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AUSTRALIAN ATOMIC ENERGY COMMISSION

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PART III CONTINUOUS PRODUCTION IN A PULSED FLUIDISED BED REACTOR

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February 1975

ISBN 0 642 99676 8

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ABSTRACT

The development of a 0.13 m diameter pulsed fluidised bed reactor for the continuous production of sinterable uranium dioxide from ammonium diuranate is described. Calcination–reduction at 670 to 680°C produced powders with surface areas of 4 to 6 $m^2\ g^{-1}$ giving pellet densities in excess of 10.6 $g\ cm^{-3}$.

Sinterability was relatively insensitive to changes in operating conditions, provided the availability of hydrogen was adequate, for gas flow rates in the range 0.95 to 1.4 $\ell\ s^{-1}$, pulse frequencies of 0.5 and 0.75 Hz and mean residence times of the solids from 0.6 to 1.4 hours. Sinterability was shown to be improved either by use of higher input concentrations, or by use of a secondary flow of hydrogen (about 5 per cent of input) fed into the powder collection system and flowing countercurrent to the UO_2 product. The maximum throughput of 17 kg $UO_2\ h^{-1}$ (0.6 hours mean residence time) required only 120 per cent of the stoichiometric requirement at an input concentration of 50 vol.% with secondary hydrogen flow.

Results are given for studies of the kinetics of reduction of calcined ammonium diuranate in hydrogen and the residence time distribution of solids in a pulsed fluidised bed. Estimates based on these data suggested that the overall conversion of ammonium diuranate to uranium dioxide in the continuously operated pulsed fluidised bed reactor was in excess of 99 per cent.

Continuous stabilisation of the UO_2 product was demonstrated at 12 kg h^{-1} of UO_2, in a 0.15 m diameter glass stabiliser, using 10 vol.% air in nitrogen and a temperature of about 50°C.

National Library of Australia card number and ISBN 0 642 99676 8

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ADU; CALCINATION; CHEMICAL REACTION KINETICS; FLUIDIZED BED REACTORS; FUEL PELLETS; POWDERS; PRODUCTION; REDUCTION; SINTERED MATERIALS; SINTERING; URANIUM DIOXIDE; VERY HIGH TEMPERATURE

CONTENTS

1. INTRODUCTION

In the first report in this series (Fane 1974), the pulsed fluidised bed reactor was selected as being particularly suitable for the direct calcination and reduction of ammonium diuranate (ADU) to sinterable uranium dioxide (UO_2) because of its good powder handling and heat transfer characteristics. The second report (Fane, Le Page & Alfredson 1974) described the successful development of a 0.13 m diameter pulsed fluidised bed reactor for the production of sinterable UO_2 from ADU, employing both simple–batch and batch–continuous operation. Both modes of batch operation are intermittent and less attractive for a production facility than continuous operation which offers improved consistency of product, easier control, reduced labour requirements, and the potential for higher throughput. However, a continuously operated fluidised bed has the disadvantage that because the bed of particles tends to be well mixed, there is the possibility that incompletely converted material will reach the outlet zone and contaminate the product. The actual significance of this contamination of the UO_2 product can be determined only by the way the powder performs in pellet fabrication tests.

In the initial stages of this study, the Canadian specification (Chalder 1961) for sinterable UO_2 powder was adopted as the standard to be achieved:

> "A compact of not less than 0.72 in. (18.3 mm) in diameter and 1.0 in. (25.4 mm) in length obtained by pressing the powder to not more than 40,000 lb in^{-2} (276 MPa) shall have a density between 4.75 and 5.50 g cm^{-3}. The pressed sample complying with the above requirements, after sintering in a hydrogenous atmosphere for not more than 1.5 h at a temperature not exceeding 1650 °C, shall form a coherent pellet of density not less than 10.4 g cm^{-3}. The rate of heating of the sample during the sintering cycle shall not be less than 200 °C h^{-1} and the density shall be determined by appropriately accurate geometric and weight determination".

During this study, the required density of sintered pellets was increased from 10.4 to 10.6 g cm^{-3} and the sintering cycle was changed to 4 hours at 1600 °C rather than 1.5 hours at 1650 °C as stated above. A surface area limitation was also imposed. Whilst powders with surface areas of 3 to 9 $m^2\ g^{-1}$ are normally suitable for cold–pressing and sintering, a narrower range of 4 to 6 $m^2 g^{-1}$ was desired for the techniques of pellet fabrication developed at the AAEC Research Establishment.

This report describes the development and assessment of the pulsed fluidised bed reactor system for the continuous production of sinterable UO_2 powder, including the continuous stabilisation (partial oxidation or increase in the O:U ratio to render it stable in air) of this product. In addition, results are presented for background studies related to the degree of conversion in the continuous system, including the kinetics of the calcination and reduction reactions, the residence time distributions of the solids in the pulsed fluidised bed and the estimated time for complete conversion of a single particle of ADU to UO_2.

2. EQUIPMENT

The equipment comprised a 0.13 m diameter stainless steel pulsed fluidised bed reactor (PFBR), a 0.15 m diameter glass pulsed fluidised bed stabiliser (PFBS), and associated gas supply and solids handling systems. The PFBR and PFBS incorporated powder feed to the top of the beds *via* a screw feeder (and a rotary valve for the PFBR), and bottom product withdrawal *via* a conical base gas distributor (*i.e.* no bed support plate) and a vibratory conveyor. The gas supply system providing a pulsed gas flow to the PFBR consisted of a 2.8 ℓ pulse chamber separated from the reactor by a solenoid valve. The gas (nitrogen and/or hydrogen) was supplied at 0.35 MPa and the solenoid was actuated to give pulse frequencies of 0.5 and 0.75 Hz. This gas supply system has been found most satisfactory in batch–continuous operation (Fane, Le Page & Alfredson 1974). As indicated in Table 1, this system was used throughout the continuous operation runs except for one run (C9) in which conventional fluidisation was used and the solenoid valve was held in the fully open position.

Figure 1 gives the equipment flowsheet which is similar to flowsheet C described by Fane, Le Page & Alfredson (1974) with the added provision for hydrogen injection into the product collector of the PFBR.

3. EXPERIMENTAL

3.1 ADU Feed Material

The ADU feed material was produced from Australian yellow cake using the pilot plant equipment described by Alfredson (1972). The ADU was precipitated with ammonium hydroxide solution from nuclear purity uranyl nitrate at pH 7.5. After filtration, the ADU was dried and then granulated to either –1000 μm or –350 μm giving size distributions with weighted mean particle diameters of 340 and 170 μm respectively. Details of physical and chemical properties are given in Table 2.

3.2 Typical Procedure for Continuous Operation

The preliminary step in a continuous experiment was the establishment of a bed of UO_2 by following the procedures for a batch–continuous run (Fane, Le Page & Alfredson 1974). In this preliminary step, approximately 3 kg of UO_2 was charged into the PFBR and heated to operating temperature in a stream of nitrogen. ADU was fed at a constant rate by the screw feeder and rotary valve system, and then calcined and reduced to UO_2 in a pulsed stream of nitrogen and hydrogen. The increase in bed level was followed by observation of the pressure drop across the bed and, when a specified level was reached, continuous operation was commenced by starting product withdrawal *via* the vibratory conveyor to the product collection hopper. The measurement of bed level, which was important for satisfactory continuous operation, was reliably achieved using a pneumatic differential pressure cell and recorder. Pressure tappings were purged with nitrogen, and the pneumatic signal from the cell was damped to minimise pulsations at the recorder.

Precautions were taken to ensure that the product collector was free of oxygen (which could react explosively with process hydrogen) by evacuation, followed by purging with nitrogen. This procedure was also adopted when product collectors were replaced. In some experiments, a portion of the hydrogen input (about 5 per cent) was introduced into the product collector, and entered the PFBR *via* the product withdrawal system, flowing countercurrent to the hot UO_2 product.

Steady state conditions were achieved by adjusting the rate of product withdrawal to give a constant bed level, as indicated by the pressure drop across the bed. Continuous operation was maintained for a number of hours, and the powder product in the final hour was collected separately and taken to be representative of the chosen experimental conditions.

The UO_2 was allowed to cool in the product collectors and then transferred to the PFBS, where stabilisation of the UO_2 powder was carried out separately, by either batch or continuous mode. For continuous operation of the PFBS, unstabilised UO_2 was fed into a bed of stabilised UO_2 at a rate corresponding to a mean residence time of about 1 hour. The feed rate, typically 12 kg h^{-1}, was adjusted to maintain a bed temperature of about 50 °C with a flow rate of 1.4 to 1.9 ℓ s^{-1} of nitrogen containing 10 vol. % air. Stabilised UO_2 product was withdrawn continuously from the bottom of the bed *via* a vibratory conveyor. Analyses and assessment of the UO_2 were carried out as described by Fane, Le Page & Alfredson (1974).

3.3 Measurement of the Kinetics of Reduction of Calcined ADU

Reaction rate measurements were made using a Cahn R.G. Electrobalance with a 20 mm diameter silica envelope to contain mixtures of hydrogen and nitrogen passing over the reacting sample. The ADU starting materials were typical of those used in the PFBR, and were precipi–

tated at pH 7.2 and 7.5. The nitrate content of the ADU varied from about 0.5 wt.% for material washed during filtration to about 2.7 wt.% for unwashed material.

