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THE PRODUCTION OF SINTERABLE URANIUM DIOXIDE FROM AMMONIUM DIURANATE IN A PULSED FLUIDISED BED REACTOR - INTERIM REPORT

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ABSTRACT

Results and operational experience are reported for the batchwise production of uranium dioxide from ammonium diuranate in a pulsed fluidised bed reactor. Alternative proposals for batch/continuous operation are assessed and compared with continuous operation. The future development programme is outlined.

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CONTENTS (continued)

1. INTRODUCTION

Uranium dioxide for fuel pellet fabrication must be readily sinterable and have consistent quality. It is most widely produced via the ammonium diuranate (ADU) route in which ADU is precipitated from a uranium solution with ammonia, then calcined and reduced with hydrogen to form uranium dioxide (UO_2).

A variety of contactors have been used for the conversion of both ADU and uranium trioxide (UO_3) to UO_2. These include batch tray reactors (Hinton 1955, Placek and North 1960, Berry 1967), moving beds (Smiley 1961, Delange et al. 1964), rotary kilns (Wirths and Ziehl 1958, Delange 1963, Smith et al. 1964) and pulsed fluidised beds (Heidt et al. 1966, Rio Algom Mines Ltd. - private communication). Batch tray operation is at present in use within Chemical Engineering Section for producing 5-kg batches of UO_2 which are satisfactory for pellet fabrication (Janov and Alfredson - A.A.E.C. unpublished work). The disadvantages of this technique are the need for manual handling in loading and unloading the furnace and the possibility of non-uniform temperatures within the static beds of powder. The susceptibility of UO_2 powder to microsintering under the exothermic reduction conditions suggests the use of equipment with good heat transfer characteristics and efficient gas-solids contacting (Alfredson 1970). Moving bed reactors are apt to have temperature gradients even when the feed material is pelletised (Smiley 1961), and rotary kilns tend to classify their contents and require a closely sized feed (Lloyd 1963). The pulsed bed technique has more efficient heat transfer and gas-solids contacting characteristics than these other methods, and is also able to handle a feed with wide size distribution, as is the case with ADU powders.

We now define a variety of reaction strategies which can be considered for the pulsed fluidised bed.

Batch operation. ADU is charged to the cold reactor, heated up and calcined before hydrogen is introduced. Product is either discharged hot, or allowed to cool within the reactor and then discharged.

Batch/continuous. This is a general term covering all types of operation in which the reactor is kept hot and from which there is intermittent product removal.

Sequential batch. ADU is charged to the hot reactor, heated up and calcined before hydrogen is introduced. Product from the reactor is discharged hot.

Intermittent feed and reduction. Similar to sequential batch except that, following an initial reduction, further ADU is added to take advantage of the volume reduction accompanying the conversion of ADU to UO_2.

Continuous feed/intermittent discharge. For most of the cycle there is simultaneous ADU feed, calcination and reduction. The bed of UO_2 is allowed to build up to a maximum level before discharge. A portion of the bed is retained as a basis for the next batch.

Continuous operation. There is a steady-state input and output of materials, and a fixed bed volume.

This report describes the initial development of pulsed fluidised bed equipment and reviews the experience and results to date for batch and sequential batch operation. The aim was to produce a UO_2 powder which complied with the A.E.C.L. specification (Chalder 1961). This specification requires a sintered density not less than 10.4 g/cm^3 after sintering in a hydrogen atmosphere for not less than $1\frac{1}{2}$ hours at a temperature not exceeding 1650°C. However it should be noted that, at the time of writing, the terms of reference have been modified so that the required sintered density is 10.6 ± 0.15 g/cm^3 with an average of 10.6 (Reeve - private communication). The other modes of batch/continuous and continuous operation are also critically assessed and discussed in the context of the proposed development programme.

2. PILOT PLANT EXPERIENCE

Approximately 75 kg UO_2 has been produced by batch operation of the pulsed bed reactor and approximately 10 kg by sequential batch operation. The major effort has been towards the production of a powder with acceptable sintering and microstructural properties, and investigation of the influence of operating conditions on these properties. In addition, information has been collected on heat transfer characteristics, efficiency of gas usage, control and reliability.

2.1 Equipment

The equipment used in batch operation is shown schematically in Figure 1 and the salient features of the reactor in Figure 2. All parts in contact with the ADU and UO_2 are stainless steel, or other suitably inert material.

The reactor body is 5 inch diameter Schedule 40 pipe, approximately 40 inches long, having a conical gas inlet section and a 10 inch diameter disengagement section housing sintered stainless steel bayonet filters. Bed support plates made from either $\frac{1}{8}$ inch thick sintered metal plate or from 200 mesh screen are used.

Calrods wrapped around the reactor body and bonded to it with copper supply the necessary heating. Cooling coils similarly attached are available for heat removal. The heaters on the main body of the reactor are connected to give two heating zones, each of 4 kW and separately controlled by on/off controllers. Additional heating, under manual control, is supplied to the gas inlet pipe, the base cone, the disengagement section and the off-gas piping.

As a safety precaution, the reactor is fitted with a graphite bursting disc which is connected to the vent system via a blow-down drum.

Gases enter the reactor in pulses through a heated pipe, from a pressure chamber isolated by electronically-actuated solenoid valves. The measurement of gas flow rates is facilitated by the use of differential flow controllers, which eliminate pulsations at the flowmeters. This gas input system permits the use of a wide range of pulsing conditions and any desired nitrogen/hydrogen ratio.

After passing through the bed of powder the gas leaves the reactor via the four bayonet filters and then passes through a backup filter before discharging to the ventilation system. Fine powder which accumulates on the filters is periodically returned to the bed by blowback of the filters.

Pressure drops across the bed and across the filters are measured either by pneumatic recorders or using strain gauge transducers connected to a high speed Brush oscillograph. System temperatures are monitored on a 12 point recorder, a push button indicator, and when required, on a Heath flat bed recorder.

A separate reactor is used for stabilisation of the UO_2 product using air diluted with nitrogen. It has many of the features of the reduction reactor except that it is designed for ambient temperature operation. The reactor body is a 6 inch diameter glass pipe, 5 feet long, with a Perspex base section and a conical bed support fabricated from stainless steel. Instead of off-gas filters within the reactor, an external cyclone separator is used. The charging hopper for the stabilisation unit can be filled with hot powder from the reduction reactor by pneumatic transport. Cooling coils on the outside of the hopper and facilities for fluidising within the hopper provide rapid powder cooling.

2.2 Batch Operation

The establishment of a procedure for batch operation required the solution of various developmental problems, which are dealt with separately (Section 2.5). This section presents typical current practice.

From 4 to 7.5 kg ADU (dried at 100°C and granulated to -20 BSS) is pneumatically conveyed to the reactor by a stream of nitrogen. The bed of ADU is heated in a stream of nitrogen to approximately 600°C over a period of 2 hours, this rate being set by the available heating capacity. Satisfactory gas-solids contacting appears to be obtainable over a range of pulsing conditions (see Section 3.2.2), typical figures being 2 std ft^3/minute gas flow from a pulse chamber of 0.1 ft^3 capacity operating at 30 cycles/minute with a corresponding maximum pulse chamber pressure of 10 psig.

