (1942) - Trans. Amer. Inst. Chem. Engrs. 38, 251.

Smith, S.E., Broadley, J.S., Brown, F. & Kent, W.C.L. (1964) - Proc. 3rd Int. Conf. on Peaceful Uses of Atomic Energy. 10, 161.

Sullivan, J.D., Maier, C.G. & Ralston, O.C. (1927) - Tech. Papers, Bureau of Mines. Washington. No.384.

Sutton, A.H., Bishop, J.C., Cohen, M.H. & Stahman, K.J. (1966) - Chem. Eng. Prog. Symp. Series. 62 (65), 20.

Taylor, R.F. & Dell, F.R. (1966a) - Trans. Instn. Chem. Engrs. 44 (3), T97.

Taylor, R.F. & Dell, F.R. (1966b) - Trans. Instn. Chem. Engrs. 44 (4), T105.

Taylor R.F. & Jenkins, T.R. (1968) - I. Chem. E. Symp. Series. No.27, 101.

Varentsov, P.V. & Yufa, M.S. (1961) - Int. Chem. Eng. 1, 88.

Walas, S.M. (1959) - Reaction Kinetics for Chemical Engineers. McGraw-Hill Book Co., New York.

Wirths, G. & Ziehl, L. (1958) - Proc. 2nd Int. Conf. on Peaceful Uses of Atomic Energy. 4, 16.

Yagi, S. & Kunii, D. (1961) - Chem. Eng. Sci. 16, 364.

Zabrodsky, S.S. (1966) - Hydrodynamics and Heat Transfer in Fluidized Beds. (tr. F.A. Zenz.) MIT Press, Cambridge.

Zabrodsky, S.S. & Bokun, I.A. (1966) - Investigation of Heat and Mass Transfer in Technological Processes and Apparatus. Minsk : Nauka : Tekhnika, p 135. (Translation USAEC Report ANL-TRANS 593, tr. E.K. Wilip.)

Zenz, F.A. & Othmer, D.F. (1960) - Fluidization. Reinhold Publications Inc. New York.

TABLE 1

QUALITATIVE CHARACTERISTICS OF SOME GAS/SOLID CONTACTORS

Contactor	Heat Transfer	Solids Conversion	Feed Material	Mechanical Complexity
Moving bed	Poor, radial temperature gradient expected.	High (plug flow of solids).	Narrow size distribution, normally pelletised. Not friable.	Relatively simple, although flow inducers may be necessary.
Vibrating tray	Poor, local overheating possible	High (plug flow of solids), unless entrainment occurs.	Narrow size distribution.	Mechanically complex. Must operate at system resonant frequency.
Rotary kiln	Poor, local overheating possible	High (plug flow of solids), unless entrainment occurs.	Narrow size distribution	Gland required to seal ends of kiln.
Stirred bed	Good for small diameter. Poor for large diameter (should be enhanced by more vigorous stirring).	High (plug flow of solids), unless entrainment occurs.	Friable powders not well suited.	Gland required to seal agitator shaft.
Conventional fluidised bed	Good (enhanced by radial diffusion of solids).	Poor, unless reaction is rapid (bed approximates to single backmix stage), or mean residence time is sufficiently long.	Restricted size distribution. Not suitable for fine powders.	Mechanically simple. No moving parts. No sealing problems.
Tapered fluidised bed	Less than conventionally fluidised bed (reduced radial diffusion of solids).	Good (bed approximates to a number of stages in series).	Narrow size distribution. Not suitable for fine powders.	Mechanically simple. No moving parts. No sealing problems.
Stirred fluidised bed	Good (should be enhanced by stirring).	Poor, unless reaction is rapid or mean residence time is sufficiently long.	Suitable for fine powders. Less suitable for friable powders.	Gland required to seal agitator shaft.
Pulsed fluidised bed	Good (may be better than conventional fluidised bed).	Poor, unless reaction is rapid or mean residence time is sufficiently long.	Suitable for wide size distribution, high fines content, and friable powders.	Relatively simple. Pulse generator will require maintenance.