A 120 mg sample of ADU was heated to the desired reduction temperature in a stream of nitrogen and allowed to reach constant weight over a period of 1000 to 1200 seconds before hydrogen was introduced. Experiments were carried out at atmospheric pressure on ADU with particle sizes of 500 to 1000 μm, 50 to 75 μm and less than 20 μm, at temperatures in the range 500 to 650°C with mixtures of 15, 32, 71 and 100 vol.% hydrogen in nitrogen. A gas flowrate of 20 $cm^3\ s^{-1}$ was used throughout, following tests which showed that the reaction rate was independent of gas flowrate over the range 15 to 25 $cm^3\ s^{-1}$. Further details are given by Le Page & Fane (1974).

3.4 Measurement of the Residence Time Distribution of the Solids

Experiments were carried out in the 0.15 m diameter glass PFBS to determine the residence time distribution of the solids in a pulsed fluidised bed. Measurements were made using UO_2 tagged with iron, which was prepared by co–precipitation of ADU and ferric hydroxide followed by reduction in hydrogen. Both tagged and untagged materials had particle sizes ranging from 1000 μm and 100 μm, corresponding to a weighted mean particle diameter of about 300 μm, which was similar to that of the UO_2 produced in most of the reduction experiments.

A step change in the feed from pure UO_2 to tagged UO_2 was made and the product was sampled continuously from the bottom of the bed. The concentration of tagged UO_2 in the product was determined by magnetic separation of the pure UO_2 and the iron impregnated material. Mass balances on the tagged material were 100 ± 2 per cent. Experiments were carried out with a pulse chamber volume of 2.8 ℓ, a pulse frequency of 0.75 Hz, static bed depths of 0.35 and 0.59 m, gas flow rates of 1.9 and 2.8 $\ell\ s^{-1}$, mean residence times for the solids from 0.5 to 1.2 hours, and ratios of the density of tagged and pure UO_2 powders of 0.68 and 0.95.

4. RESULTS AND DISCUSSION

4.1 Degree of Conversion of Solids in the Continuous Reactor

The overall degree of conversion of ADU to UO_2 achieved in a continuous pulsed fluid–ised bed is an important factor in determining the suitability of the type of equipment for a production facility. Whereas the batch modes of operation described by Fane, Le Page & Alfred–son (1974) can be arranged to give complete conversion, there is no guarantee that it will be achieved with continuous operation. Attempts to determine experimentally the degree of con–version at near completion of the reaction in these continuous experiments were unsuccessful. Errors in sampling and analysis made it difficult to distinguish between oxygen to uranium ratios of, for example, 2.00 and 2.02 which corresponded to UO_3 contents in the UO_2 of zero and 2 per cent respectively. However, it is possible to estimate the overall degree of conversion from a knowledge of the kinetics of the calcination and reduction reactions, and the residence time dis–tribution of the solids in the pulsed fluidised bed. This section describes a model for such studies.

4.1.1 Kinetics of the calcination of ADU to UO_3

The kinetics of the calcination of ADU to UO_3 were estimated from data obtained by differential thermal analysis (DTA) of ADU, (Fane, Le Page & Alfredson 1974). The method of estimation involved analysis of the DTA trace as described by Borchardt & Daniels (1957) and detailed in Appendix A.

For the simplified case, which assumes the calcination of ADU to UO_3 to be a single reaction, an estimate of the activation energy was 86 kJ mol^{-1} and of the pre–exponential con–stant was $2.0 \times 10^8\ s^{-1}$ for an approximately first order reaction with respect to unconverted solid. The resultant equation giving the rate of formation of UO_3 was:

$$\frac{dx_{UO_3}}{dt} = 2.0 \times 10^8 \, (1-x_{UO_3}) \cdot \exp\left(\frac{-86.0 \times 10^3}{RT}\right) \qquad (1)$$

where x_{UO_3} = fraction of UO_3 existing at time t.

4.1.2 Kinetics of reduction of calcined ADU

The weight of sample in the thermobalance after calcination in nitrogen and prior to reduction, corresponded closely to the composition of UO_3 at 550°C and below, and U_3O_8 at 600°C and above, irrespective of the type of ADU used.

The thermobalance traces for the reduction of UO_3 in hydrogen–nitrogen mixtures at 550°C showed inflections at a weight corresponding to U_3O_8. Similar observations have been made by Tanford, Tichner & Lardner (1945); they are also supported by the work of Notz & Mendel (1960), who showed by X–ray diffraction that the complete formation of U_3O_8 separated the two steps and that UO_3 and UO_2 did not coexist during reduction. From these observations the kinetic data for the conversion of UO_3 to UO_2 have been separated into two independent consecutive steps: UO_3 to U_3O_8 and U_3O_8 to UO_2. Additional data for the U_3O_8 to UO_2 step were obtained from reductions carried out at 600°C and above.

The rates of the UO_3 to U_3O_8 reactions between 500°C and 550°C were found to be independent of particle size over the range studied; they were correlated by the following equation:

$$\frac{dx_B}{dt} = A\,(y_{H_2})^m \exp(-E_a/RT) \qquad (2)$$

where x_B = fraction of reactant solid converted;

y_{H_2} = mole fraction of hydrogen in the reducing gas (supplied at atmospheric pressure);

A = $14.9\ s^{-1}$;

m = 0.90 by least squares analysis with a standard deviation of 0.04; and

E_a = 44.0 kJ mol^{-1} by least squares analysis with a standard deviation of 2.9 kJ mol^{-1}.

The rates of the U_3O_8 to UO_2 reaction between 500°C and 650°C were also found to be independent of particle size over the range studied and were correlated by the following equation:

$$\frac{dx_B}{dt} = A(y_{H_2})^m(1-x_B)^n \exp(-E_a/RT) \qquad (3)$$

where A = $7.8 \times 10^3\ s^{-1}$;

m = 0.88 by least squares analysis with a standard deviation of 0.05;

E_a = 88.4 kJ mol^{-1} by least squares analysis with a standard deviation of 1.7 kJ mol^{-1}; and

n was found to be a function of temperature and hydrogen concentration varying from 0.65 at lower temperatures and hydrogen concentrations to zero at higher values of these parameters. This variation is shown in detail in Figure 2. A full discussion of these results was given by Le Page & Fane (1974).

4.1.3 Time for complete conversion of an ADU particle

When a particle of ADU is introduced into a hot bed of UO_2, fluidised by a mixture of hydrogen and nitrogen, it undergoes the following changes during conversion to UO_2:

- heat is transferred from and to the bed;
- the ADU is calcined to UO_3;
- the UO_3 is reduced to U_3O_8; and
- the U_3O_8 is reduced to UO_2.

A model which incorporates a heat balance for the particle and the kinetics of the chemical reactions is described in detail in Appendix B.

Figure 3 shows the computed history of a 1000μm particle of ADU following introduction into a bed of UO_2 at 670°C, fluidised by gas having a mean concentration of 23.4 vol.% hydrogen in nitrogen. The time for complete conversion is about 100 seconds, of which about 90 seconds is taken up by the consecutive reactions, UO_3 to U_3O_8 and U_3O_8 to UO_2. Particle heating and calcination are achieved rapidly.

Figure 4 shows the estimated times of complete conversion for ADU particle sizes of 200 and 1000 μm introduced into a bed of UO_2 at 670°C for a range of mean hydrogen concentrations. It should be noted that although the kinetics of the reaction steps are independent of particle size (Section 4.1.2), the larger particle experiences a more rapid conversion than the smaller because of the higher intraparticle temperature generated in the larger particle. Peak temperatures estimated by the model range from about 680 to 780°C depending on reaction conditions.

4.1.4 Residence time distribution of the solids

In this work, interest centred on the 'toe', or initial portion of the residence time distribution because it is the particles which pass through the bed rapidly which will be inadequately reduced. The toe of a typical residence time distribution curve is shown in Figure 5.

The data were interpreted in terms of the equivalent number of backmix stages connected in series. A single backmix stage represents a well mixed system and an increasing number of backmix stages approaches a plug flow system. The fractional concentration of tagged material in the outlet stream of a series of backmix stages following a step change from untagged to tagged feed can be represented by the following equation:

$$\text{one stage} \quad c_1 = 1 - \exp -(t/\bar{t}) \tag{4}$$

$$\text{two stages} \quad c_2 = 1 - \exp -(2t/\bar{t}(1 + 2t/\bar{t})) \tag{5}$$

where c_1, c_2 = fractional concentrations of tagged material in the outlet stream,

t = time from initiation of the step change, and

$\bar{t}$ = total mean residence time in the system.

As can be seen from Figure 5, the measured data were intermediate between those given by Equations (4) and (5) and have, therefore, been interpreted as the equivalent number of fractional backmix stages. The relevant equation for this condition is developed in Appendix C, and is:

$$c_2 = 1 - \left(\frac{\bar{t}_1}{\bar{t}_1 - \bar{t}_2}\right) \exp-(t/\bar{t}_1) + \left(\frac{\bar{t}_2}{\bar{t}_1 - \bar{t}_2}\right) \exp-(t/\bar{t}_2) \qquad (6)$$

with $\bar{t}_1 > \bar{t}_2$, and

$\bar{t}_1 + \bar{t}_2 = \bar{t}$

where $\bar{t}_1, \bar{t}_2$ = mean residence times in first and second stages respectively, and

the number of backmix stages, $N = \frac{\bar{t}}{\bar{t}_1}$.

Values of $\bar{t}_1$ and $\bar{t}_2$ giving the best fit for the data were used to estimate N for the four experimental runs, and the results are summarised in Table 3. For these conditions, the pulsed fluidised bed was equivalent to approximately 1.1 stages, from which it could be implied that it corresponded to two unequal size, well mixed systems in series having a volume ratio of 10 to 1.

