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# AUSTRALIAN ATOMIC ENERGY COMMISSION
## RESEARCH ESTABLISHMENT
## LUCAS HEIGHTS

# INVESTIGATION OF BATCH-TRAY CALCINATION-REDUCTION OF AMMONIUM DIURANATE TO URANIUM DIOXIDE

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# INVESTIGATION OF BATCH-TRAY CALCINATION-REDUCTION OF AMMONIUM DIURANATE TO URANIUM DIOXIDE

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## ABSTRACT

Process cycles have been developed on the half-kilogram scale for the conversion of ADU to $UO_2$ powder of specified surface area in the range 3-10 $m^2/g$. The recommended cycle involves calcination of ADU in nitrogen during heating to the reduction temperature, followed by reaction with 30 volume per cent hydrogen in nitrogen and stabilisation at ambient temperature with 2 volume per cent oxygen in nitrogen. $UO_2$ surface area increased from 3 to 10 $m^2/g$ as the reduction temperature changed from 700 to 500°C, but was not sensitive to the surface area of the precursor ADU or the hydrogen flow rate.

# CONTENTS

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## 1. INTRODUCTION

Uranium dioxide powder for the fabrication of dense fuel pellets is usually produced from ammonium diuranate (ADU). The strong influence of ADU precipitation conditions on the sinterability of $UO_2$ powder has been discussed previously (Janov et al. 1971). The calcination-reduction cycle used for converting the ADU to $UO_2$ also influences the sinterability of the $UO_2$ powder; in particular, the temperatures of calcination and reduction determine the surface area of the $UO_2$ powder. As the surface area of $UO_2$ powder (produced from the same ADU) increases, the density of pellets pressed and sintered under standard conditions also increases (Driear 1961). $UO_2$ powders for fabrication into fuel pellets by cold-pressing and sintering should have surface areas in the range 3-9 $m^2/g$ because powders with surface area less than 3 $m^2/g$ do not generally give sufficiently dense pellets while powders with surface area greater than 9 $m^2/g$ are difficult to stabilise with respect to oxygen content (Reeve, A.A.E.C. private communication).

Although other properties such as packing and pressing characteristics may also be important in pellet fabrication, these are affected by the type of equipment used for reduction as well as the process cycle. This report is concerned only with control of the surface area of the $UO_2$ powder. The development of standard process cycles for the batch-tray calcination-reduction of ADU to $UO_2$ using hydrogen-nitrogen mixtures to produce $UO_2$ powders with surface areas in the range 3-10 $m^2/g$ is described.

## 2. LITERATURE REVIEW

Ammonium diuranate can be converted to $UO_2$ by two routes, both of which are considered in this investigation:

(i) Calcination of ADU to $UO_3$ or $U_3O_8$ in an inert or oxidising atmosphere followed by reduction of the calcined product to $UO_2$.

(ii) Direct conversion of ADU to $UO_2$ where a reducing atmosphere is maintained throughout the process.

Woolfrey (1968) has given a comprehensive review of the preparation and calcination-reduction of ammonium uranates which emphasises the composition and morphology of the various compounds. In this section we consider only published information relating to the process cycles used for calcination-reduction and particularly the effect of temperature on the surface area of $UO_2$ and the intermediate products. Various techniques for the stabilisation of $UO_2$ powders are also briefly reviewed.

### 2.1 Calcination of ADU to $UO_3$ and $U_3O_8$

The decomposition of ADU in air has been studied by a number of authors including Landspersky et al. (1963), Notz et al. (1960) and Ippolitova et al. (1961). Although their results are not in complete agreement, there is general agreement about the main features of ADU decomposition. As the calcination temperature is increased, ADU loses water and then in the range 350-450°C ammonia is liberated to form $UO_3$. According to Notz et al. (1960) and Ippolitova et al. (1961), further heating results in the exothermic formation of some $U_3O_8$ by reaction with evolved ammonia in the temperature range 450-500°C. The decomposition terminates at 640°C when all the solid has been converted to $U_3O_8$.

The surface area changes associated with calcination in air are shown in Figure 1. Various workers have used different techniques for measuring surface area (conventional BET, continuous flow BET, or permeability) and this often complicates comparison of their results. The surface area of the calcined ADU increases with temperature to about 350°C after which micro-sintering apparently commences and the surface area of the $UO_3$ and $U_3O_8$ decreases with increasing temperature. The discontinuity seen in Figure 1 at 600°C may be due to the use of different techniques for measuring surface area.

Similar data were obtained by Delmas and Holder (1963) using a rotary kiln furnace but the maximum surface area occurred at approximately 450°C (Figure 2). The residence time at the specified temperature was 15 to 20 minutes, but no details were given about the temperature gradient in the furnace. It is likely that some of the material reacted in the inlet side of the furnace at temperatures lower than specified. Delmas and Holder measured surface areas by the BET method, but unfortunately expressed them on a volumetric basis and, as the density of their samples is not given, a direct comparison cannot be made with the results of other workers.