TABLE 2

A COMPARISON OF THE PERFORMANCE OF SOME CONTACTORS USED FOR THE PRODUCTION OF UO_2

Contactor	Diameter (m)	Feed Material	Throughput ($kg(UO_2)\ h^{-1}$)	Capacity ($kg\ h^{-1}m^{-3}$)	ΔT, Wall to Bed (K)	Stoichiometric Hydrogen (x theoretical)	Reference
Moving bed	0.15	UO_3 (ADU calcined at about 400°C) as flakes 1 to 2 cm thick.	19.5	340	-	1.15	Delange *et al* (1964)
Rotary kiln	0.15	UO_3 (ADU calcined at 380-400°C)	10	78	-	~ 2	Delmas & Holder (1963)
	0.15	UO_3/U_3O_8 (ADU calcined at 450-500°C)	2.3	-	80	>10	Caputo & Perry (1961)
Stirred bed	0.05	Hydrated UO_3 (ex fluid bed denitration)	2.5	390	<20	2	Taylor & Dell (1966a)
	0.40	UO_3 (pot denitration)	230	115	300		Smiley (1961)
Conventional fluidised bed							
(a) 1 stage	0.15	UO_3 (ex pot denitration)	~ 7	~ 270	-	-	Smiley (1961)
(b) 2 stage	0.15	UO_3 (ex pot denitration)	~ 20	~ 390	-	-	
	0.34	UO_3 (ex pot denitration)	~450	~ 390	<15	1.5	
Pulsed fluidised bed	0.13	ADU (oven dried)	12 *	230	-	~ 2	This report
	0.3		150 *	230	-	~ 2	