Previous work on conventionally fluidised beds (Yagi & Kunii 1961; Kunii & Levenspiel 1969) suggested that the particulate phase was well mixed and equivalent to a single backmix stage, although Bowling & Watts (1963) observed in their experiments that the proportions of particles having short residence times were less than expected from Equation (4). Bowling & Watts (1963) suggested that the deviation resulted from the fact that the solid material was fed into the top of the bed and withdrawn from the base, and that there was inevitably a finite mixing time for the bed of particles.

Similar reasoning may be applied to the present studies, although an additional factor may have been that the tagged material was less dense than the normal feed. According to recent studies (Rowe, Nienan & Agbim 1972) with conventionally fluidised beds, mixtures of particles with only small density differences will readily segregate, although the degree of segregation diminishes as the fluidising gas flowrate is increased. If segregation occurred in the experiments now reported, it would have competed with the mixing process and delayed appearance of tagged material in the outlet.

However, the fact that similar results were obtained with both light and heavy tagged material suggests that either the gas flow rates were high enough to mask the effects of density difference, or that the findings of Rowe, Nienan & Agbim (1972) cannot be applied to the pulsed fluidised bed. If segregation owing to density difference was of any significance, the arrangement adopted for the PFBR would have taken full advantage of it, because the ADU (tap density ~ 1.2 g cm^{-3}) was fed to the top of the bed and the UO_2 product (tap density ~ 2.8 g cm^{-3}) was withdrawn from the bottom of the bed.

Although equivalence to 1.1 backmix stages appears to be a minor deviation from well mixed behaviour, the smaller proportion of material having short residence times was quite significant; this point is discussed below.

4.1.5 Estimation of degree of conversion

Partially converted material would have appeared in the product from the PFBR if any particles had a residence time less than the time for complete conversion. The experimentally determined residence time distribution (Figure 5) which shows residence times approaching zero, was used to estimate the portion of partially converted material in the product. For example, for the particle considered in Section 4.1.3, the time for complete conversion was about 100 seconds, and with a mean particle residence time of, say, 1 hour, Figure 5 indicates that about 0.4 per cent of the outlet stream would not have been fully converted. The mean conversion of this material would be about 50 per cent, assuming linear (zero order) kinetics for the conversion of UO_3 to

U_3O_8 to UO_2, which is a reasonable approximation judging from Figure 3. Thus overall conversion, for this example, would have been about 99.8 per cent. It should be noted that if the pulsed fluidised bed was equivalent to a single backmix stage, the amount of incompletely reduced material would have been about 2.5 per cent, giving an estimated overall conversion of 98.75 per cent.

The degree of conversion for each experimental run was estimated using the kinetic data of Figure 4 and the residence time distribution data of Figure 5. An average hydrogen concentration was assumed, based on the known inlet concentration and an outlet concentration which allowed for dilution by the gaseous products of calcination. The results of these estimates of the degree of conversion have been included in Table 3 which gives the detailed results of the experimental runs. It is important to note that the estimated degree of conversion does not include an allowance for conversion occurring in the product withdrawal system for those experiments in which hydrogen was injected in that system.

The estimated conversions ranged from 98.4 to 99.8 per cent with the majority in excess of 99 per cent. The relationships between conversion, operating conditions and product quality, assessed in terms of sintered density, are discussed in the following section.

4.2 Effect of Operating Variables on UO_2 Properties

Although all experimental runs were carried out at similar operating temperatures (670 to 680°C), the surface areas of the UO_2 powders ranged from 4.0 to 5.8 $m^2\ g^{-1}$ (mean value 5.0 and standard deviation 0.5 $m^2\ g^{-1}$). Whereas previous work on batch operation (Fane, Le Page & Alfredson 1974) had indicated a dependence of surface area on the temperature of reduction in the PFBR, there was no simple correlation between the surface area of UO_2 powder produced on a continuous basis and the estimated intraparticle temperature excursion (Section 4.1.3). A similar spread about the mean surface area for a given temperature of reduction was also observed in the batch experiments (Fane, Le Page & Alfredson 1974).

Differences between powders were less obvious following pellet fabrication by standard techniques, with sintered densities having a mean value of 10.66 g cm^{-3} and a standard deviation of 0.05 g cm^{-3}. Acceptable powders were produced by continuous operation under a variety of conditions (see Table 1), with sintered densities in excess of 10.60 g cm^{-3} being obtained for:

(a) ADU types 1 and 2 (particle sizes 1000 μm and 350 μm respectively);

(b) production rates from 6 to 17 kg h^{-1} of UO_2;

(c) mean residence times from 0.6 to 1.4 hours;

(d) bed contents from 10 to 14 kg UO_2, corresponding to bed depth to diameter ratios (H/D) of 5 to 7 approximately;

(e) gas flowrates of 0.95 to 1.4 $\ell\ s^{-1}$;

(f) hydrogen concentrations from 25 to 75 vol.% (the lower concentration required hydrogen injection – see (h) below);

(g) hydrogen inputs of 120 to 300 per cent of the stoichiometric requirement, based on the reduction of UO_3 (the lower inputs required hydrogen injection (h), or higher hydrogen concentrations (f));

(h) operation with and without hydrogen injection (5 per cent of total input) into the product removal system of the PFBR; and

(i) pulse frequencies of 0.5 and 0.75 Hz.

Pellet fabrication tests were carried out on the UO_2 powders produced in the final hour of each run, and it was assumed that these samples were representative of steady state operation. This assumption is justified on the grounds that the steady state concentration of unreduced material in the bed will be achieved very quickly because only a short time is required for complete conversion of a fresh particle. In support of this assumption, the data from runs C10 and C17 with identical operating conditions show that very similar results were obtained for runs of 2.5 and 6.5 hours respectively.

The lowest sintered density (10.54 g cm^{-3}) was produced in run C1 (Table 1) which used 25 vol.% hydrogen, a supply rate of 110 per cent of the stoichiometric requirement and a mean residence time of 0.8 h. These conditions corresponded to an estimated conversion of 98.8 per cent. An improved density was achieved by increasing the supply rate to 167 per cent and the residence time to 1.4 hours (run C2).

Further improvements in density were achieved by injecting about 5 per cent of the hydrogen into the product collector (runs C3 and C5 to C14), which allowed the product to contact hydrogen in the discharge system for about a minute in a plug flow situation at a temperature where reduction could take place. Densities well in excess of 10.60 g cm^{-3} were achieved using this technique even though, for run C7, the estimated conversion was only 98.4 per cent. This suggests that low conversion in the bed was compensated by hydrogen injection. However, the results of runs C4 and C15 to C17 indicated that the use of hydrogen injection was not mandatory provided the inlet hydrogen concentration was in excess of 37.5 vol.% and the hydrogen supply was greater than 150 per cent of the stoichiometric requirement. The estimated conversions for those conditions were 99.6 per cent or greater.

The maximum throughput of UO_2 attained in the experiments was 17 kg h^{-1} which was the upper limit of operation of the feeding system. The trend of results in Table 3 suggests that the maximum production capacity of the reactor could be higher than 17 kg h^{-1}. The runs giving the maximum capacity included C14, for which the hydrogen supply was only 120 per cent of the stoichiometric requirement with an inlet gas concentration of 50 vol.%.

Conventional fluidisation (run C9) also produced satisfactory UO_2. Similar results were obtained with both simple-batch and batch–continuous operation (Fane, Le Page & Alfredson 1974). These observations suggest that conventional fluidisation may be acceptable for the conversion of ADU to sinterable UO_2 contrary to the experience of Hawthorn, Shortis & Lloyd (1960), and further work is clearly necessary to demonstrate whether conventional fluidisation is a satisfactory method of processing. In the meantime, it is believed that pulsed fluidisation offers distinct advantages over conventional fluidisation in reducing elutriation, improving heat transfer (Alfredson & Doig 1970) and being able to handle powders with a wide size range and a large percentage of fine particles (Levey 1959, 1965).

4.3 Stabilisation

The UO_2 powders produced directly from reduction in the PFBR are of surface area such that they are pyrophoric in air. To render them stable in air, they are partially oxidised or stabilised (increase in the O : U ratio) with nitrogen containing 10 vol.% air. UO_2 powders produced in runs C8 to C10 (Table 3) were stabilised on a continuous basis at a throughput of about 12 kg h^{-1} using the technique described in Section 3.2. The oxygen to uranium ratios (Table 1) were similar to those of materials produced by batch stabilisation. As observed in an earlier report (Fane, Le Page & Alfredson 1974), UO_2 produced by the simultaneous calcination–reduction process (*i.e.* batch–continuous operation) tended to reach a lower oxygen to uranium ratio for a given surface area than UO_2 produced by consecutive calcination and reduction (*i.e.* simple–batch operation). These observations were confirmed by the results of continuous operation. Thus for an average surface area of 5 m^2 g^{-1}, the continuously produced UO_2 had an oxygen to uranium ratio of about 2.11, whereas that produced by simple–batch operation had ratios in the range 2.13 to 2.14. In practice, the product from continuous operation would be more desirable since lower oxygen to uranium ratios are preferred for ease of pellet fabrication.

5. CONCLUSIONS

Sinterable UO_2 was produced by the continuous calcination and reduction of ADU in the 0.13 m diameter pulsed fluidised bed reactor. For operating temperatures in the range 670 to 680 °C, powders were produced with surface areas in the range 4 to 6 $m^2\ g^{-1}$, which gave pellets with densities in excess of 10.6 g cm^{-3} after sintering at 1600 °C for four hours in hydrogen. Sinterability was relatively insensitive to the operating conditions within the range of experimental conditions as follows:

(a) ADU feed material with particle sizes of –1000 μm and –350 μm respectively;

(b) UO_2 production rates from 6 to 17 kg h^{-1} ;

(c) mean residence times from 0.6 to 1.4 hours;

(d) bed contents from 10 to 14 kg UO_2, corresponding to bed depth to diameter ratios (H/D) of 5 to 7 approximately;

(e) gas flowrates from 0.95 to 1.4 $\ell\ s^{-1}$; and

(f) pulse frequencies of 0.5 to 0.75 Hz.