When hydrogen is admitted to the reactor, the exothermal heat generation causes a rise in the bed temperature, the magnitude and duration of which can be explained from heat and mass balance considerations (Section 3.3). Typically 2 std ft^3/minute of gas, with a hydrogen content of 25 vol.% in nitrogen passing into a bed derived from 4 kg ADU, results in a temperature rise of approximately 20 to 25°C. Under these conditions, the reactor wall temperature is controlled at a temperature approximately 5 to 10°C higher than the bed temperature. The temperature history of the bed is depicted in Figure 3, showing a reaction plateau at 625°C which terminates after the passage of approximately 1.5 stoichiometric volumes of hydrogen (see Section 3.3 for more detailed analysis). To ensure complete reduction, excess hydrogen is passed through the bed.

The UO_2 powder is discharged to the stabiliser cooling hopper where it is fluidised with nitrogen to assist cooling, and is brought to ambient temperature in approximately 15 minutes. The stoichiometric UO_2 is stabilised by pulsing with a mixture of 2 vol.% oxygen in nitrogen for approximately 40 minutes, reaching a composition of 2.10 ± 0.05 depending on the UO_2 surface area. The stabilisation process is exothermic and bed temperature excursions of 10 to 15°C lasting 5 to 10 minutes are encountered. Stabilised material is discharged through the base of the stabiliser to a glass product collector, and transferred to a fume hood for sampling and storage. Bottom discharge is also proposed for the pulsed bed reactor in future development studies.

The overall process time is of the order of 3.5 hours, of which 2 hours are required for heating the reactor and contents. To process a 7.5 kg batch of ADU takes marginally longer, the extra time being contributed by the extended reaction plateau. Simple batch studies have been a useful precursor to the batch/continuous and continuous studies described below.

2.3 Sequential Batch Operation

Batch operation involving charging the ADU to the cold reactor is of limited use. To avoid the time-consuming heating period, tests have been carried out in which the reactor is kept at the reaction temperature and the ADU is 'hot charged' in increments. Since ADU evolves at least 2 moles of gas per mole U on thermal decomposition, the amount charged per increment has to be restricted to approximately 2 kg. Larger increments of ADU result in reactor pressure surges to greater than 10 psig, caused by the sudden evolution of gas. As shown in Figure 3, two 2-kg increments can be charged and brought to reaction temperature in about 20 minutes. The subsequent treatment of the batch is the same as that described in Section 2.2, and on discharging the hot UO_2 a fresh batch of ADU is charged.

By this means, two 6-kg batches of ADU have been processed in approximately

2 hours. It must be pointed out that this test was only intended to demonstrate the feasibility of the approach and should not be considered as an optimum. Further batch/continuous experiments are planned and the alternative strategies are discussed in Section 4.

2.4 Powder Testing

The pulsed bed product is sampled and measurements made of O/U ratio, chemical purity, surface area, pour and tap density and, in some cases, particle size distribution. In addition, fabrication tests are carried out by Ceramics Section using either automatic or isostatic pressing under the following conditions:

(i) automatic pressing, precompaction at 10,000 lb/in^2, pressing at 20 $tons/in^2$, or

(ii) isostatic pressing at 20 $tons/in^2$.

The sintering conditions used are 4 hours in hydrogen at 1500°C. Results of these tests are given in Section 3.

2.5 Developmental Problems

During the batch studies a number of difficulties were encountered which required equipment modification; these are outlined below.

Small quantities of incompletely reduced material were present in the UO_2, even after vast excesses of hydrogen had been passed through the bed. This was caused by the entrainment of fine powder from the bed to the disengagement section. The fine particles lodged on the walls and filters and could be held there, out of the hot zone, during the reduction reaction. During the cooling period, some of these incompletely reduced particles returned to the bed. The problem was overcome by heating the disengagement section to approximately 500°C and by hot-discharging the product immediately after reduction to minimise the likelihood of partly reduced material being returned to the bed.

Unacceptable microstructures, characterised by areas of segregated porosity, were observed in pellets fabricated from some powders. These defects were related to microsintering of the powder during reduction because poor fluidisation resulted in the formation of hot-spots. This was attributed to a broken bed support plate which probably encouraged gas channelling and the formation of static bed areas. The sintered metal plate has been replaced by a support made from 200 mesh screen sandwiched between 50 mesh screen and has given satisfactory performance. Future tests will aim at eliminating the bed support plate altogether.

2.6 Reliability and Maintenance

Comments on these aspects of equipment behaviour are made from the limited experience of 27 batch runs, giving 100 to 150 hours running time of which up to a half was at temperatures above 550°C.

The use of sintered metal bed support plates was an apparent weakness in the original design, although they have been widely used in fluid bed production plants. The plates were clamped between flanges at the bottom of the reactor. Various ways of installing the plates were tried without success. Recently the sintered plate was replaced with 200 mesh screen, which appears to be more reliable. However it is intended to eliminate this type of bed support altogether, and relevant tests have been successfully carried out in the stabilisation pulsed bed using a simple conical bed support.

The off-gas filters and blowback system have operated satisfactorily over the plant life time. If a filter were to fail it would be readily detected by a change in pressure drop). A back-up filter provides an added safeguard in the event of failure. The use of a cyclone separator for off-gas cleaning has been tried in the stabilisation unit without success.

The solenoid valves used to control blowback of the filters and to pulse the fluidising gas are a potential source of trouble, although malfunction is readily detected by abnormal pressure drop fluctuations. In a production facility, it would be prudent to have by-pass solenoid valves installed to allow maintenance without shut-down. An alternative to solenoid valves would be to use the type of cam-actuated poppet valves used in air-pulsed solvent extraction columns.

The reactor calrod heaters have performed without failure, having been subjected to a considerable amount of temperature cycling. However, should a heater fail, considerable maintenance problems exist with the current design. Fewer problems would be experienced if the reactor and heater (furnace) were mechanically separate, although heat transfer from the heaters to the reactor would be much less efficient.

The only other aspect of the operation which is specific to this equipment is the powder handling. Reliable techniques have been developed for conveying powders from vessel to vessel and no insurmountable problems are foreseen.

Compared with other types of gas/solids contactors (rotary kilns, moving beds etc.) the pulsed fluidised bed is probably the most reliable.

3. EXPERIMENTAL RESULTS

3.1 Product Characteristics

The results of tests on some of the powders produced since the problems discussed in Section 2.5 were identified are given in Table 1. The ADU feed materials in all experiments were precipitated in a continuous precipitator at pH 7.2. All powders gave pellets with a uniform microstructure free from cracks and segregated porosity, except Experiments 26 and 27 where some segregated porosity was observed. This problem could readily be overcome by micronising these powders (Ramm - A.A.E.C. private communication). The hour glass taper on all pellets was less than 0.005 inches. Densities up to 10.6 g/cm^3 have been obtained, and it is anticipated that higher sintered densities can be achieved by using ADU precipitated at higher pH (Janov and Afredson - A.A.E.C. unpublished work).

3.2 Product Variation with Operating Conditions

The physical characteristics of the UO_2 can be expected to be sensitive to the thermal history of the powder, the ADU precursor and the fluidising conditions. Product surface area decreased with an increase in reduction temperature, as shown in Figure 4. The data show a spread of approximately $\pm$ 0.5 m^2/g about a mean curve, but this is not surprising considering the differences between ADU batches, the batch sizes and the fluidising conditions. It appears that a change of 20°C in reduction temperature in the range 600 to 700°C is accompanied by a change of approximately 0.5 m^2/g in the surface area of the UO_2 powder.

Runs 22 to 25 inclusive were carried out at a reduction temperature of 620°C to examine the influence of fluidising conditions on the pellet density and microstructure. The tests were conducted as a half replicate fractional factorial design (Davies 1961); the factors and levels chosen are given in Table 2. All four powders gave pellets with acceptable microstructures and the differences between pellet densities were small (Table 1). At the levels chosen, the factors do not appear to have any significant effect on the sintering characteristics of the powders.