* *Estimated continuous operation.*

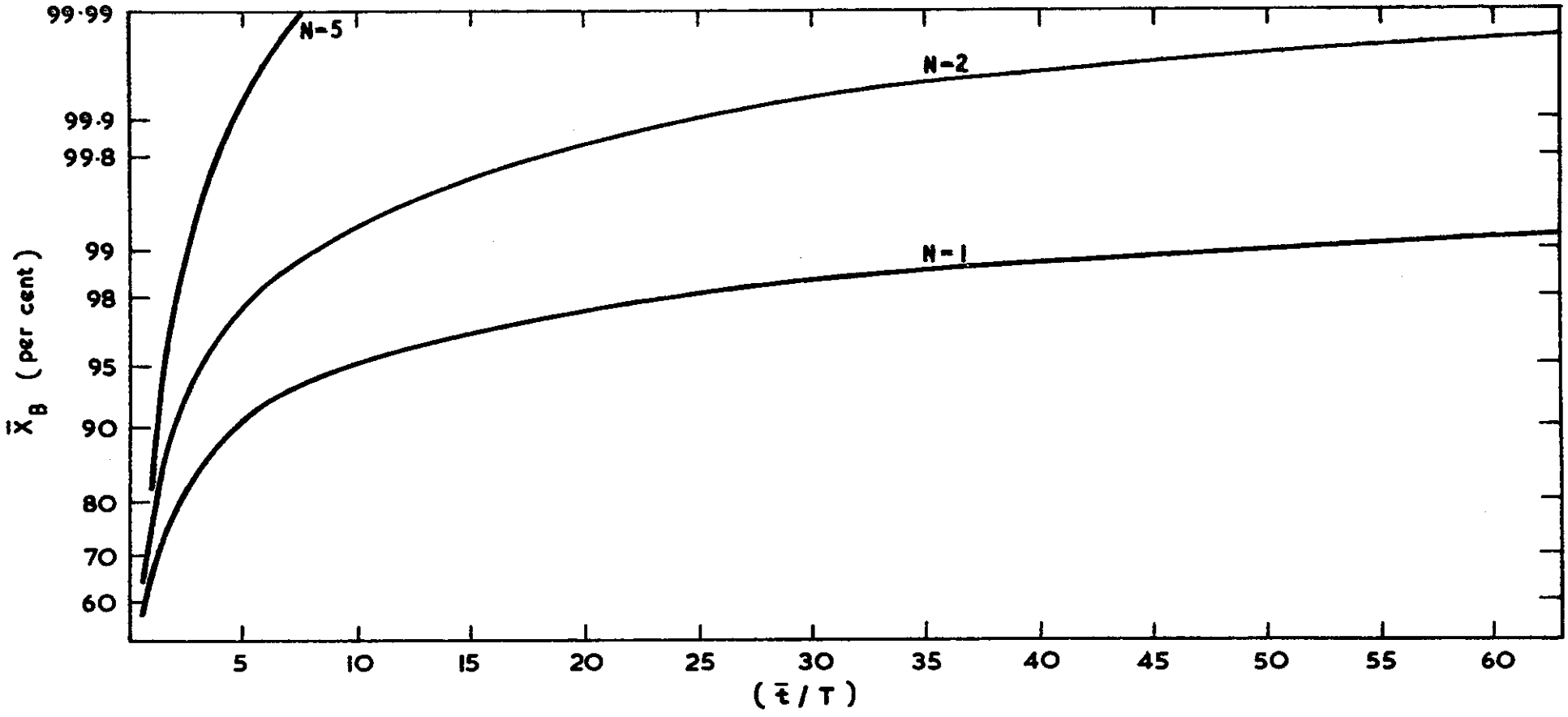

FIGURE 1. MEAN CONVERSION ($\bar{X}_B$) VERSUS RESIDENCE TIME PARAMETER ($\bar{t}/\tau$) FOR N BACKMIX STAGES IN SERIES AND ZERO ORDER KINETICS

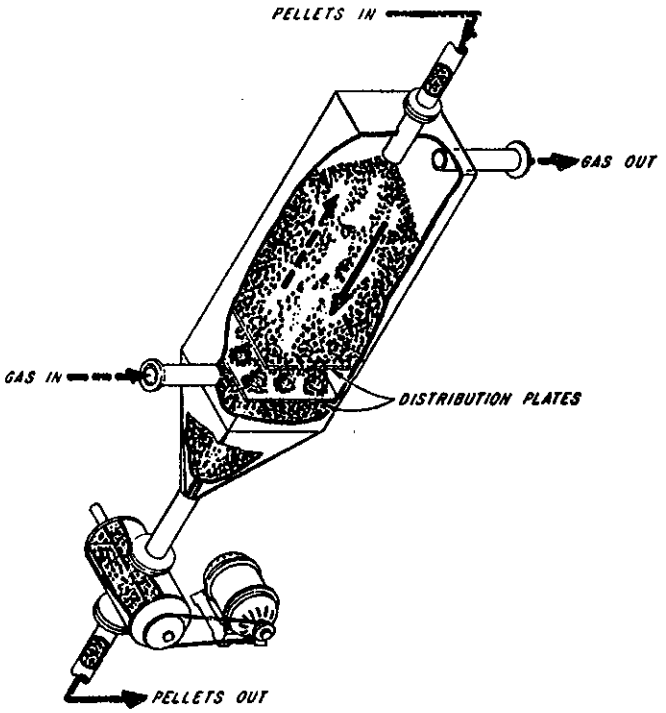

FIGURE 2. THE MOVING BED REACTOR
(after Smiley & Brater 1958b)