Sintered densities below 10.6 g cm^{-3} were obtained with powders produced using a hydrogen input concentration of 25 vol.% for supply rates of 167 per cent of the stoichiometric requirement. Improved sinterability was obtained, either by using greater input concentrations (50 per cent input concentration at 120 per cent of stoichiometric requirement) or by using a secondary flow of hydrogen (about 5 per cent of total input) which was fed into the powder collection system and flowed countercurrent to the UO_2 product.

On the basis of these results, the continuously operated fluidised bed reactor is a feasible choice for the conversion of ADU to UO_2 in a production facility.

The reduction of calcined ADU in hydrogen between 500 and 650 °C was observed to take place as two consecutive steps, UO_3 to U_3O_8 and U_3O_8 to UO_2. The order of reaction with respect to unconverted solid was zero for the UO_3 to U_3O_8 step and varied from 0.65 to zero for the U_3O_8 to UO_2 step, depending on hydrogen concentration and temperature. In both reactions, the order with respect to hydrogen concentration was 0.9. The activation energies were 44.0 kJ mol^{-1} for the UO_3 to U_3O_8 reaction and 88.4 kJ mol^{-1} for the U_3O_8 to UO_2 reaction. For both steps, the reaction rate was independent of ADU particle size, within the range 1000 to 20 μm.

A model has been developed which combines the kinetics of calcination and reduction with a heat balance to estimate the time for complete conversion of an ADU particle introduced into a hot bed of UO_2 fluidised by a gas of known composition.

The residence time distribution of the solids in the pulsed fluidised bed showed a small deviation from well mixed behaviour. The bed was found to be equivalent to about 1.1 backmix reactors in series.

Combination of the reaction kinetics and residence time distribution data indicates that an overall conversion of ADU to UO_2 of 99 per cent or better was obtained in the continuously operated PFBR.

Continuous stabilisation was demonstrated at a rate of 12 kg h^{-1} UO_2 for a temperature of 50 °C in the 0.15 m diameter glass stabiliser. The properties of the product were similar to materials produced by batch stabilisation.

6. ACKNOWLEDGEMENTS

The authors wish to thank Messrs. H. Barton and J. Taylor who assembled the initial PFBR system, and Messrs. W. A. Layton and J. Taylor who assembled the PFBS system. The major development work was assisted by Messrs. H. Barton, J. Sarbutt, who also carried out surface area determinations, and Mr. G. P. Shaw. Thanks are also due to Mr. V. Vilkaitis for the supply of ADU, Mr. P. Pakalns and staff for chemical analyses, Mr. E. J. Ramm and staff for pellet fabrication and assessment, Mr. K. Thompson (vacation student – University of Auckland, N.Z.) for carrying out the residence time distribution experiments, and Mr. G. Price for guidance and loan of equipment for the kinetic studies. The authors also wish to thank Dr. P. G. Alfredson for helpful discussion and assistance in compiling this report.

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TABLE 1

EXPERIMENTAL DATA

Run No.	ADU Type (see Table 2)	Operating Conditions [1]									Estimated Conversion to UO_2	UO_2 Properties		
		Gas Flow ($\ell\ s^{-1}$)	Hydrogen Concentration (vol.%)	Hydrogen × Stoichiometric (%)	Hydrogen Injection (% Total Input)	Pulse Frequency (Hz)	Duration of Experiment (h)	Bed Content (kg UO_2)	Mean Residence Time (h)	Production Rate (kg $UO_2\ h^{-1}$)	(%)	Surface Area ($m^2\ g^{-1}$)	O : U Ratio	Sintered Density [2] ($g\ cm^{-3}$)
C1	1	1.2	25.0	110	0	0.75	2.5	10	0.8	12	98.8	5.2	2.16	10.54
C2	1	0.95	25.0	167	0	0.75	2.5	10	1.4	6	99.6	4.0	2.13	10.57
C3	1	0.95	25.0	167	~5	0.75	2.5	10	1.4	6	99.7	5.0	2.11	10.62
C4	2	0.95	50.0	200	0	0.75	2.5	10	1.0	10	99.8	5.2	2.10	10.69
C5	2	0.95	50.0	200	~5	0.75	2.5	10	1.0	10	99.8	4.3	2.12	10.70
C6	1	0.95	75.0	176	~5	0.75	2.5	10	0.6	17	99.7	4.3	2.09	10.67
C7	1	1.4	25.0	132	~5	0.75	2.5	10	0.6	17	98.4	5.4	2.12	10.67
C8	1	0.95	25.0	167	~5	0.5	2.5	10	1.4	6	99.7	4.7	2.12	10.65
C9	1	0.95	25.0	167	~5	Conventional Fluidisation	2.5	10	1.4	6	99.7	5.4	2.10	10.64
C10	1	0.95	37.5	150	~5	0.75	2.5	10	1.0	10	99.6	4.4	2.09	10.68
C11	1	0.95	75.0	300	~5	0.75	2.5	10	1.0	10	99.9	5.5	2.13	10.68
C12	2	0.95	50.0	200	~5	0.75	2.5	14	1.4	10	99.8	4.7	2.09	10.67
C13	2	0.95	37.5	150	~5	0.75	2.5	10	1.0	10	99.6	5.7	2.10	10.63
C14	1	0.95	50.0	120	~5	0.75	2.5	10	0.6	17	99.4	5.7	2.12	10.73
C15	1	0.95	75.0	150	0	0.75	2.5	10	0.6	17	99.7	5.8	2.12	10.74
C16	1	1.4	50.0	300	0	0.75	3.5	10	1.0	10	99.8	5.3	2.10	10.66
C17	1	0.95	37.5	150	0	0.75	6.5	10	1.0	10	99.6	4.6	2.10	10.68

Notes: *(1) Operating temperature of bed 670 to 680 °C.*

(2) Pellet fabrication by micronisation, precompaction at 70 MPa, granulation to −100 mesh, automatic pressing at 276 MPa, and sintering in hydrogen at 1600 °C for four hours.

TABLE 2

TYPICAL PROPERTIES OF ADU FEED

pH of Precipitation 7.5

ADU Type	Surface Area ($m^2\ g^{-1}$)	Analysis			Granulated to Less Than (μm)	Particle Size Distribution				Pour Density ($g\ cm^{-3}$)	Tap Density ($g\ cm^{-3}$)
		$\frac{NH_3}{U}$ ($mol\ mol^{-1}$)	$\frac{H_2O}{U}$ ($mol\ mol^{-1}$)	$\frac{NO_3}{U}$ ($mol\ mol^{-1}$)		> 350 m < 1000 m (%)	> 150 μm < 350 μm (%)	> 100 μm < 150 μm (%)	< 100 μm (%)		
1	11.0	0.50	1.20	0.57	1000	45	23	12	20	0.65	1.17
2	13.8	0.52	1.28	1.40	350	6	48	18	28	0.69	1.24

TABLE 3

RESIDENCE TIME DISTRIBUTION DATA FOR SOLIDS IN A PULSED FLUIDISED BED

Run No.	Static Bed Height (m)	Mean Residence (h)	Gas Flowrate ($\ell\ s^{-1}$)	Ratio Density Tagged UO_2 to Untagged UO_2	No. of Backmix Stages in Series
RTD 1	0.36	0.50	1.9	0.65 : 1	1.10
RTD 2	0.36	1.17	1.9	0.95 : 1	1.12
RTD 3	0.36	0.83	1.9	0.95 : 1	1.09
RTD 4	0.58	0.67	2.8	0.95 : 1	1.10