Figure 1 also shows the effect of time of calcination on the surface area of ADU decomposition products. When samples were maintained at the maximum temperature, their surface areas (at temperatures above 350°C) were significantly lower than the surface areas of samples brought to the maximum temperature at 10°C per minute and then immediately withdrawn from the furnace. Most of this reduction of surface area with time occurred in the first four hours and increased soaking periods up to 70 hours had no significant effect. Delmas and Holder (1963) also found that the surface area of ADU decomposition products decreased with time (at least up to 3 hours) at 500 and 600°C, but at higher temperatures there was a negligible effect (Figure 3).

Very little work has been carried out on the decomposition of ADU in inert atmospheres. Woolfrey (A.A.E.C. private communication) studied the effect of calcination temperature on the surface area of ADU decomposition products in helium and obtained results qualitatively similar to those shown in Figure 1 with a sharp maximum in surface area at approximately 350°C. He also found that

ADU materials precipitated at different pH gave decomposition products with different surface areas.

### 2.2 Reduction of $UO_3$ and $U_3O_8$ to $UO_2$

The reduction of calcined ADU to $UO_2$ takes place in stages with the most commonly reported intermediate phase being $UO_{2.56}$ (Huntington et al. 1958, De Marco and Mendel 1960). The kinetics of the reactions are linear and the reported activation energies are in the range 26 to 39 kcal/mole.

The surface area of $UO_2$ produced from calcined ADU is dependent on the surface area of the starting $UO_3$ or $U_3O_8$ as well as the reduction temperature. The results obtained by Delmas and Holder (1963) using a rotary kiln furnace show the influence of both these factors on the surface area of $UO_2$ (Figure 4). As explained in Section 2.1, it is likely that some of the material reacted at temperatures lower than specified because of temperature gradients in the furnace. The $UO_2$ surface area decreased with increasing reduction temperature in the range 500 to 800°C for ADU calcined at 380 to 600°C. For calcination temperatures of 700 and 800°C, a maximum $UO_2$ surface area occurred at a reduction temperature of 600°C and it decreased with a further increase in reduction temperature. Similar results showing the dependence of $UO_2$ surface area on the temperature of ADU calcination in air have been reported by Imris et al. (1965), Jakes and Landspersky (1964) and Landspersky et al. (1963).

One of the main requirements of $UO_2$ powder production is that the powder must have uniform properties throughout a batch as well as between batches. To achieve this the temperature of ADU calcination and reduction must be closely controlled. The reduction of $UO_3$ and $U_3O_8$ to $UO_2$ in hydrogen is exothermic,

$$UO_3 + H_2 \longrightarrow UO_2 + H_2O(g) \qquad \Delta H_{298} = -23.8 \text{ kcal/mole}$$

$$\frac{1}{3} U_3O_8 + \frac{2}{3} H_2 \longrightarrow UO_2 + \frac{2}{3} H_2O(g) \qquad \Delta H_{298} = -12.9 \text{ kcal/mole}$$

To minimise temperature excursions during the reaction, Delange (1963) suggested the use of ammonia gas as the reductant because the dissociation of ammonia is an endothermic process and would tend to balance the heat liberated from the reduction reaction:

$$2NH_3 \longrightarrow N_2 + 3H_2 \qquad \Delta H = 22.1 \text{ kcal mole}$$

Delmas and Holder (1963) and others have also used a dilute mixture of hydrogen in nitrogen so that the nitrogen would remove the excess heat of reaction without causing undesirable temperature excursions with resultant product non-uniformity.

### 2.3 Direct Reduction of ADU to $UO_2$

Direct reduction of ADU to $UO_2$ in hydrogen was investigated extensively by Bourns and Watson (1961). Unfortunately, most of their reactions were characterised in terms of the final temperature reached. It is the temperature at which reduction actually occurs and not the final temperature during the reduction cycle which determines the surface area of the $UO_2$ powder, because $UO_2$ does not lose appreciable amounts of surface area by sintering below 800°C in hydrogen (Belle 1961).

Jakes and Landspersky (1964) reported a relationship (shown in Figure 5) between reduction temperature and $UO_2$ surface area in the range 600-900°C but their reduction procedure was not described. As the surface area of their $UO_2$ powders was quite high and did not vary greatly with temperature, it is probable that the temperature which they quote is the final temperature reached and that all the reductions actually occurred at some lower temperature during heating. Jakes and Landspersky also reported that $UO_2$ prepared from ADU calcined in the temperature range 200-500°C had a surface area twice that of $UO_2$ produced directly from ADU. Clayton and Aronson (1958) also found that $UO_2$ prepared from ADU calcined at 500°C had a higher surface area than $UO_2$ prepared directly from ADU when the final reduction temperature was 800-900°C. In their work, however, hydrogen was present during both heating and cooling, so reduction presumably took place at some lower temperature.

Woolfrey (A.A.E.C. private communication) has recently reduced ADU to $UO_2$ at precisely measured temperatures. His surface area results show a maximum at approximately 325°C after which there is a rapid decrease. Further, Woolfrey found that different parent ADU powders give $UO_2$ products with different surface areas. Jakes and Landspersky (1964) also found an influence of ADU precipitation conditions on $UO_2$ surface area, while others have found no relationship (Clayton and Aronson 1958).