3.3 Heat and Mass Balance Considerations

Complete reduction of calcined ADU in excess hydrogen at 600°C takes approximately 2 minutes (Huntington et al. 1958). To achieve this rate of conversion in a pulsed fluidised bed charged with 4 kg of ADU would require a hydrogen supply rate in excess of 5 std ft^3/minute and a heat removal rate of 260 Btu/minute, corresponding to a wall temperature approximately 100°C lower than the bed temperature. Figure 3 shows an observed temperature excursion resulting from a hydrogen input of only 2 std ft^3/minute. Since it is important to reduce the bulk of the material at the same temperature to produce a uniform product, this type of temperature excursion must be avoided. Thus for batch operation the reaction rate should be controlled by the hydrogen supply rate, with the establishment of steady state temperature conditions for the majority of the reduction period (R on Figure 3).

From laboratory data (Price - A.A.E.C. private communication) the effective reduction reaction can be assumed to be

$$U_3O_8 + 2H_2 = 3UO_2 + 2H_2O \quad ,$$

as a result of the self-reduction of ADU at approximately 420°C. Taking the steady state period referred to earlier as the time for complete reduction, the efficiency of hydrogen utilisation in our experiments is estimated to vary from 50 to 75 per cent. Off-gas analysis will provide further information on the hydrogen economy.

From an analysis of the steady state conditions during and after the reaction, the bed to wall heat transfer coefficient is estimated as 85 Btu/h ft^2 F°, which compares favourably with a figure of 80 Btu/h ft^2 F° estimated from heat transfer studies in a glass mock-up pulsed fluidised bed (Alfredson - A.A.E.C. unpublished work). A coefficient of 85 corresponds to a gas inlet temperature of 135°C, which suggests that the gas preheat system should be improved.

4. DISCUSSION OF ALTERNATIVE OPERATING CYCLES

Sequential batch operation does not represent an optimum use of reactor space, since there is a reduction in bed volume of at least 50 per cent when ADU is converted to UO_2. Thus in the 5 inch diameter reactor, the maximum bed height which we would consider corresponds to approximately 8 kg ADU or as much as 16 kg UO_2, which is equivalent to a static bed height to diameter ratio of 5. Two alternative schemes of batch/continuous operation can be considered which allow the bed to build up close to the maximum before discharge. These two schemes are discussed briefly in this section and compared with continuous operation.

4.1 Intermittent Feed and Reduction

Approximately 8 kg ADU is charged to the hot reactor at a steady rate of 1 kg/minute. This material is heated up to 600°C in nitrogen and then reduced with N_2/H_2 at 625°C. After reduction, a further 4.5 kg ADU is added, brought to temperature and reduced. A third charge of 2.5 kg ADU can then be added, leaving a fully reduced bed of 12 kg UO_2. As a consequence of the 50 per cent volume reduction from ADU to UO_2, the size of successive ADU batches decreases by approximately half, and a stage is reached when the batch size is insignificant. In this example, the feed sequence is terminated after the third batch. The amount of UO_2 produced is estimated at 12 kg over a period of 1 hour.

In this type of operation, control of the bed temperature requires careful consideration, since during calcination, heat passes from the wall to the bed, whereas during reduction the position is reversed. This can be achieved by having a temperature controller adjusting the wall heaters or coolers respectively, to keep a constant wall temperature or a specified bed temperature. Since the reactor body has a large heat capacity, the wall temperature will have a slow response and the bed temperature is the preferred control parameter. However this will require a set point adjustment from say 600 to 625°C as the hydrogen is introduced. Obviously this type of operation is labour intensive, requiring almost continuous manual control of powder feeding operations, inlet gas composition etc.

4.2 Continuous Feed/Intermittent Discharge

4.2.1 Alternative Cycles

This scheme is similar to continuous operation with simultaneous ADU feed, calcination and reduction, except that the bed is allowed to build up to the maximum level, approximately 16 kg UO_2, before discharging any product. A portion of the UO_2 is retained in the reactor to provide adequate bed depth for wall to bed heat transfer at the beginning of the next cycle.

The rate of addition of ADU is determined from the reactor heat balance, which must consider the sensible heat increases of the gas and solid feed, the heat of decomposition of the ADU, the exothermic heat of reduction and the wall to bed heat transfer. The allowable ADU feed rate increases with bed depth, that is, with wall to bed heat transfer. Thus the initial feed rate is determined by the initial bed depth, which is selected either as a minimum for adequate fluidisation (say, 4 kg UO_2 corresponding to a bed depth of 8 inches), or as sufficient to support the heat transfer requirements of a significant feed rate (say, greater than 2 kg ADU/h). In this work, the latter consideration determines the initial feed rate. The final feed rate may be limited by the hydrogen supply rate required for the reduction reaction.

Many alternative strategies are possible, and some examples are summarised in Table 3, and discussed below. In each case, the hydrogen flow is continued for approximately 5 minutes after the ADU feed is stopped to ensure complete conversion to UO_2 before the product is discharged.

Example 1. This is based on a total gas flow of 2 std ft^3/min (the same gas flow has proved to be adequate for beds of 7 kg ADU, which corresponds to a bed length/diameter ratio (L/D) of approximately 4.5). Cracked ammonia is used as the fluidising gas.

Example 2. A flow rate of 2 std ft^3/min may not be adequate for a 16 kg bed of UO_2, with a L/D ratio of 5. This example shows the marginal drop in throughput and hydrogen economy if the maximum L/D ratio is lowered to 4.

Example 3. An alternative to reducing the maximum L/D ratio is to increase the input gas stream with increasing bed depth. This example considers the effect of increasing the hydrogen flow from 1 std ft^3/min initially to a final 3 std ft^3/min, with a constant nitrogen supply of 1 std ft^3/min. Comparison of Examples 1 and 3 shows that the latter strategy results in a slight drop in throughput and a more significant drop in hydrogen economy.

Example 4. This example shows that for an unchanging gas flow rate of 4 std ft^3/min with 75 vol.% hydrogen, the hydrogen usage is poor.

Example 5. For the increasing gas rate method (see Example 3), further hydrogen economy is achieved by replacing the hydrogen with cracked ammonia.

Example 6. All previous examples have been based on a wall-to-bed temperature difference of 25°C. This is considered an acceptable figure since, although typical values experienced during batch operation have been 5 to 10°C, higher values have been encountered without obvious detriment. Comparison of this example with Example 1 gives a clear indication of the marked loss in throughput and hydrogen economy if the maximum temperature difference is only 10°C.

Example 7. This shows the benefit to be gained from improving the inlet gas preheat system; compare Examples 6 and 7.

The most promising strategies are given by Examples 1, 2 and 5. Of these, Example 1 is the least conservative since it assumes that 2 std ft^3/min gas rate is adequate for an L/D of 5. The other two examples adopt a more conservative approach by either reducing the maximum bed or by increasing the final gas rate. This latter approach is favoured since it promises a higher throughput and a better hydrogen economy. Further improvements would be expected by improving the gas preheat system.