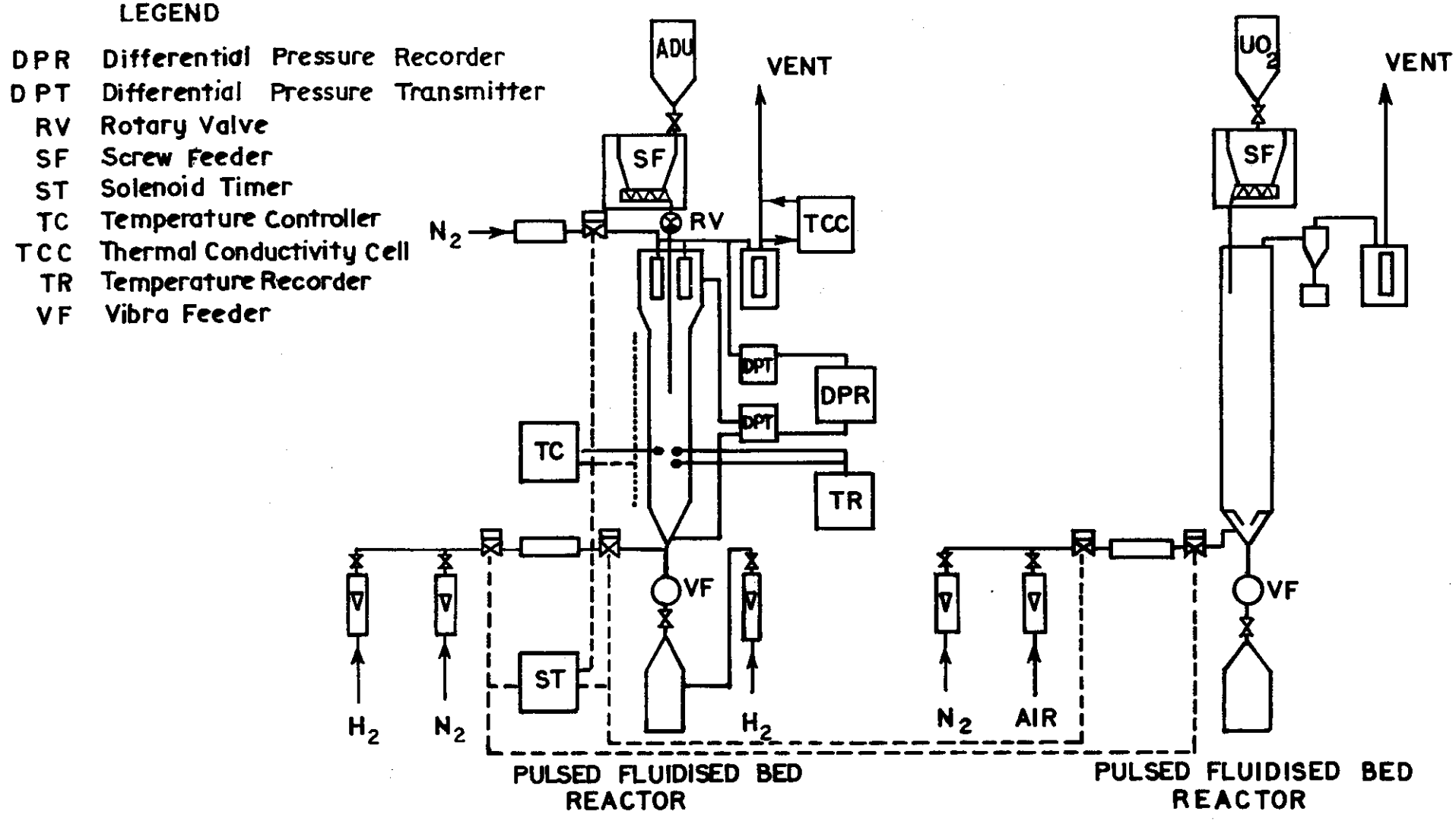


FIGURE 1. CONTINUOUS PULSED FLUIDISED BED REACTOR SYSTEM

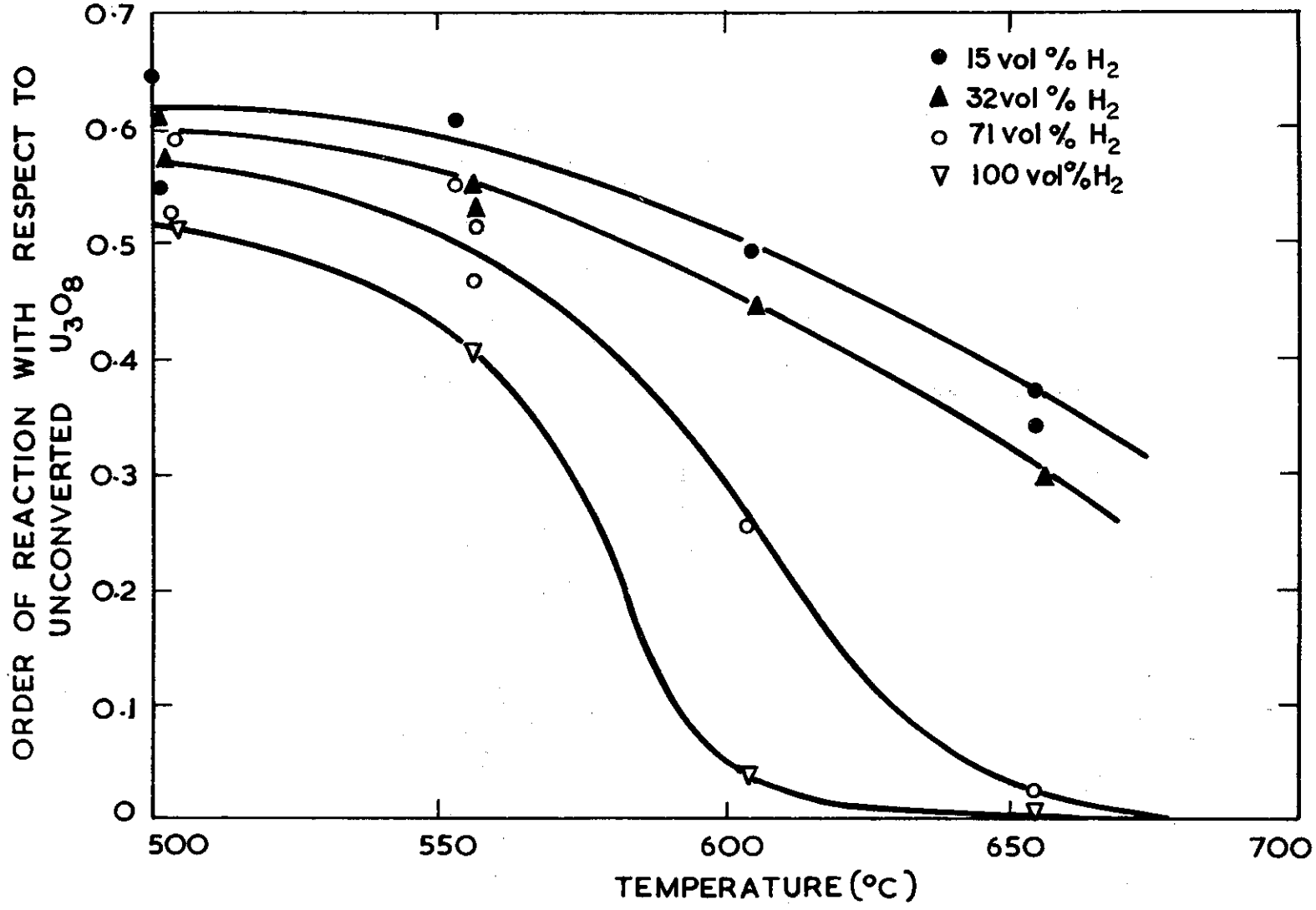


FIGURE 2. VARIATION OF THE ORDER (n) OF THE REDUCTION REACTION U_3O_8 TO UO_2 WITH TEMPERATURE AND HYDROGEN CONCENTRATION