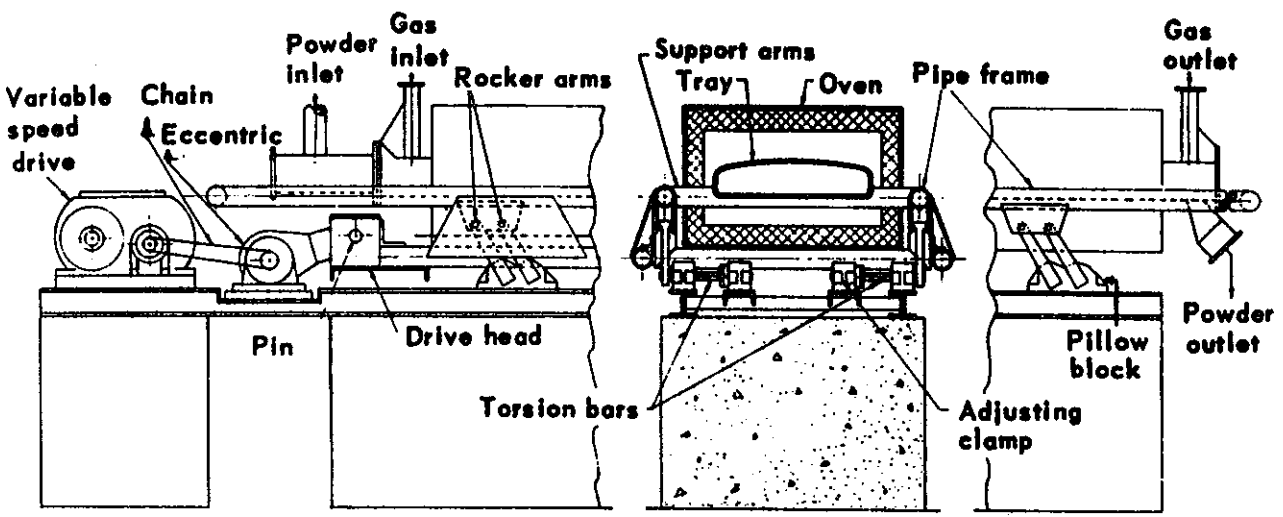

FIGURE 3. THE VIBRATING TRAY REACTOR
(after Smiley & Brater 1958a)

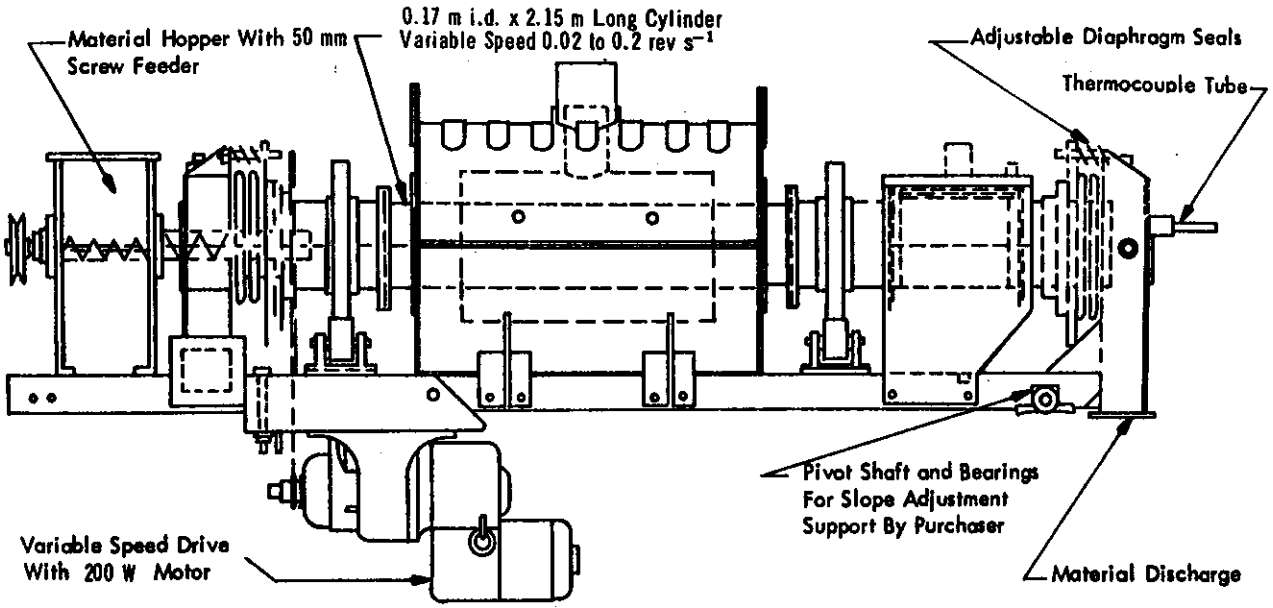

FIGURE 4a. THE ROTARY KILN REACTOR
(after Caputo & Perry 1961)