### 2.4 Self-Reduction of ADU

ADU contains variable amounts of ammonia in its structure, the level depending upon the precipitation conditions and the manner in which it is washed, but typically there are 0.3-0.5 moles of ammonia per mole of $UO_3$ (Deptula 1962). When ADU is heated, this ammonia can cause substantial reduction of the solid decomposition product.

Pedregal and Solano (1958) produced $UO_{2.076}$ by heating ADU at 700°C in an enclosed furnace in the absence of a reducing gas. They postulated that the ammonia was first expelled from the solid and then dissociated in the gas phase to produce hydrogen which reduced the solid residue to $UO_{2.076}$. Price (A.A.E.C. private communication) recently showed that much of the self-reduction occurred before the ammonia was evolved from the solid and that when ADU was calcined in an inert atmosphere, $U_3O_8$ was nearly always produced irrespective of the initial ammonia content of the ADU. When ADU was calcined in air $UO_3$ was produced because the ammonia was oxidised before temperatures high enough to effect self-reduction were reached. When ADU was heated in hydrogen at 5°C per minute, self-reduction occurred at 400°C before reduction by hydrogen commenced at 430°C.

### 2.5 Stabilisation of $UO_2$ Powder

Stoichiometric $UO_2$ powder has a tendency to absorb oxygen exothermically on exposure to air and if the rate of absorption is not controlled the powder may ignite (Bannister 1967, 1968). The fabrication behaviour of the powder may be adversely affected by excessive absorption of oxygen and this should also be controlled. Stoichiometric $UO_2$ powders with surface areas greater than 3 $m^2/g$ must be treated before exposure to the atmosphere to control the absorption of excess oxygen. This process is termed stabilisation, and can be achieved by chemisorption of oxygen at low temperatures (Caputo and Perry 1961) or under conditions of limited oxygen access (EURAEC 1961). Caputo and Perry contacted $UO_2$ powder and cooled air at 10-15°C in a screw feeder. The EURAEC method used two volume per cent oxygen in nitrogen to effect stabilisation at room temperature over a period of 40 hours.

Stabilisation can also be effected by absorbing other species on the surface of the $UO_2$ powder. These probably retard or perhaps even prevent oxidation of the $UO_2$ surface. Bourns and Watson (1961) cooled $UO_2$ to room temperature in hydrogen and then covered it with dry ice. Stabilisation was complete when the dry ice had sublimed. Other gaseous inhibitors which have been used include water vapour, ammonia, carbon tetrachloride, various alcohols, ketones and hydrocarbons (Bannister 1967, 1968).

## 3. EXPERIMENTAL

### 3.1 Equipment

The calcination-reduction experiments were carried out in trays inside a closed reaction vessel which was inserted in an electrical resistance furnace. The cylindrical furnace and the disassembled reaction vessel with four trays in position are shown in Figure 6.

The reaction vessel and trays were made of A.I.S.I. 321 stainless steel. Fourteen trays, each 0.29 m diameter by 32 mm deep, could be accommodated on the frame which was connected to the top flange of the reaction vessel. The top flange and the main body of the reaction vessel, 0.31 m diameter by 0.95 m deep, were bolted together with a teflon gasket between them. The process gases were introduced through the top of the reaction vessel and directed via two tubes (vertical supports in the frame on which the trays rested) to the bottom of the vessel where they were released. The gases left the reaction vessel through a port located in the top cover, passed through a water-cooled condenser and were then released into a fume duct. A slight positive gas pressure was maintained inside the reaction vessel to prevent air from entering through any possible leaks.

The 5.4 kW furnace used three separate heating elements to give an even temperature profile and allow flexibility in operation. Nine stainless steel sheathed chromel-alumel thermocouples were located within the reaction vessel. Three were used with proportional controllers to control the temperature of the furnace and the remaining six provided a continuous temperature trace on a twelve-point recorder. The temperature within the trays did not vary by more than 20°C in the radial direction when checked with an inert powder at approximately 600°C. In the vertical direction the temperature did not vary by more than 25°C in the bottom 7 trays. However, all the reduction results given in this report were obtained with 500 g samples of ADU spread on one tray only and therefore the temperatures quoted are believed to be accurate to within 10°C.

### 3.2 Reaction Gases

Three gases were used: hydrogen to effect reduction, air to stabilise freshly reduced $UO_2$ and nitrogen as a diluent in the previous two cases and as the calcining atmosphere at other times. The hydrogen was 99.5 per cent pure and contained 10 p.p.m. oxygen and approximately 1000 p.p.m. water vapour. High purity cylinder nitrogen (28 p.p.m. water, 30 p.p.m. oxygen) was used in early experiments, but later service nitrogen containing 50 p.p.m. oxygen and 85 p.p.m. water vapour was used. The change had no effect. The oxygen for stabilisation was obtained from compressed air supplied to the laboratory ( ~ 1000 p.p.m. water).