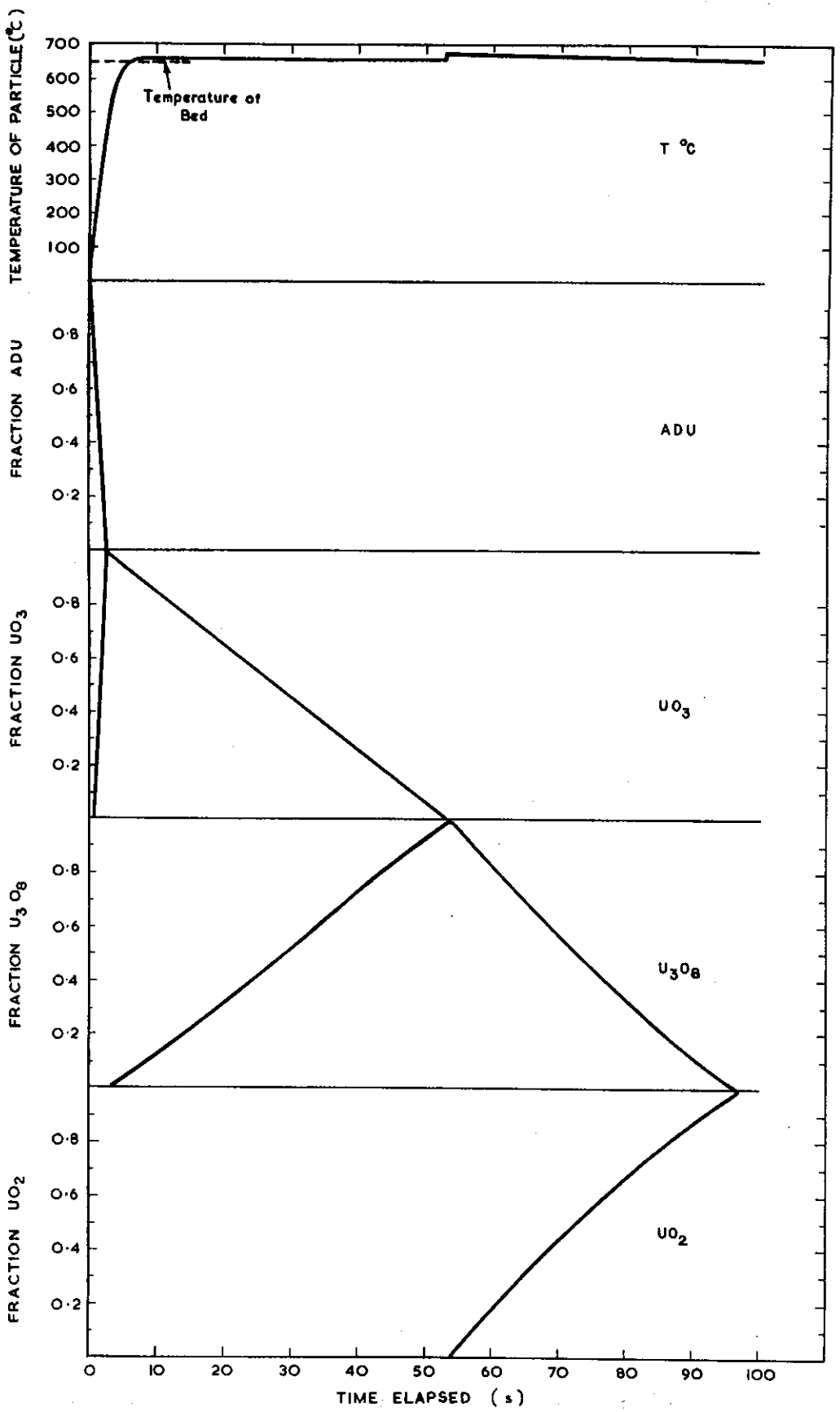


FIGURE 3. TEMPERATURE AND CONVERSION HISTORY FOR 1000 μm PARTICLE OF ADU

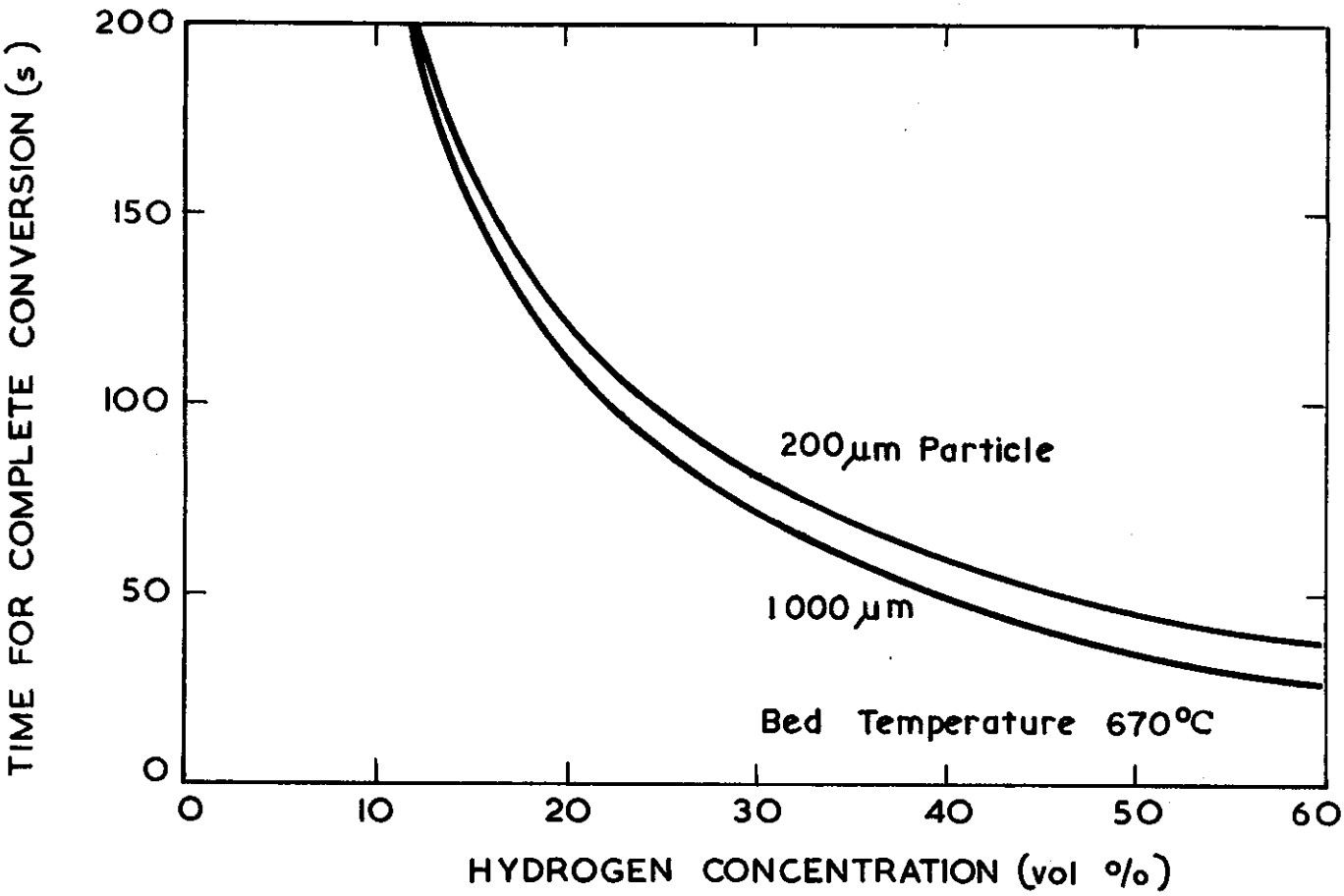


FIGURE 4. ESTIMATED TIME FOR COMPLETE CONVERSION OF A PARTICLE OF ADU

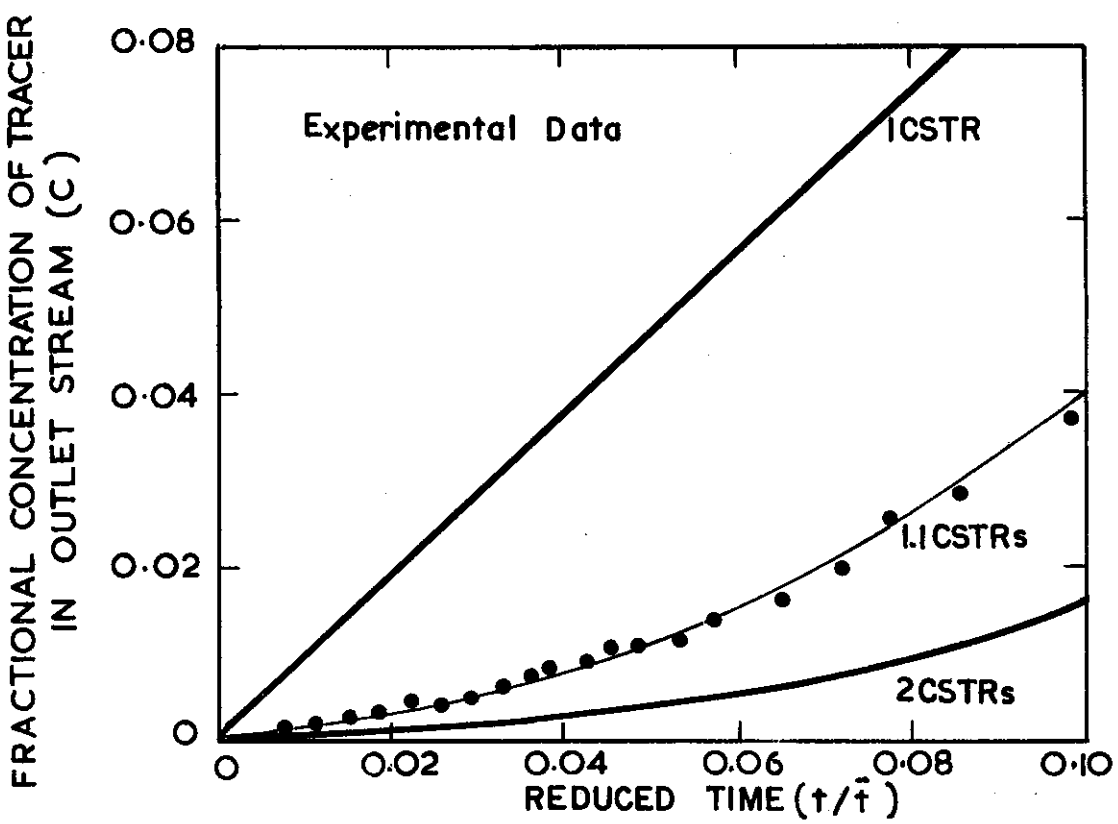


FIGURE 5. RESIDENCE TIME DISTRIBUTION DATA, RUN RTD 2 - TABLE 3

APPENDIX A

KINETICS OF THE CALCINATION OF ADU TO UO_3

The method used to estimate the kinetics of the calcination of ADU to UO_3 involves analysis of the DTA trace as described by Borchardt & Daniels (1957). For the case of an endo– or exothermic reaction which is first order with respect to unconverted solid, the rate constant is given by

$$k = \frac{\Delta T}{\alpha - a} \qquad \text{(A1)}$$

where k = value of the rate constant at temperature T;

ΔT = differential temperature at temperature T;

α = total area of the endo– or exotherm on the trace; and

a = area of the endo– or exotherm on the trace for temperatures less than T.

A typical DTA trace is shown in Figure A1. The calcination reactions are represented by the endothermic temperature excursion between 100 and 250 °C associated with the liberation of water and ammonia, and the minor endotherms and exotherms between 250 and 400 °C, possibly associated with the decomposition of nitrate and partial self–reduction (Price 1971). To simplify this complex picture, the analysis was limited to the major endotherm between 100 and 250 °C.

Accurate integrations of the primary calcination endotherm gave rate constant values over the temperature range 100 to 250 °C. The calculated rate constants gave a straight line Arrhenius plot (Figure A2) which confirmed the first order nature of the reaction (Borchardt & Daniels 1957) and justified the use of Equation (A1). From the slope of the Arrhenius plot, the activation energy was 86 kJ mol^{-1} and, from the absolute magnitude of the rate constant, the pre–exponential constant was calculated as 2.0×10^8 s^{-1}. The kinetics of the calcination of ADU to UO_3 were therefore described by the following equation:

$$\frac{dx_{UO_3}}{dt} = 2.0 \times 10^8 \, (1 - x_{UO_3}) \cdot \exp\left(\frac{-86.0 \times 10^3}{RT}\right) \qquad \text{(A2)}$$

where x_{UO_3} = fraction of UO_3 existing at time t.