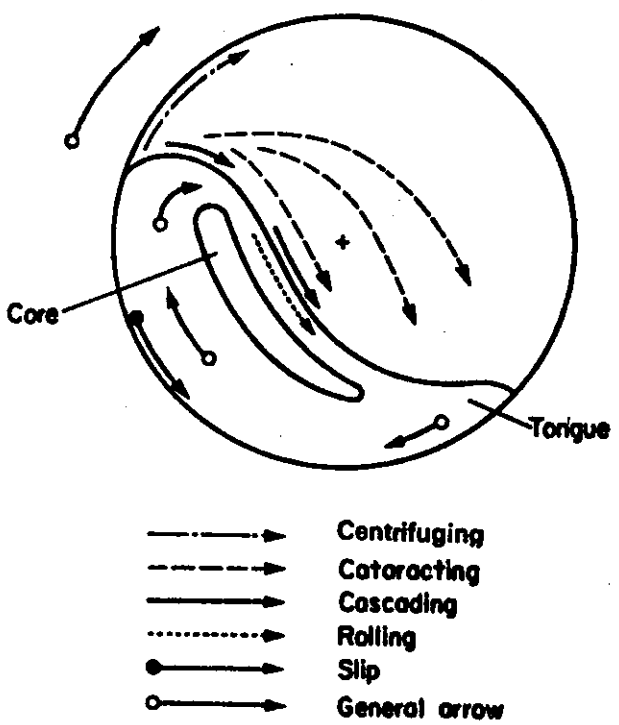

FIGURE 4b. REGIMES OF SOLIDS MOVEMENT IN A ROTARY KILN REACTOR (after Rutgers 1965a)

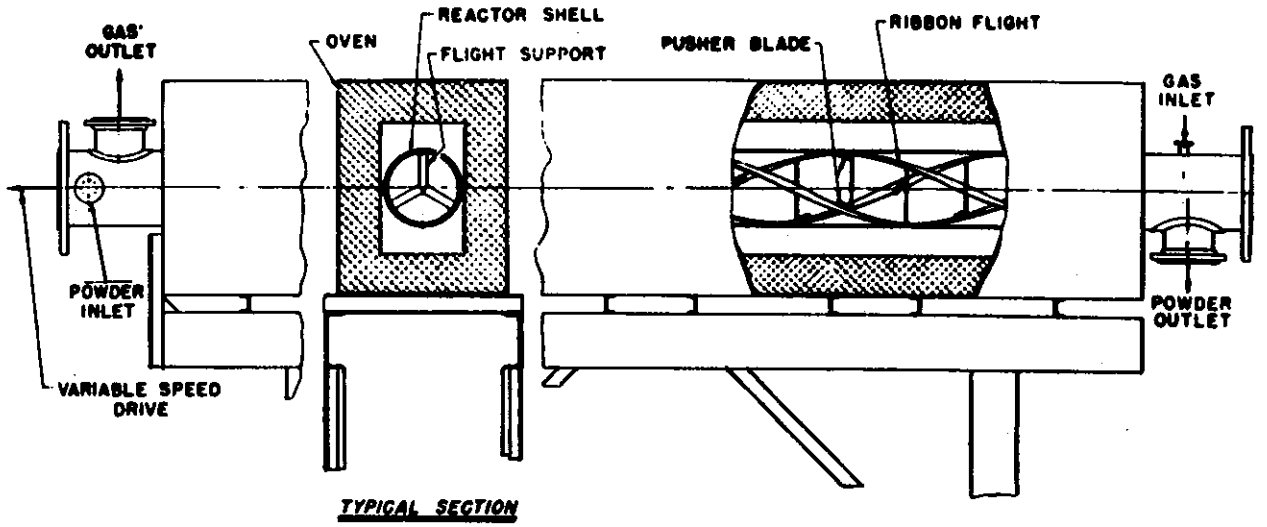

FIGURE 5. THE STIRRED BED REACTOR (after Smiley & Brater 1958a)