### 3.3 Reduction Cycles

Two different process cycles were used. The first (subsequently referred to as Cycle I) was based on the work of Bourns and Watson (1961), the temperature of the furnace being raised at 100°C per hour in the manner shown in Figure 7a. The maximum temperature was sometimes varied, but in all cases a plateau was maintained at 450°C for one hour. With this cycle 30 volume per cent hydrogen in nitrogen was used until the end of the 450°C plateau, then the nitrogen was replaced by hydrogen to give a pure hydrogen atmosphere. A few runs with different initial hydrogen concentrations were also made. The total quantity of hydrogen used above 400°C was 4.2 times the theoretical amount required to convert $U_3O_8$ to $UO_2$ although a few experiments were made using different ratios. This was the same as that used by Bourns and Watson (1961) although they reported their usage as 2.8 times the theoretical amount required to convert $UO_3$ to $UO_2$. The hydrogen flow was maintained while the reduction furnace was cooled to room temperature.

In the second process cycle (Cycle II), the temperature of the furnace was raised as rapidly as possible (250°C/h) to a specified temperature and then maintained at that temperature for two hours (Figure 7b). Hydrogen was usually not admitted until the maximum temperature had been reached and only nitrogen was used during the heating period. A 30 per cent hydrogen/nitrogen mixture was used for reduction and 4.2 times the theoretical quantity of hydrogen was passed through the furnace during the reduction period. After the reduction period, the hydrogen was turned off and the reaction vessel was cooled to room temperature in a stream of nitrogen.

Variations from these basic cycles were also used and they will be described as they are encountered.

### 3.4 Stabilisation Cycles

Two different stabilisation procedures were used: dry ice stabilisation (Bourns and Watson 1961) and controlled oxidation with two volume per cent oxygen in nitrogen (EURAEC 1961). In the first procedure, dry ice was spread manually over the $UO_2$ powder as soon as the reaction vessel was opened. The powder was not disturbed until all the dry ice had sublimed; the powder was then sufficiently stable. Controlled oxidation was carried out by passing two volume per cent oxygen in nitrogen through the cold reaction vessel for 40 hours at a rate sufficient to supply five times the amount of oxygen required to convert the $UO_2$ to $UO_{2.1}$. It was later found to be sufficient to pass the same gas mixture at the same rate for only 16 hours (overnight) to effect satisfactory stabilisation (i.e. twice the amount of oxygen required to convert $UO_2$ to $UO_{2.1}$). Stabilisation using nitrogen saturated with ethyl alcohol for 2 hours (Cordfunke and Van der Giessen 1967) was also tested without much success.

### 3.5 Procedure

The weighed ADU (500 g) was placed on a segment of a circular tray to maintain a powder depth of 10-20 mm. This shallow bed depth was used to minimise variations in powder properties which have been observed with deeper beds (Bancroft and Watson 1958). These variations may be due to microsintering of crystallites during the exothermic reduction as a result of temperature excursions under the poor heat transfer conditions which exist in deep static beds of powder. The tray was positioned centrally on the frame so that it was in the most uniform temperature zone of the furnace. Several thermocouples were then imbedded in the powder, the reaction vessel was sealed, placed in the furnace, and purged with nitrogen before the reduction cycle was commenced. At the completion of the reduction cycle, the reaction vessel was removed from the furnace and cooled to room temperature. After stabilisation of the $UO_2$ powder, the reaction vessel was disassembled and samples for chemical analysis, surface area measurement and sintering tests were prepared by riffling.

### 3.6 Thermal Conductivity Cell

In a few experiments, a Gow-Mac 24-100 thermal conductivity cell with nickel filaments was used to continuously monitor the concentration of hydrogen in the off-gas from the reaction vessel. The off-gases were first passed through an absorption train consisting of molecular sieves and silica gel to remove traces of water vapour and ammonia and then metered at the rate of 600 $cm^3$/min through the sample side of the cell. Hydrogen analysis was unaffected by flow-rate variations in the range 100-700 $cm^3$/min. Nitrogen was passed through the reference side of the cell at 600 $cm^3$/min. The cell was operated at 85°C with a bridge current of 100 mA and was calibrated against known hydrogen-nitrogen mixtures.

### 3.7 Surface Area Measurements

The procedures used to measure the surface areas of $UO_2$ and ADU powders have been described previously (Janov et al. 1971). Both the classical BET method (Brunauer et al. 1938) and the continuous flow method developed by Nelsen and Eggertsen (1958) were used. The $UO_2$ was conditioned overnight at 300°C and the ADU at 50°C prior to these measurements. A vacuum of $10^{-5}$ torr was applied during conditioning in the classical BET method while a stream of nitrogen was passed over the samples during conditioning in the continuous flow method.

## 4. RESULTS AND DISCUSSION

### 4.1 Preliminary Experiments

Initially, Cycle I was investigated using various concentrations of hydrogen (10, 30 and 100 volume per cent) during the early part of the cycle and varying the quantity of hydrogen used above 400°C from 4.2 to 22.5 times that theoretically required to convert the uranium as $U_3O_8$ to $UO_2$. Although on some occasions $UO_2$ powders with surface areas less than 9 $m^2/g$ were produced (CE 1, 11 and 30, Table 1), high surface area $UO_2$ powders were generally obtained with this cycle. Various ADU starting materials were used in these experiments and this could partly account for the spread in $UO_2$ surface areas. However, even ADU powders of similar surface area, reduced in an identical manner (e.g. CE 26, 29, 30, 31 and 35, Table 1) gave markedly different $UO_2$ powders. As Cycle I did not give a reproducible $UO_2$ product and because the surface area of the $UO_2$ was generally greater than the required range (3-9 $m^2/g$) other reduction methods were tried.