Continuous feed / intermittent discharge operation could be readily automated, requiring manual control for a short period at the end of each cycle. It is an attractive proposal for a production plant. Figure 5 shows the proposed equipment flowsheet and includes the control system. The wall temperature is held steady to ± 5°C by conventional on/off temperature controllers. The ADU feed rate increases with time, as observed earlier, and in Example 5 the hydrogen (or cracked ammonia) flow also increases with time. The bed temperature is used as the input signal to the ADU feeder controller, since bed temperature is sensitive to changes in ADU feed rate. The reactant gas flow is arranged to increase in proportion to the ADU feed rate. Alternatively, by measurement of the off-gas composition, the reactant gas flow could be adjusted to give a fixed excess of hydrogen. If it is desired to put a limit on the input hydrogen rate to increase the cycle time, the feeder/bed temperature control loop will be self-adjusting and give a reduced rate of increase of ADU feed rate.

4.2.2 Scale-up

Table 4 gives calculated data for 5 and 10 inch diameter reactors showing the effects of scale-up on process data. Increasing the reactor diameter by a factor of 2, increases the cycle time by a similar factor and the throughput by a factor of 4. These factors are consistent with the observation that, for a given maximum L/D ratio, bed volume increases with $(\text{diameter})^3$, and feed rate, which is controlled by the heat transfer surface, increases with $(\text{diameter})^2$. In general for this type of batch/continuous operation:

$$\text{throughput} \propto (\text{diameter})^2$$

$$\text{cycle time} \propto \text{diameter}.$$

It should be noted that Reaktor-Brennelemente GmbH (RBG) in Germany use the continuous feed/intermittent discharge approach for the calcination and reduction of ammonium uranyl carbonate (AUC) to UO_2 in a 30 cm (12 inch) diameter stirred fluidised bed (RBG - private communication). Approximately 330 kg AUC is fed into the reactor at a steadily increasing rate over a period of 4 hours, producing 150 kg UO_2 product. The hydrogen usage is approximately twice stoichiometric. The RBG cycle has a UO_2 throughput of 37.5 kg/h, which is somewhat less than that calculated for the 10 inch diameter pulsed bed reactor in Table 4. A major factor contributing to the lower throughput is that the RBG reactor is fully discharged at the end of the cycle. For the assumptions made in this report, it can be shown that bed weight increases exponentially with time. Since the allowable feed rate is a function of the size of the bed and the surface area available for heat transfer, only small feed rates can be used at the beginning of a process cycle with a near empty bed. A time penalty is incurred whilst the bed builds up to a reasonable level; the smaller the initial bed, the greater the penalty. For the proposed pulsed bed cycles, a portion of the batch (not less than one quarter) is assumed to be retained in the reactor at the end of each cycle.

The proportion of bed retained is somewhat arbitrary, and for the purpose of this exercise has been chosen to give a significant feed rate. If, however, it is thought necessary to increase the batch cycle time, to reduce labour costs, accepting the lower throughput per unit reactor volume, this can be arranged by retaining a smaller proportion of the bed and having a very low initial feed rate. A simpler expedient may be to limit the hydrogen flow rate, which puts a constraint on the ADU feed rate in the later stages of the cycle. As observed in Section 4.2.1, the proposed control system will reduce the rate of increase of ADU supply rate under conditions of limiting hydrogen supply.

4.3 Continuous Operation

Compared with the batch cycles discussed earlier, continuous operation is much more amenable to automatic control and should also give a more consistent product since steady state operating conditions are maintained. The proposed equipment flow sheet is shown in Figure 6.

There is, however, an inherent difficulty associated with continuous flow systems which derives from the spread of residence times of the particles. Thus if a fraction of the particles escape from the reactor before the time for complete conversion has elapsed, the overall product conversion will be less than 100 per cent. Obviously this situation need not arise with the batch cycles considered.

To estimate the product conversion and throughput it is necessary to combine chemical kinetic data with residence time distribution data. From the available kinetic data (Huntington et al. 1958, and Belle 1961), the time required for complete conversion of calcined ADU, in excess hydrogen, is estimated as 100 seconds in 100 per cent hydrogen, 133 seconds in 75 vol.% hydrogen and 200 seconds in 50 vol.% hydrogen in nitrogen. Residence time distribution studies on conventionally fluidised beds (Kunii and Levenspiel 1969) have shown that the bed is well mixed, that is, all particles have an equal chance of leaving in the product stream. This situation probably will not apply to the proposed pulsed bed arrangement in which ADU is fed to the top of the bed and UO_2 product removed from the bottom. However the overall conversion data have been calculated on the basis of a well-mixed bed to obtain conservative figures.

Table 5 gives the estimated throughputs, conversions and stoichiometric hydrogen requirements for mean particle residence times of 1 hour and $1\frac{1}{2}$ hours, assuming a total gas flow rate of 2 std ft^3/min and an L/D ratio of 4.

These estimates should be compared with the figures available for the continuous calcination and reduction of ADU in a 6 inch diameter pulsed bed reactor at Rio Algom Mines Ltd. in Canada. Acceptable UO_2 was produced at 14.5 kg/h with a 1 hour mean residence time, reaction temperatures in the range 600 to 650°C, and a gas flow of about 3 std ft^3/min with 50 vol.% hydrogen, representing approximately twice the stoichiometric requirement (Rio Algom Mines Ltd. - private communication). Since no unreduced ADU could be detected in the UO_2 product by the Rio Algom workers, this confirms the conservative nature of our assumptions in that Table 5 indicates only 97.2 per cent conversion under these conditions.

As a conservative estimate of continuous reactor throughput, the $1\frac{1}{2}$ hours residence time and 75 vol.% hydrogen in nitrogen gas stream are nevertheless recommended. The poor hydrogen economy is determined by the scale of operation, as is shown in the next section.

4.3.1 Scale-up

Reactor volume, and hence throughput, increases with (diameter)^3, for a fixed L/D ratio, whereas gas flow rate can only increase with (diameter)^2. These factors combine to improve the hydrogen economy in larger reactors. Projected data for a 10 inch diameter reactor, with a mean residence time of $1\frac{1}{2}$ hours are shown below:

Gas flow rate	8 std ft^3/min
Hydrogen concentration	75 vol.%
UO_2 throughput	70 kg/h
Conversion	98.8 wt.%
Hydrogen required	1.8 x stoichiometric

4.4 Comparison of Continuous Feed/Intermittent Discharge and Continuous Operation

As observed earlier, continuous operation should have a lower labour demand and give a more consistent product than any type of batch operation. Table 6 compares the estimated data for 5 and 10 inch diameter reactors for both modes of operation. For the 5 inch diameter reactor, continuous-feed/intermittent-discharge operation has advantages over continuous operation for throughput, conversion and hydrogen economy. However for the larger reactor, continuous operation has advantages, although the differences would be reduced if higher gas inlet temperatures, larger wall-to-bed temperature differences and a shorter cycle time were used for the batch/continuous operation (changes in these factors would not affect continuous operation).

5. PROPOSED DEVELOPMENT PROGRAMME

It has been demonstrated that the pulsed bed reactor, operated batchwise, can produce powders which can be sintered to greater than 10.5 g/cm^3; it is proposed to accept this figure as an interim target. Further development of the pulsed bed reactor is to be an investigation of continuous feed/intermittent discharge operation and continuous operation. During these investigations higher sintered densities will be sought by using ADU precipitated at a higher pH and by sintering at 1600°C.

5.1 Continuous Feed/Intermittent Discharge Operation

The immediate aim of the programme will be to demonstrate the feasibility of this type of operation for the production of ceramic grade UO_2, using a flow-sheet similar to that shown in Figure 5; the necessary modifications are being carried out at present. Initially manual control of feed rates will be used. The particular goals, many of which are interdependent, are as follows:

(i) to determine the maximum allowable bed depth,
(ii) to determine the optimum gas and solid feed rate strategy,
(iii) to obtain further data on heat transfer,
(iv) to improve the gas preheat system,
(v) to assess the quality control of the product, and
(vi) to establish a viable control system.