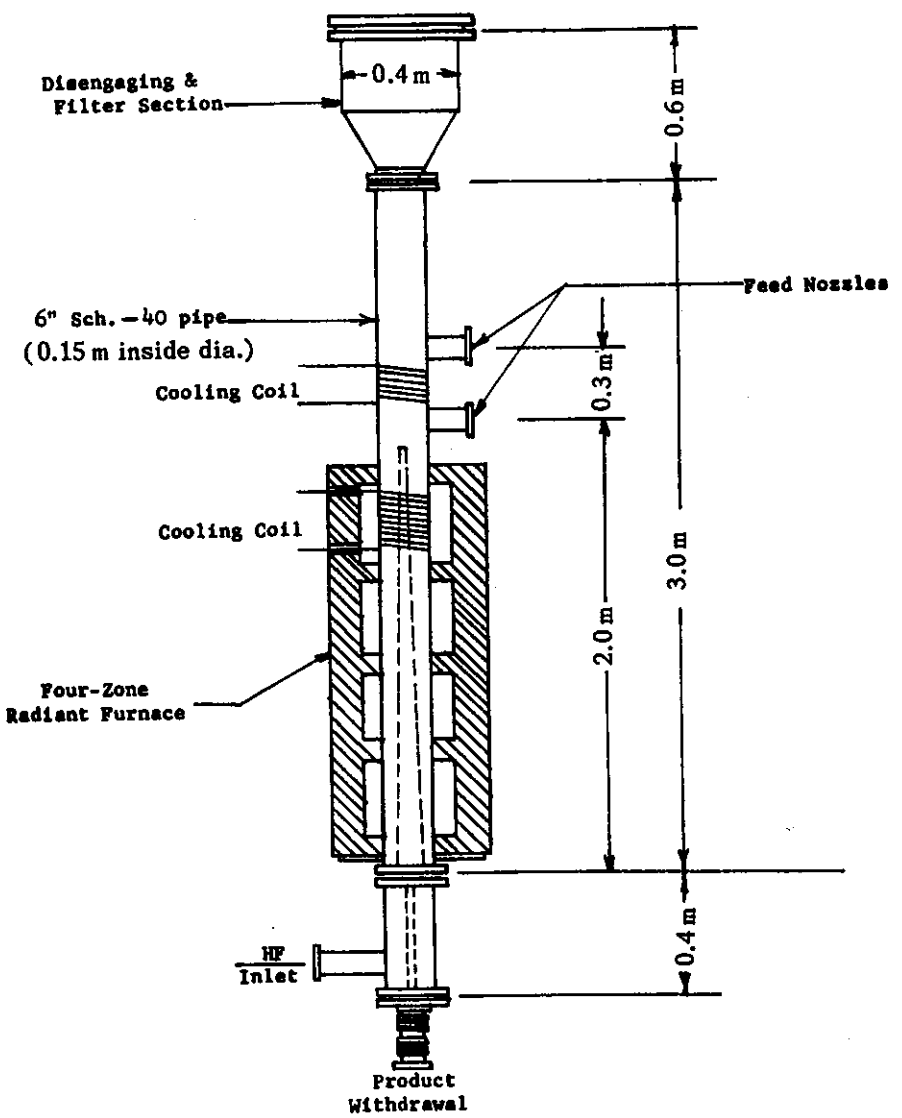

FIGURE 6a. THE TAPERED BED (after Simecek & Trask 1963)