Direct reduction of ADU to $UO_2$ with Cycle II using 100 per cent hydrogen from the beginning was investigated briefly. In four experiments, the maximum temperature was 500°C while in a further experiment the final temperature was 850°C. In each case, hydrogen was added at a rate sufficient to supply at least the theoretically required amount of hydrogen between 400 and 500°C. The surface areas of the $UO_2$ powders produced were 13.1, 12.9, 13.6 and 7.1 $m^2/g$ for the 500°C cycles while the 850°C cycle yielded a $UO_2$ powder with surface area 14.1 $m^2/g$. In the last case, the reduction obviously took place at approximately the same temperature as for the other four powders (400-500°C) and the further heating to 850°C had little effect on the surface area.

### 4.2 Effect of Reduction Temperature on $UO_2$ Surface Area

In the preliminary experiments described above, reduction could take place over a range of temperatures since hydrogen was present from the beginning of the cycle. Depending on the reactivity of the powder, a smaller or larger proportion of it reacted at the lower temperatures as the powder was progressively heated. However, if hydrogen is introduced at one temperature only then no doubt exists about the reduction temperature. In a series of experiments using Cycle II, ADU was heated to the reduction temperature in nitrogen only and 4.2 times the theoretically required quantity of hydrogen was then added as 30 volume per cent hydrogen in nitrogen at the specified temperature over two hours. Figure 8 shows the effect of reduction temperature on the surface area of $UO_2$ powders produced from the same ADU. The $UO_2$ surface area decreased from approximately 10 $m^2/g$ for a reduction temperature of 500°C to approximately 3 $m^2/g$ at 700°C. This trend is in agreement with the results of Delmas and Holder (1963) for ADU calcined below 600°C (Figure 4). These results indicate that in most of the preliminary calcination-reduction experiments in which high surface area $UO_2$ powders were obtained, the reduction reaction actually occurred at temperatures below 500°C.

Conversion of ADU to $UO_2$ by calcination in nitrogen followed by reduction at a fixed temperature in a 30 per cent hydrogen/nitrogen mixture (Cycle II) was therefore adopted as a standard cycle which allowed $UO_2$ powders of any surface area in the range 3-10 $m^2/g$ to be prepared by altering the reduction temperature in the range 500-700°C. Routine pilot-plant production has demonstrated the reproducibility of the $UO_2$ surface areas prepared by this method (Janov et al. - A.A.E.C. unpublished report).

### 4.3 Effect of Hydrogen Availability on $UO_2$ Surface Area

When Cycle I was used for reducing ADU to $UO_2$, the rate of hydrogen addition determined the temperature range over which reaction occurred because it governed the availability of hydrogen for reduction. This was demonstrated in a series of experiments in which the quantity of hydrogen available for reduction was varied from 4.2 to 1.5 times the theoretical requirement (Table 2). As the ratio of actual hydrogen supplied above 400°C to hydrogen theoretically required to convert $U_3O_8$ to $UO_2$ was decreased, the surface area of the $UO_2$ produced was lowered indicating that the reduction was forced to occur at higher temperatures. Results for two experiments carried out on the same ADU using Cycle II with reduction at 600°C are included in Table 2 for comparison and demonstrate the lower surface area obtained when all reduction actually occurred at 600°C.

Reduction at 600°C using Cycle II was not sensitive to the rate at which hydrogen became available within the experimental range. In two experiments using ADU powder with surface area 10.5 $m^2/g$, 4.2 times the theoretically required amount of hydrogen was introduced into the reaction vessel as a 30 per cent hydrogen/nitrogen mixture with reduction periods of two and four hours. There was no significant difference in the surface areas of the $UO_2$ powders produced (4.3 and 4.8 $m^2/g$).

### 4.4 Properties of Calcined ADU in Standard Process Cycle II

With the standard Cycle II process outlined in Section 4.2, control of the $UO_2$ surface area is achieved by varying both calcination and reduction temperatures. The composition and surface area of the intermediate calcined ADU product were therefore examined by interrupting the process cycle after calcination and cooling the furnace to room temperature. After sampling the calcined ADU, the furnace was reheated in nitrogen and the reduction completed by the standard cycle. Table 3 summarises the results of these experiments.

Above 600°C, the product of calcination was very nearly $U_3O_8$ in agreement with the results of Price (A.A.E.C. Private Communication) while at 500°C the oxygen/uranium ratio was 2.74. The surface area of the calcined ADU decreased with increasing temperature in the range 500-700°C in agreement with previous work for calcination in air (Section 2.1). The surface area of the subsequent $UO_2$ powders was lower than that of the calcined ADU except for calcination at 700°C. In this instance, $UO_2$ powders with essentially the same surface area as the calcined ADU were obtained for reduction at both 500°C and 700°C.