5.2 Continuous Operation

Continuous operation will not be attempted until the above-mentioned batch/continuous programme has been concluded. However, some relevant studies have been initiated; they are:

(i) a determination of ADU reduction kinetics,

(ii) measurement of pulsed bed residence time distributions,

(iii) the development of a suitable bed level indicator for control purposes, and

(iv) the development of continuous powder feeding techniques.

Continuous operation requires additional equipment, such as feeders, product take-off devices, and containers. The aims of the programme will be briefly:

(i) to determine the maximum throughput, and/or the minimum mean residence time,

(ii) to determine the hydrogen economy, and

(iii) to assess the control of the plant.

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TABLE 1

RESULTS OF TESTS ON UO_2 POWDERS PRODUCED

UNDER BATCH OPERATING CONDITIONS

Experiment No.	Surface Area (m^2/g)	O/U	Pressing and Sintering Conditions	Green Density (g/cm^3)	Sintered Density (g/cm^3)
22	5.6	2.15	A	5.5	10.56
23	4.9	2.14	A	5.5	10.60
23M	4.9	2.14	B	5.48	10.48
23M	4.9	2.14	C	5.63	10.64
24	6.5	2.10	A	5.40	10.50
25	6.9	2.19	A	5.35	10.50
25M	6.9	2.19	B	5.51	10.39
25M	6.9	2.19	C	5.51	10.56
26	5.3	2.17	A	5.55	10.44
27A	6.1	2.15	A	5.5	10.50
27B	4.9	2.11	A	5.6	10.50

M UO_2 powder was micronised before pellet fabrication

Pressing and sintering conditions

A Isostatic pressing, 20 tons/in^2, 4 h at 1500°C in hydrogen

B Automatic pressing, 10,000 lb/in^2 precompaction, 20 tons/in^2 press, 4 h at 1500°C in hydrogen

C Automatic pressing, 10,000 lb/in^2 precompaction, 25 tons/in^2 press, 4 h at 1600°C in hydrogen

TABLE 2

DESIGN OF FACTORIAL EXPERIMENT ON PULSED FLUIDISATION

Factor	Symbol	+ Level	- Level
ADU particle size	A	-20 mesh	-100 mesh
Pulsing conditions	B	0.1 ft^3 pulse chamber 2 std ft^3/min 30 cycles/min	0.4 ft^3 4 ft^3/min 40 cycles/min
Inert gas purity	C	oxygen-free nitrogen (< 5 ppm O_2)	service nitrogen (up to 500 ppm O_2)

TABLE 3

ALTERNATIVE STRATEGIES FOR CONTINUOUS FEED/INTERMITTENT DISCHARGE OPERATION

Example No.	Fluidising Gas				Bed Weight		L/D Ratio Max.	Cycle Time (minutes)	Wall-Bed ΔT (°C)	Gas Inlet Temperature (°C)	Throughput (kg UO_2/h)	Hydrogen Required (x stoichiometric)
	Initial		Final		Initial	Final						
	Flow Rate (ft^3/min)	Hydrogen Concentration (vol.%)	Flow Rate (ft^3/min)	Hydrogen Concentration (vol.%)	kg UO_2	kg UO_2						
1	2	75	2	75	4	16	5	55	25	125	12	2
2	2	75	2	75	4	13	4	50	25	125	11	2.5
3	2	50	4	75	4	16	5	60	25	125	11.5	3
4	4	75	4	75	6	16	5	65	25	125	9.5	6
5	2	37.5	4	56	4	16	5	60	25	125	11.5	2
6	2	75	2	75	8	16	5	100	10	125	5	6
7	2	75	2	75	6	16	5	90	10	325	7	4.5

TABLE 4

A COMPARISON OF PROCESS DATA FOR 5 INCH AND 10 INCH DIAMETER REACTORS:

CONTINUOUS FEED / INTERMITTENT DISCHARGE OPERATION

Reactor Diameter (in.)	Fluidising Gas				Cycle Time (minutes)	Throughput (kg UO_2/h)	Hydrogen Required (x stoichiometric)
	Initial		Final				
	Flow Rate (ft^3/min)	Hydrogen Concentration	Flow Rate (ft^3/min)	Hydrogen Concentration			
5	2	37.5	4	56	60	11.5	2
10	8	37.5	16	56	120	50	2.5

Assumptions (i) wall-bed ΔT = 25°C

(ii) gas inlet temperature = 125°C

(iii) maximum L/D ratio = 5

TABLE 5

ESTIMATED PROCESS DATA FOR THE CONTINUOUS OPERATION OF A 5-INCH DIAMETER PULSED BED REACTOR

Mean Residence Time (hours)	Gas Composition (hydrogen vol.%)	Throughput (kg UO_2/h)	Conversion (wt.% UO_2)	Hydrogen Required (x stoichiometric)
1	50	13	97.2	1.6
1	75	13	98.1	2.4
1.5	50	8.7	98.2	2.3
1.5	75	8.7	98.8	3.5

TABLE 6

COMPARISON OF CONTINUOUS FEED/INTERMITTENT DISCHARGE OPERATION AND CONTINUOUS OPERATION

Conditions	5 inch Diameter Reactor		10 inch Diameter	
	Batch/ Continuous	Continuous	Batch/ Continuous	Continuous
	A	B	C	D
Throughput (kg UO_2/h)	11.5	8.7	50	70
Product composition (wt.% UO_2)	100	98.8	100	98.8
Hydrogen requirements (x stoichiometric)	2	3.5	2.5	1.8

A 1 hour cycle; gas flow increases from 2 std ft^3/min at 37.5 vol.% hydrogen to 4 std ft^3/min at 56 vol.% hydrogen. L/D (max.) ratio = 5 (Example 5, Table 3).

C 2 hour cycle; gas flow increases from 8 std ft^3/min at 37.5 vol.% hydrogen to 16 std ft^3/min at 56 vol.% hydrogen. L/D (max.) ratio = 5. (Table 4).

B 1.5 hours mean residence time, 2 std ft^3/min at 75 vol.% hydrogen. L/D (max.) ratio = 4. (Table 5).

D 1.5 hours mean residence time, 8 std ft^3/min at 75 vol.% hydrogen. L/D (max.) ratio = 4.

BB Blowback
BF Backup filter
FC Differential flow controller
FM Flowmeter
PC Pulse chamber
ST Solenoid timer
SV Solenoid valve
TC Temperature controller
TR Temperature recorder