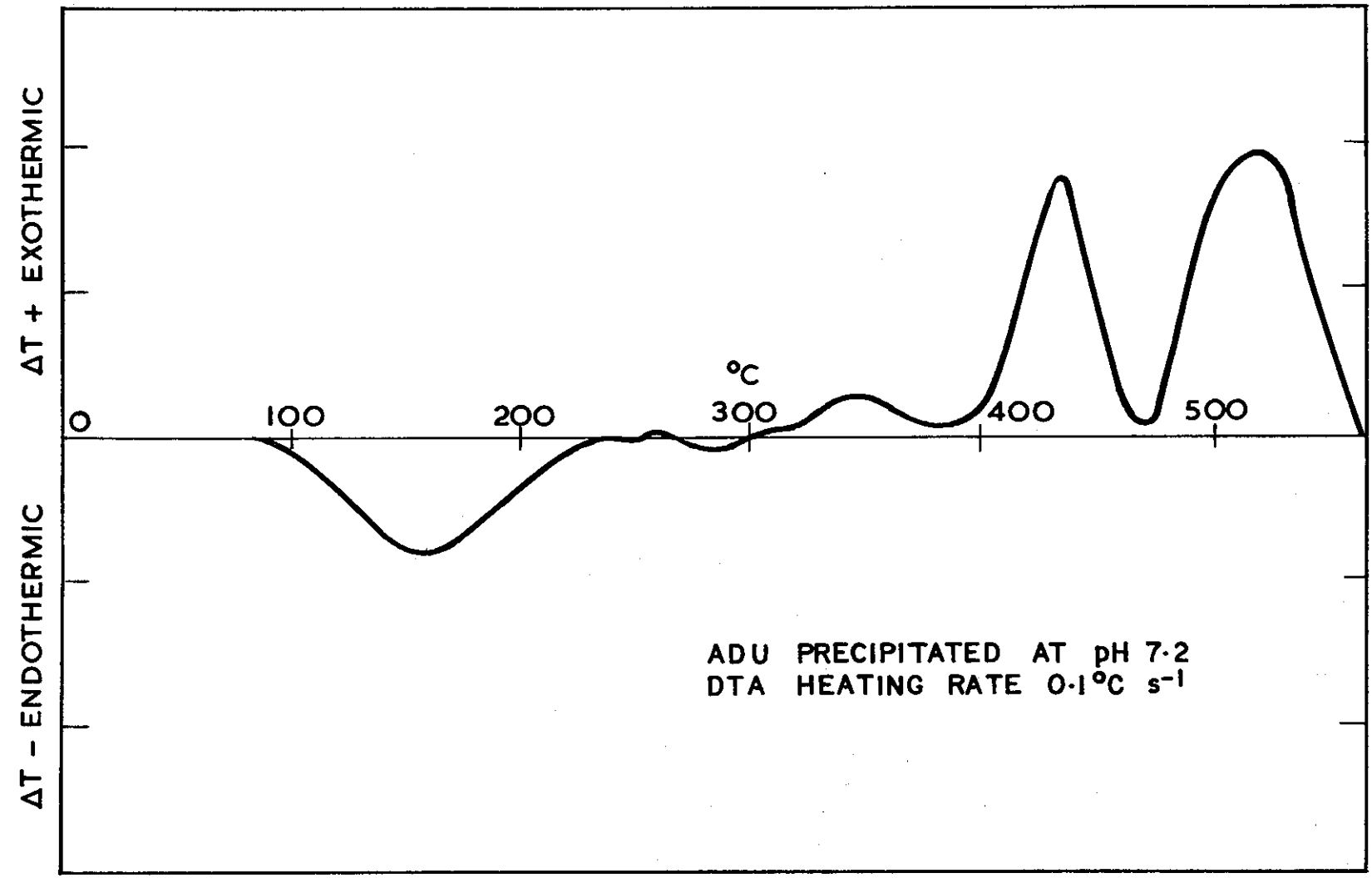


FIGURE A1. TYPICAL DTA TRACE FOR CALCINATION AND REDUCTION OF ADU IN HYDROGEN

APPENDIX B

MODEL FOR DETERMINATION OF TIME FOR CONVERSION OF AN ADU PARTICLE

The assumed conversion history of an ADU particle introduced into a hot bed of UO_2 fluidised by a hydrogen–nitrogen mixture is depicted in Figure B1. The basic components of the model are as follows:

B1 PARTICLE HEAT BALANCE

The particle temperature increases due to contact with the hot gas stream, other particles in the bed and with the reactor walls. Heat transfer coefficients from the gas stream to particles in a fluidised bed are given by the correlation of Kunii & Levenspiel (1969):

$$Nu_p = 0.3\, Re_p^{1.3} \quad , \qquad \text{(B1)}$$

where Nu_p and Re_p are the particle Nusselt and Reynolds numbers respectively.

For a particle diameter of 1000 μm and a gas flowrate of 0.95 (standard) $\ell\ s^{-1}$ of a 25 vol.% mixture of hydrogen in nitrogen, Equation (B1) estimates a gas to particle heat transfer coefficient of about 60 $W\ m^{-2}\ K^{-1}$ based on a gas temperature equal to the bed temperature of about 650 °C. This value can be compared to the measured value for the wall to bed coefficient of 485 $W\ m^{-2}\ K^{-1}$ (Fane, Le Page & Alfredson 1974). In practice, the phenomenological coefficient for the particle would be expected to lie between these two extremes, therefore, an intermediate value of 200 $W\ m^{-2}\ K^{-1}$ is assumed for the particle to bed heat transfer coefficient.

The heat balance for the particle also takes into account the endothermic and exothermic reactions of the particle. The following heats of reaction are used in the model:

Endothermic heat of calcination ADU → UO_3 = 25.2 kJ $(mol\ U)^{-1}$.

Exothermic heat of reaction $UO_3 \rightarrow U_3O_8$ = 46.0 kJ $(mol\ U)^{-1}$.

Exothermic heat of reaction $U_3O_8 \rightarrow UO_2$ = 59.0 kJ $(mol\ U)^{-1}$.

The value for the $U_3O_8 \rightarrow UO_2$ reaction was calculated from the data of Rand & Kubaschewski (1963), and the values for the other reactions were estimated by comparison of areas from the DTA traces described by Fane, Le Page & Alfredson (1974).

B2 KINETICS OF THE THREE REACTIONS

Equations describing the kinetics of the three reactions are of the form:

$$\frac{dx_B}{dt} = A.(y_{H_2})^m (1-x_B)^n \exp(-E_a/RT) \quad , \qquad \text{(B2)}$$

where x_B = fraction of reactant solid converted, and

y_{H_2} = mole fraction of hydrogen in the gas stream.

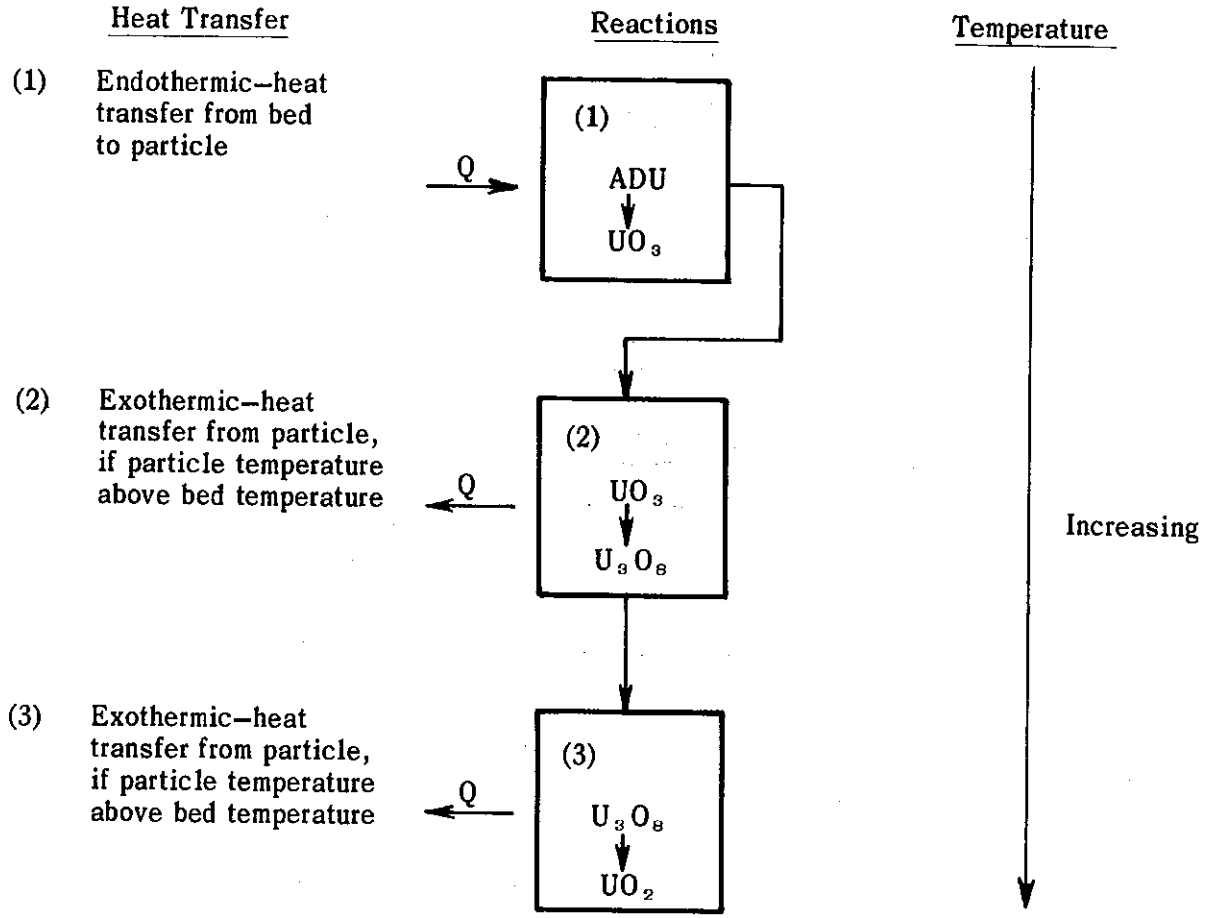
The values of the coefficients and exponents in Equation (B2) for the three reactions involved are summarised below:

Reaction	A (s^{-1})	m	n	E_a (kJ mol^{-1})
ADU $\rightarrow UO_3$	2.0×10^6	0	1	86.0
$UO_3 \rightarrow U_3O_8$	14.9	0.9	0	44.0
$U_3O_8 \rightarrow UO_2$	7.8×10^3	0.9	variable (see Fig.A2)	86.4

The sequence of the three reactions is obviously calcination of ADU to UO_3, reduction of UO_3 to U_3O_8 and reduction of U_3O_8 to UO_2. The model allows freshly formed UO_3 to react to U_3O_8 before the completion of the ADU to UO_3 reaction but does not allow the conversion of U_3O_8 to UO_2 to commence until all the UO_3 is converted to U_3O_8. This is based on observations detailed in Section 4.1.2.

B3 PROGRAM OF THE MODEL

The model combines the heat balances and the kinetics of the reactions for a single particle. A simplified flowsheet of the computer program of the model is shown in Figure B2. The output from this program is in the form of Figure 3 where the molar fraction of the various uranium compounds and the intraparticle temperatures are plotted as functions of time.



Note: Steps (1) and (2) can occur concurrently.

Steps (2) and (3) occur consecutively.

FIGURE B1. CONVERSION HISTORY OF AN ADU PARTICLE

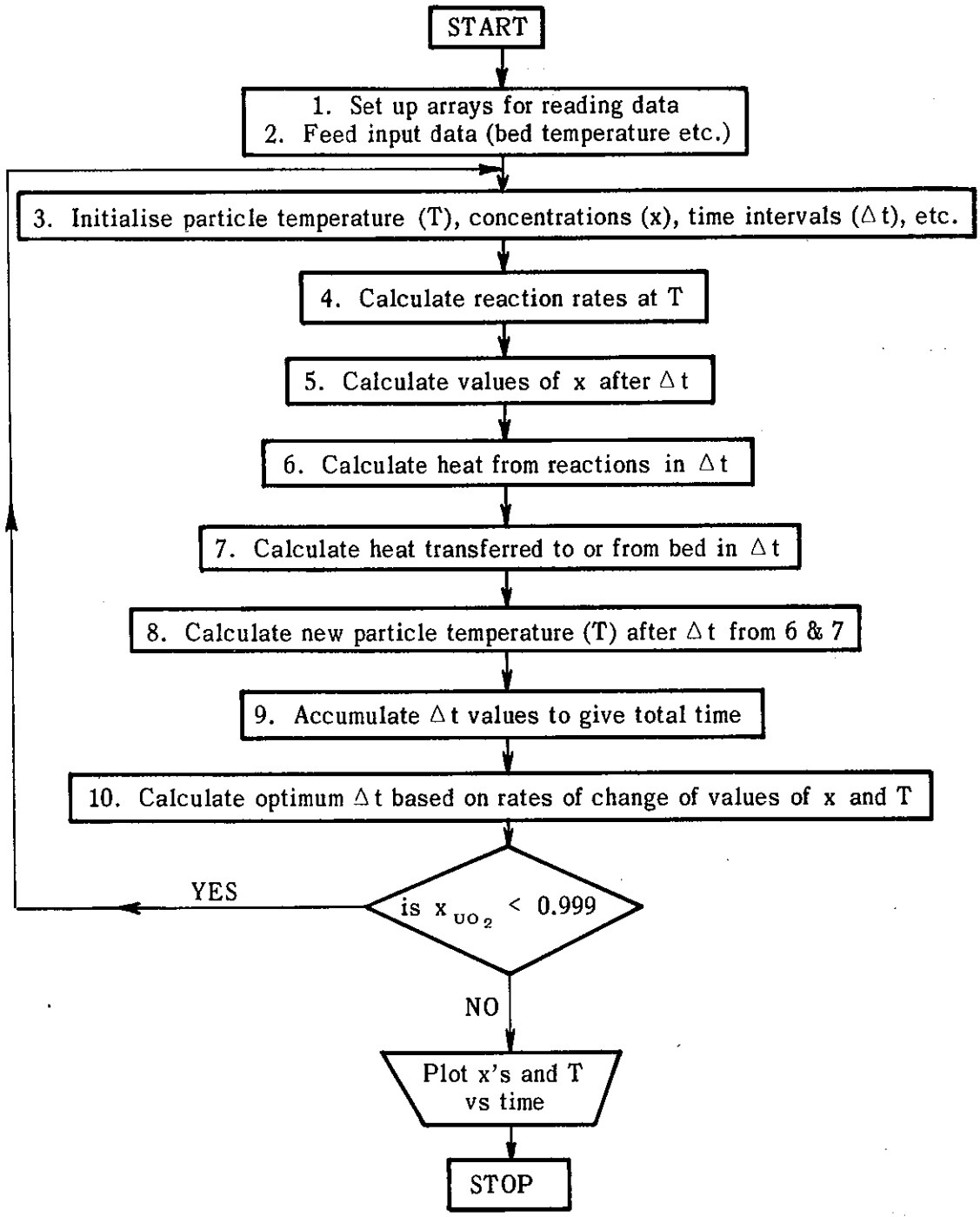


FIGURE B2. FLOW CHART FOR COMPUTER PROGRAM OF MODEL

APPENDIX C

EXIT CONCENTRATION FOR TWO UNEQUAL SIZE BACKMIX REACTORS IN SERIES

When a step change from normal to tagged feed is imposed upon a system comprising N equal sized backmix stages (also known as continuous stirred tank reactors) connected in series, the concentration of tagged material in the outlet is given (Bowling & Watts 1963) by the following:

$$C_N = 1 - (e^{-Nt/\bar{t}}) \sum_{n=1}^{N} \frac{(Nt/\bar{t})^{n-1}}{(n-1)!} \qquad (C1)$$

where C_N = concentration of tagged material in the outlet of the Nth stage;

t = time from the initiation of the step change;

$\bar{t}$ = total mean residence time in the system (*i.e.* total volume of N stages/volumetric flowrate); and

n = stage number.

Thus for one backmix stage

$$C_1 = 1 - e^{-t/\bar{t}} \quad , \qquad (C2)$$

and for two backmix stages of equal volume

$$C_2 = 1 - e^{-2t/\bar{t}} \left(1 + \frac{2t}{\bar{t}}\right) \quad . \qquad (C3)$$

Systems which exhibit behaviour intermediate between one and two stages can be considered to be equivalent to two stages of unequal size, or alternatively as one backmix stage connected to a fractional stage. Thus if the behaviour can be represented by one stage of mean residence time $\bar{t}_1$ and one of the mean residence time $\bar{t}_2$ (where $\bar{t}_1 > \bar{t}_2$, and $\bar{t}_1 + \bar{t}_2 = \bar{t}$), the number of equivalent backmix stages is $\bar{t}/\bar{t}_1$ (where $1 < (\bar{t}/\bar{t}_1) < 2$). The concentration of tagged material in the outlet of the 'second' stage may be calculated as follows:

Let Q = volumetric flowrate,

V_1, V_2 = volumes of the stages,

$\bar{t}_1, \bar{t}_2$ = mean residence times in the stages, and

C_1, C_2 = concentration of tagged material in the outlets of the stages.

Balance of tagged material for 'second' stage over time dt,

(Accumulation = input − output),

$$\frac{d\,(C_2 V_2)}{dt} = Q(C_1 - C_2) \quad ,$$

which gives

$$\frac{dC_2}{dt} + \frac{C_2}{\bar{t}_2} = \frac{1}{\bar{t}_2} \left(1 - e^{-t/\bar{t}_1}\right) \quad . \qquad (C4)$$

The solution of (C4), which is a linear first order differential equation, is obtained from

$$C_2 = e^{-t/\bar{t}_2}\left[\int e^{t/\bar{t}_2}\left(\frac{1-e^{t/\bar{t}_1}}{\bar{t}_2}\right) dt + k\right] ,$$

$$\therefore \quad C_2 = 1 - \left(\frac{\bar{t}_1}{\bar{t}_1-\bar{t}_2}\right) e^{-t/t_1} + k\, e^{-\bar{t}/\bar{t}_2} \quad .$$

Boundary condition $C_2 = 0$, when $t = 0$ gives

$$k = \frac{\bar{t}_2}{\bar{t}_1-\bar{t}_2} ,$$

hence

$$C_2 = 1 - \left(\frac{\bar{t}_1}{\bar{t}_1-\bar{t}_2}\right) e^{-t/\bar{t}_1} + \left(\frac{\bar{t}_2}{\bar{t}_1-\bar{t}_2}\right) e^{-t/\bar{t}_2} , \qquad (C5)$$

where $\bar{t}_1 > \bar{t}_2$,

$\bar{t}_1 + \bar{t}_2 = \bar{t}$, and

the number of backmix stages is $N = \bar{t}/\bar{t}_1$.