### 4.5 Analysis of Off-Gases During Reduction Reaction

Figure 9 shows typical data for the hydrogen concentration in the off-gases from the furnace during reduction at 600°C in the standard process

Cycle II. The reduction usually occurred in steps but it is not known whether this was chemically or physically induced. The total time required for reduction varied from 70 to 120 minutes and indicated that the cycle time could not be reduced below 2 hours at these hydrogen flow rates.

### 4.6 Influence of Parent ADU on $UO_2$ Surface Area

The surface area of $UO_2$ powder reduced at 600°C is fairly insensitive to the surface area and method of preparation of the parent ADU (Janov et al. 1971). Figure 10 shows the surface areas of $UO_2$ powders produced from a wide range of ADU powders using standard process Cycle II with reduction at 600°C in a 30 per cent hydrogen/nitrogen mixture. The ADU powders were produced both by single- and two-stage precipitation and cover a wide range of precipitation conditions. The surface areas of the ADU powders range from 4 to 37 $m^2/g$ but after reduction at 600°C all the $UO_2$ powders have surface areas in the range 3.4 to 6.4 $m^2/g$.

### 4.7 Stabilisation of $UO_2$ Powders

Both the controlled oxidation and dry ice methods were used for stabilising $UO_2$ powders in the surface area range 3 to 16 $m^2/g$. After stabilisation the powders were no longer pyrophoric, although their oxygen content continued to increase for many months. There was a strong positive correlation between O/U ratio and the surface area of $UO_2$ powders. A few days after stabilisation, the O/U ratio of powders with surface area 5 $m^2/g$ was approximately 2.08 and the O/U ratio of powders with surface area 14 $m^2/g$ was approximately 2.20.

Approximately one hour was allowed for dry ice stabilisation. However the controlled oxidation method was used exclusively in later experiments because it is probably more adaptable to plant operation. No attempt was made to shorten the controlled oxidation cycle below 16 hours (overnight) since it would not have effected a saving in working hours. In the Bouchet plant in France, controlled oxidation periods as short as 15-20 minutes have been used in rotary kiln furnaces (Delange et al. 1964) and similar results have been observed with pulsed fluidised beds (Fane and Alfredson, A.A.E.C. unpublished work).

### 4.8 Effect of $UO_2$ Surface Area on the Density of Sintered Pellets

Figure 11 shows the effect of $UO_2$ surface area on the density of pellets sintered at 1600°C for four hours. The powders were all produced from the same ADU precipitated at pH 7.2 but reduced at different temperatures (Figure 8). Sintered density increased slightly from 10.64 $g/cm^3$ for a $UO_2$ powder with a surface area of 3 $m^2/g$ to 10.85 $g/cm^3$ for a powder with a surface area of 10.1 $m^2/g$. This trend is in agreement with previous published data (Driear 1961).

## 5. CONCLUSIONS

Process cycles for the conversion of ADU to $UO_2$ powder with a surface area in the range 3-10 $m^2/g$ were examined with the following conclusions:

1. Direct reduction of ADU to $UO_2$ with hydrogen is sensitive to the availability of hydrogen during the heating cycle, results in a variable (usually high) $UO_2$ surface area, and is not recommended.
2. The recommended process cycle involves calcination of ADU in nitrogen during heating to the reduction temperature followed by reaction with 30 volume per cent hydrogen in nitrogen for two hours using 4.2 times the amount of hydrogen required to convert the uranium as $U_3O_8$ to $UO_2$. The $UO_2$ surface area increased from 3 to 10 $m^2/g$ as the reduction temperature was reduced from 700° to 500°C.
3. The recommended process for stabilisation of the $UO_2$ powders involves controlled oxidation with 2 volume per cent oxygen in nitrogen for 16 hours using twice the amount of oxygen required to convert the $UO_2$ to $UO_{2.1}$.
4. The surface area of $UO_2$ powder reduced at 600°C is insensitive to the surface area of the precursor ADU.
5. The density of sintered pellets increases with an increase in the surface area of the $UO_2$ powder (decrease in reduction temperature) for the same precursor ADU.