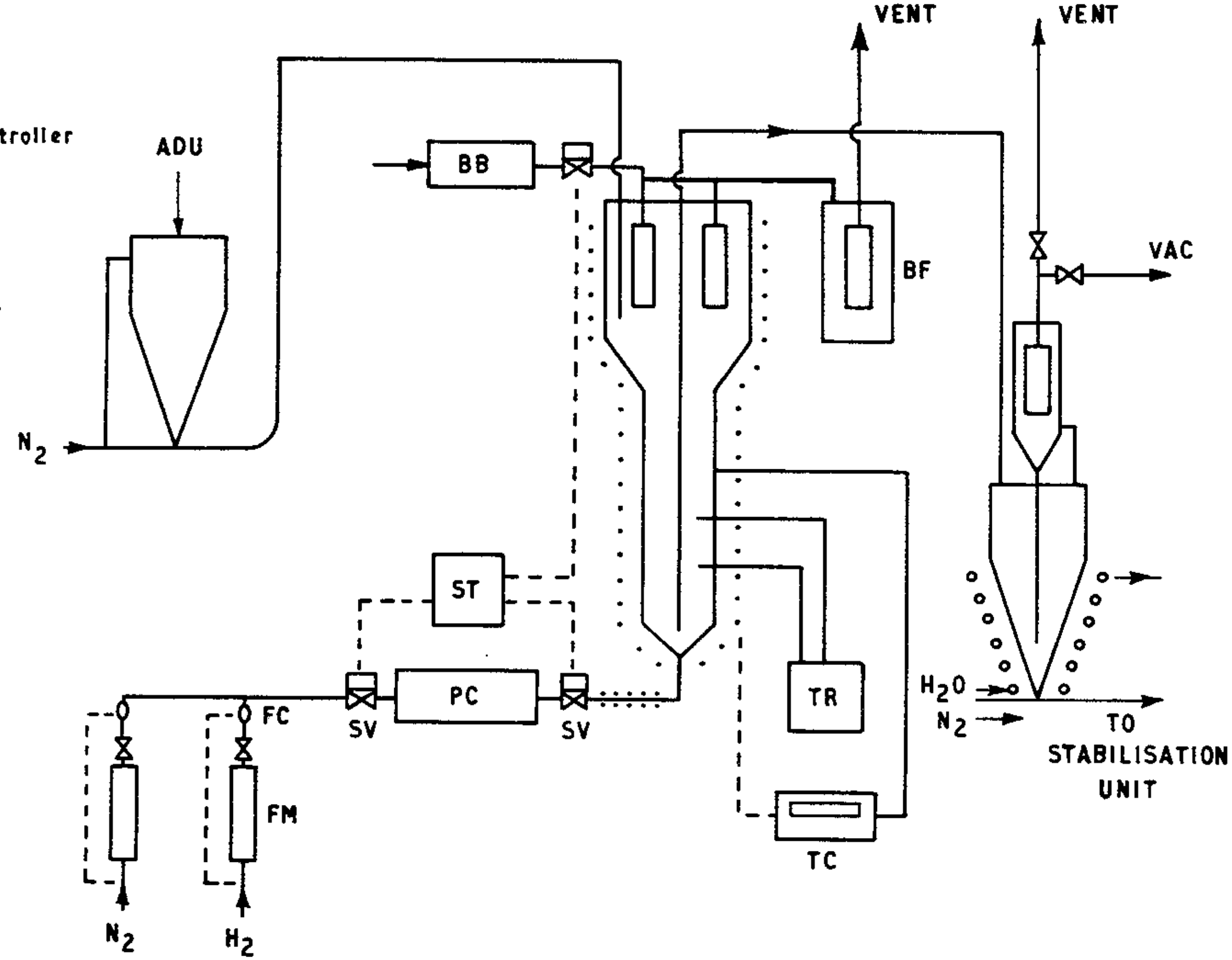

FIGURE 1. EQUIPMENT FLOWSHEET FOR BATCH OPERATION

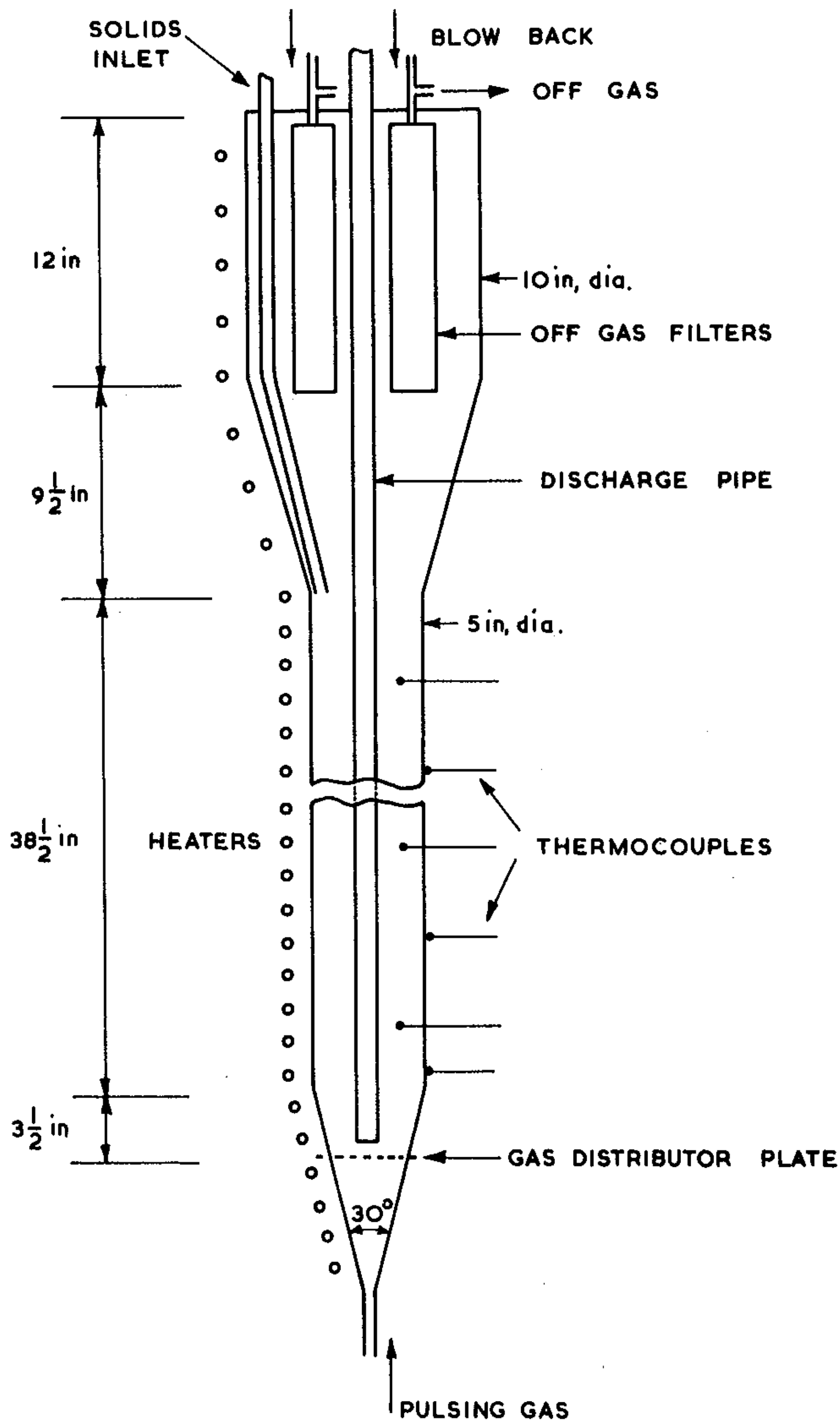

FIGURE 2. PULSED FLUIDISED BED REACTOR