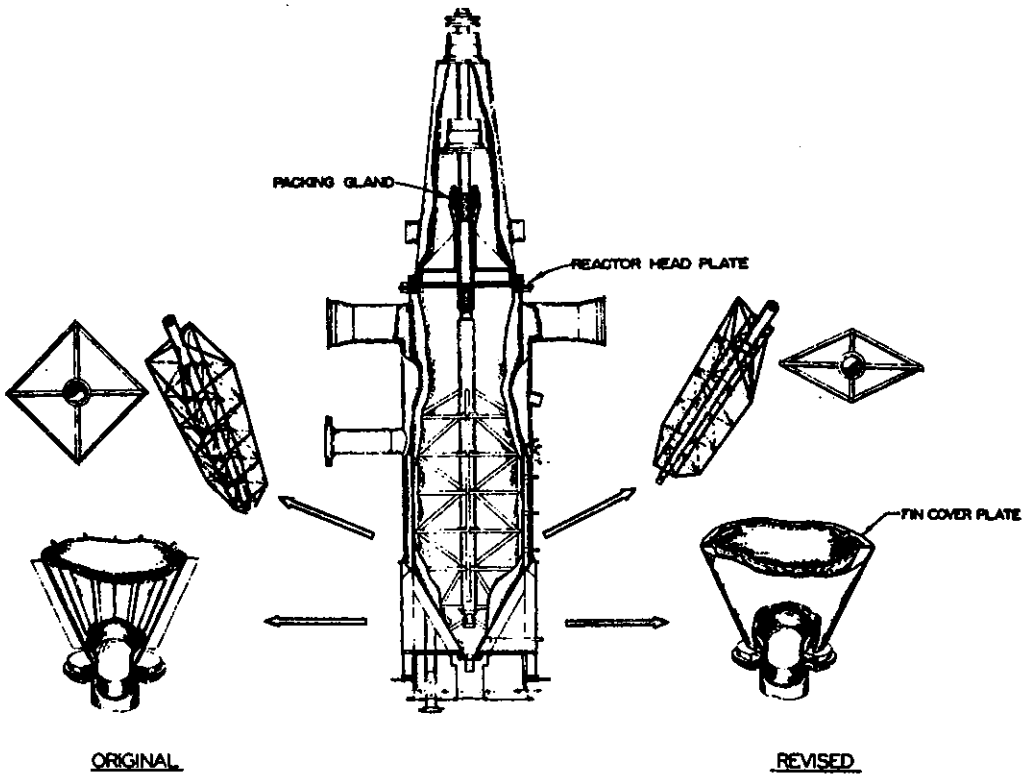

FIGURE 6b. THE STIRRED FLUIDISED BED (after Brater et al. 1966)

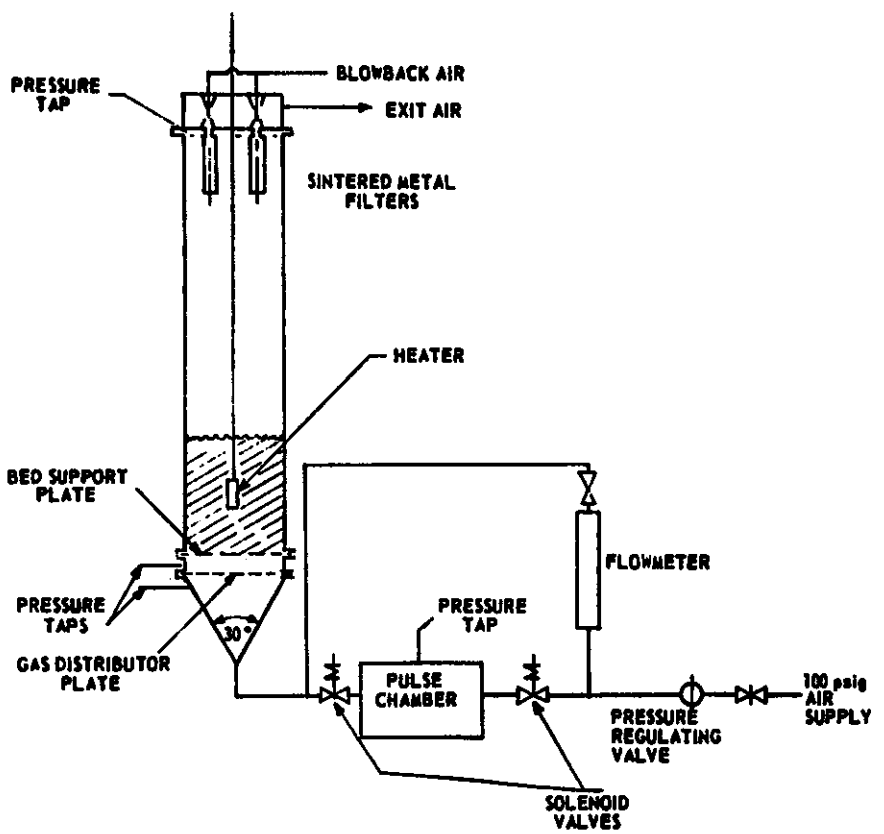

FIGURE 6c. THE PULSED FLUIDISED BED (after Alfredson & Doig 1970)