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## TABLE 1

## PRELIMINARY BATCH-TRAY CALCINATION-REDUCTION RESULTS (PROCESS CYCLE I)

| Batch Number | Details of Calcination-Reduction Cycle* | Stabilisation Method | ADU Surface Area $m^2/g$ | $UO_2$ Surface Area $m^2/g$ | O/U Ratio of $UO_2$ |
|---|---|---|---|---|---|
| CE1 | A-22.5 | Nitrogen saturated with ethyl alcohol for 2 hours | 22.8 | 7.5 | |
| CE2 | A-22.5 | Dry ice | 22.8 | 18.6 | 2.16 |
| CE3 | A-22.5 | 0.5 - 2.0 vol. % $O_2$ in $N_2$ | 22.8 | 12.9 | 2.26 |
| CE4 | A-11.3 | Dry ice | 20.0 | 14.0 | 2.20 |
| CE5 | B-12 | " " | 25.0 | 12.5 | |
| CE6 | C-12 | " " | 25.0 | 16.5 | |
| CE7 | B-12 | " " | 15.5 | 14.2 | |
| CE8 | B-4.2 | " " | 7.0 | 11.2 | 2.13 |
| CE11 | B-4.2 | 2 vol. % $O_2$ in $N_2$ | 8.0 | 5.3 | 2.09 |
| CE13 | B-4.2 | " " | 15.5 | 8.1 | 2.13 |
| CE14 | B-4.2 | " " | 25.0 | 13.1 | |
| CE18 | B-4.2 | " " | 14.0 | 9.9 | 2.18 |
| CE19 | B-4.2 | " " | 16.8 | 12.3 | 2.23 |
| CE25 | B-4.2 | " " | 9.7 | 18.3 | 2.27 |
| CE26 | B-4.2 | " " | 5.6 | 16.0 | 2.24 |
| CE27 | B-4.2 | " " | 22.1 | 10.6 | 2.17 |
| CE28 | B-4.2 | " " | 8.0 | 11.1 | 2.17 |
| CE29 | B-4.2 | " " | 5.0 | 15.1 | 2.21 |
| CE30 | B-4.2 | " " | 5.9 | 7.9 | 2.14 |
| CE31 | B-4.2 | " " | 5.6 | 13.6 | 2.20 |
| CE32 | B-4.2 | " " | 22.1 | 10.9 | 2.16 |
| CE33 | B-4.2 | " " | 8.0 | 10.2 | 2.19 |
| CE34 | B-4.2 | " " | 14.0 | 10.2 | |
| CE35 | B-4.2 | " " | 6.3 | 10.5 | |
| CE36 | B-4.2 | " " | 3.7 | 13.1 | |

* Details of Calcination-Reduction Cycles

The figure in the second column indicates the number of times theoretical amount of hydrogen used above 400°C in the reduction cycle.

A. Furnace heated to 450°C at 100°C per hour with 10 per cent $H_2$ in $N_2$, held at 450°C for one hour, gas then changed to 100 per cent $H_2$ and temperature raised to 600°C at 100°C per hour and held there for one hour.

B. As for A except that 30 per cent $H_2$ in $N_2$ was used during heating to 450°C.

C. As for A except that 100 per cent $H_2$ was used during heating to 450°C.

## TABLE 2

## EFFECT OF HYDROGEN AVAILABILITY ON $UO_2$ SURFACE AREA

Surface Area of ADU 8.5 $m^2/g$

| Batch Number | Calcination-Reduction Cycle | Actual $H_2$ Supplied/Theoretical $H_2$ Required | $UO_2$ Surface Area $m^2/g$ |
|---|---|---|---|
| CE42 | Cycle I, 30 vol. % $H_2$ from 400°C to end of 450°C plateau, then 100 vol. % $H_2$ | 4.2 | 9.3 |
| CE41 | As above | 2.3 | 7.2 |
| CE44 | As above | 1.5 | 6.0 |
| CE38, 39 | Cycle II, $N_2$ only until 600°C then 30 vol. % $H_2$ for two hours | 4.2 | 3.8, 4.2 |

## TABLE 3

## SURFACE AREA AND COMPOSITION OF CALCINED ADU AND SUBSEQUENT $UO_2$ POWDER

ADU precipitated at pH 7.5 with ammonium hydroxide

| Final Temperature of Calcination °C | Surface Area of Calcined ADU $m^2/g$ | O/U Ratio of Calcined ADU | Temperature of Reduction °C | Surface Area of $UO_2$ $m^2/g$ | O/U Ratio of $UO_2$ |
|---|---|---|---|---|---|
| 500 | 14.2 | 2.74 | 500 | 8.9 | 2.21 |
| 600 | 9.5 | 2.72 | 600 | 6.2 | 2.16 |
| 600 | 7.0 | 2.72 | 600 | 4.6 | 2.10 |
| 600 | 8.6 | 2.70 | - | - | - |
| 630 | 7.3 | 2.68 | 630 | 4.2 | 2.09 |
| 700 | 2.9 | 2.68 | 500 | 3.0 | 2.10 |
| 700 | - | - | 700 | 3.0 | 2.06 |