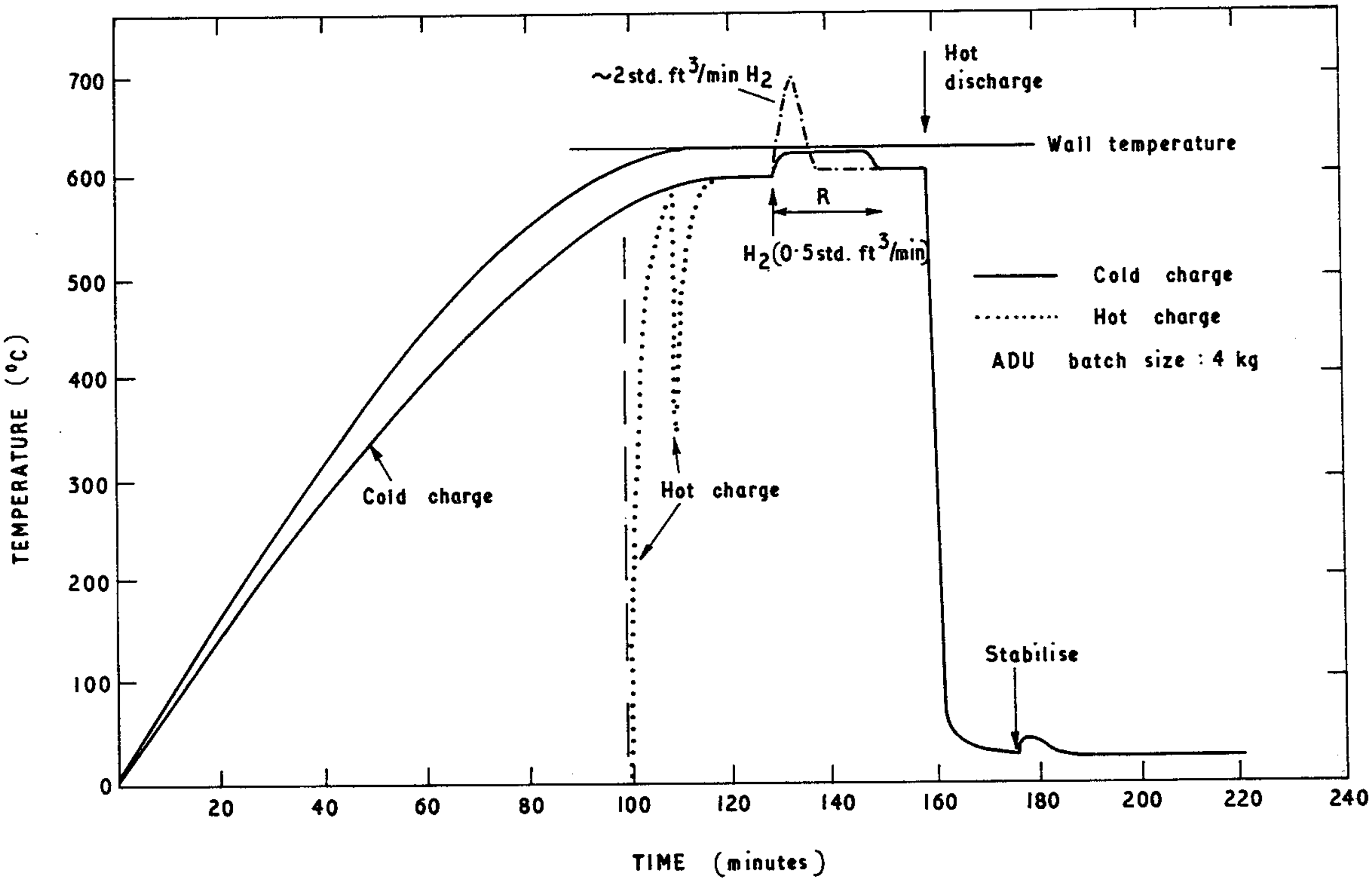

FIGURE 3. TEMPERATURE HISTORY FOR BATCH OPERATION

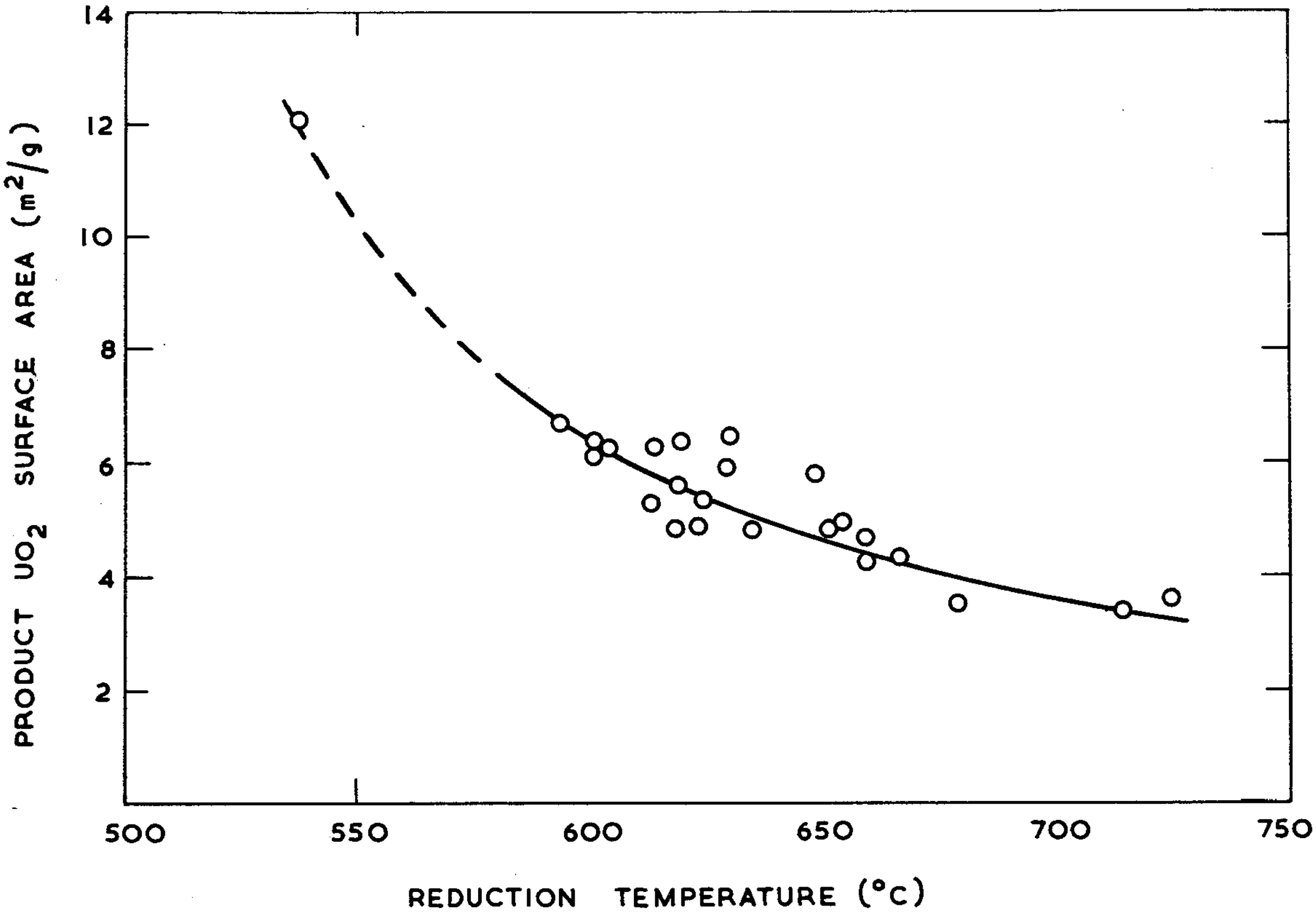

FIGURE 4. UO_2 SURFACE AREA AS A FUNCTION OF REDUCTION TEMPERATURE