APPENDIX A

CONVERSION OF THE SOLID PHASE BY GAS/SOLID REACTION IN A REACTOR COMPRISING N BACKMIX STAGES IN SERIES AND ZERO ORDER KINETICS

For a zero order reaction, thermobalance data gives steady weight loss, *i.e.*

$$\frac{dW}{dt} = -k_1 \quad .$$

For the reaction, solid A → solid B (gas phase in excess)

$$\frac{dX_B}{dt} = k_2 \quad .$$

Thus,

$$1-X_B = 1-t/\tau, \quad t \leqslant \tau \qquad \ldots(A1)$$

where τ is the time for complete conversion.

Equation (A1) shows how the conversion, X_B, of reactant in a single particle depends on its residence time in the reaction zone.

For a reactor comprising one or more backmix stages in series the residence time in the reaction zone varies from particle to particle, *i.e.* there is a distribution of residence times. The overall conversion $\bar{X}_B$ can be found from:

$$1-\bar{X}_B = \int_0^{\tau} (1-X_B)E(t)\, dt \qquad \ldots(A2)$$

where E(t) is the exit age distribution of the solids leaving the reactor, *i.e.* the fraction of the exit stream which has stayed in the reactor for a time between t and t + dt.

For N equal-sized backmix stages in series, the age distribution is:

$$E(t) = \frac{1}{(N-1)!\ \bar{t}_i} \left(\frac{t}{\bar{t}_i}\right)^{N-1} e^{-t/\bar{t}_i} \qquad \ldots(A3)$$

where $\bar{t}_i$ is the mean residence time in each stage (Kunii & Levenspiel 1969, p 492),

i.e. $\bar{t}_i$ = volumetric holdup per stage/volumetric throughput.

Putting Equations (A1) and (A3) in Equation (A2) and rearranging gives:

$$1-\bar{X}_B = \frac{1}{(N-1)!\,(t_i)^N} \left\{ \int_{t=0}^{t=\tau} t^{N-1}\, e^{-t/\bar{t}_i}\, dt - \frac{1}{\tau} \int_{t=0}^{t=\tau} t^N\, e^{-t/\bar{t}_i}\, dt \right\}$$

$$\ldots(A4)$$

In general

$$\int x^n e^{ax}\, dx = \frac{e^{ax}}{a} \sum_{m=0}^{m=n} \frac{(-1)^m n! x^{n-m}}{(n-m)!\, a^m} \quad .$$

Thus Equation (A4) gives

$$\bar{X}_B = \frac{N}{\gamma} - e^{-\gamma} \left\{ \sum_{m=0}^{m=N} \frac{N}{(N-m)!} \gamma^{N-m-1} - \sum_{m=0}^{m=N-1} \frac{1}{(N-m-1)!} \gamma^{N-m-1} \right\} \quad \ldots (A5)$$

where $\gamma = \tau/\bar{t}_i$.

For total residence time equal to $\bar{t}$ and $\bar{t}_i = \bar{t}/N$

$$\gamma = \tau N/\bar{t} = \beta N \quad i.e. \quad \beta = \tau/\bar{t}$$

The final form of Equation (A5), after further simplification is,

$$\text{Conversion } \bar{X}_B = \frac{1}{\beta} - e^{-\beta N} \left\{ \frac{1}{\beta} + \sum_{m=0}^{m=N-1} \frac{m(N\beta)^{N-m-1}}{(N-m)!} \right\} \quad \ldots (A6)$$

This gives the mean conversion of solids passing through a reactor of N backmix stages in series, for zero order kinetics. The parameter β is the ratio of the time for complete conversion of a single particle to the mean solids residence time in the reactor system. Some of the computations from Equation (A6) are shown in Figure 1.