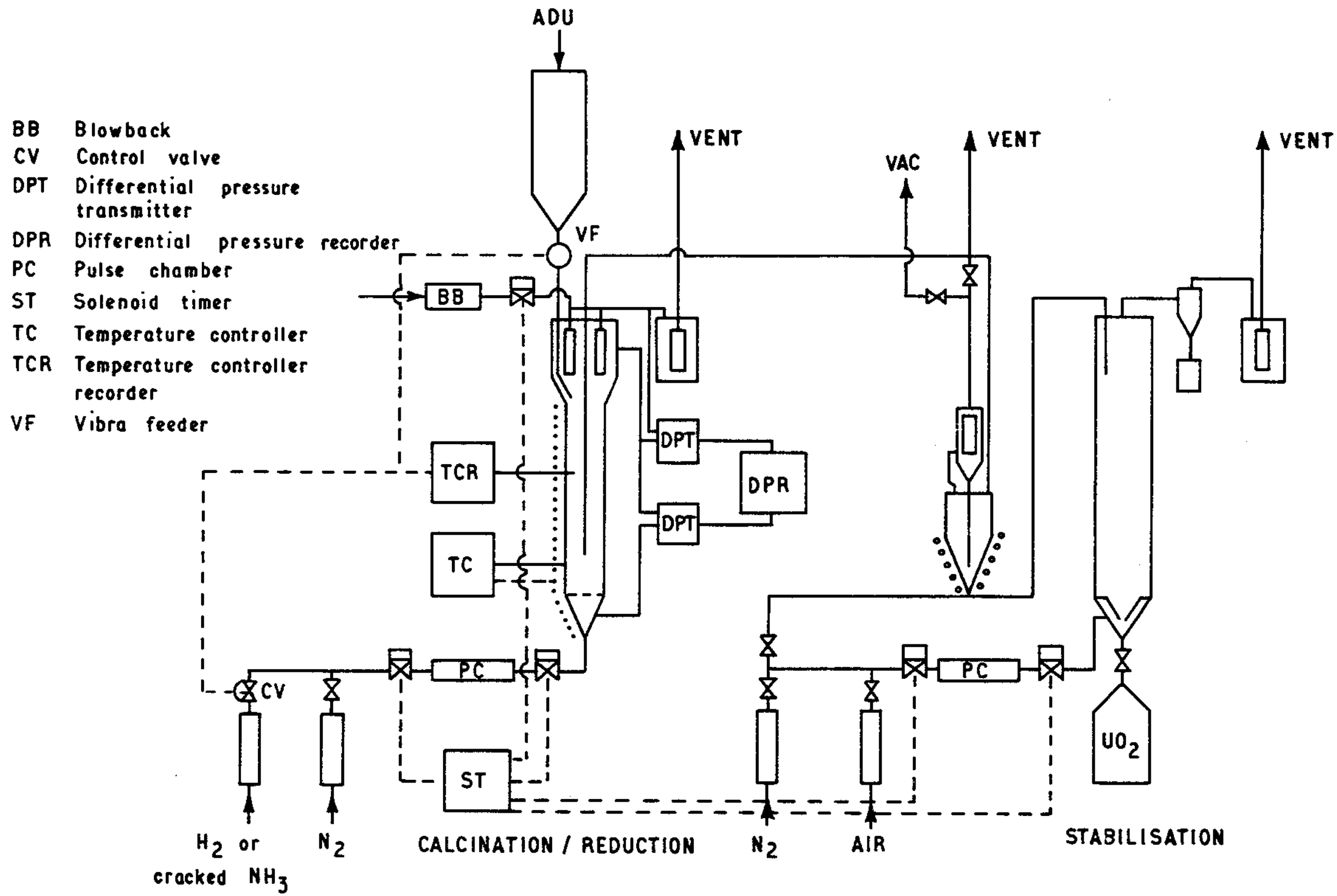

FIGURE 5. EQUIPMENT FLOWSHEET FOR BATCH/CONTINUOUS OPERATION

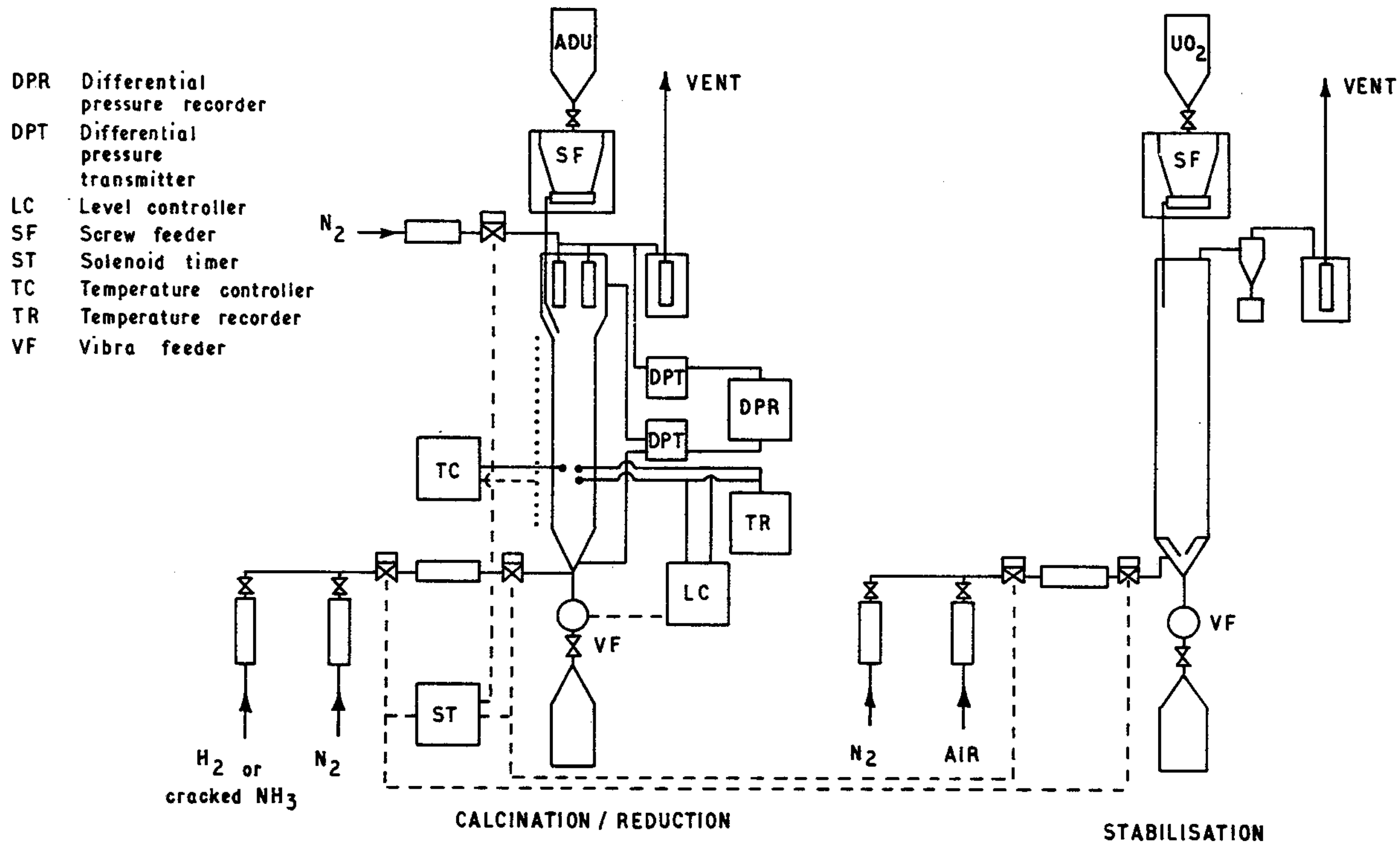

FIGURE 6. EQUIPMENT FLOWSHEET FOR CONTINUOUS OPERATION