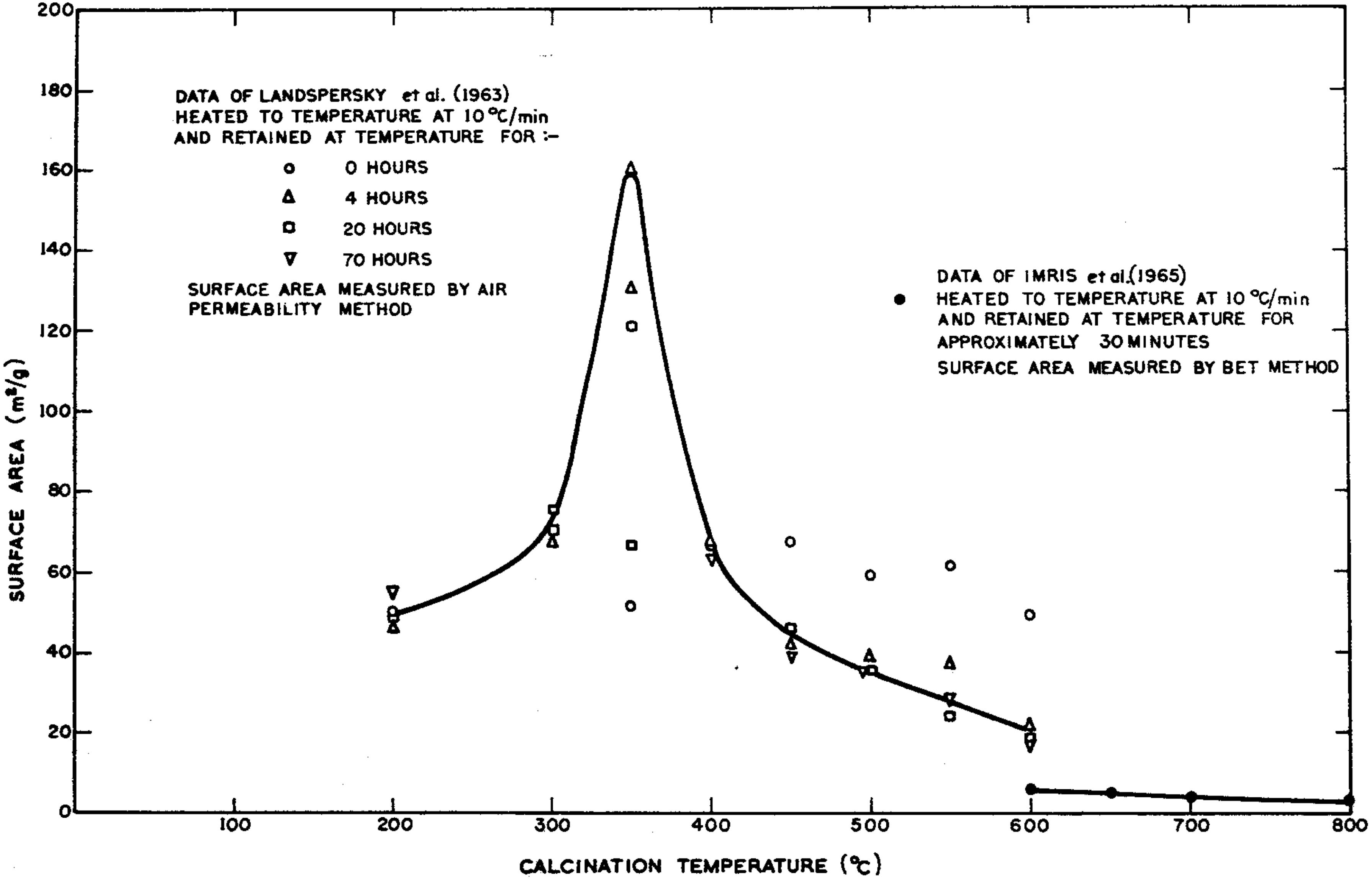


FIGURE 1. EFFECT OF CALCINATION TEMPERATURE ON THE SURFACE AREA OF ADU DECOMPOSITION PRODUCTS (After Landspersky et al. 1963, Imris et al. 1965)

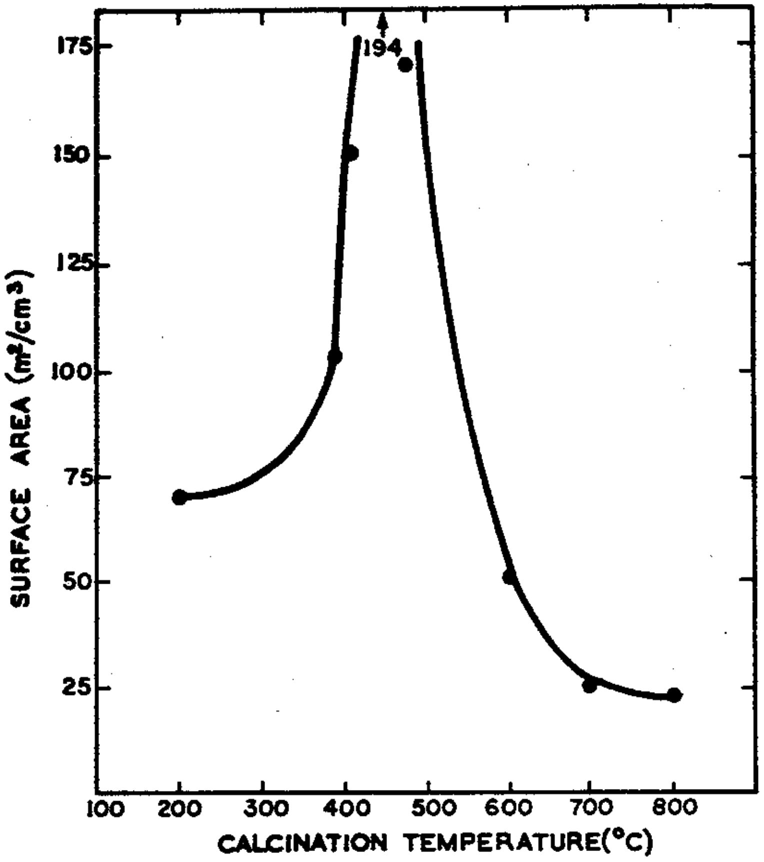


FIGURE 2 EFFECT OF CALCINATION TEMPERATURE ON THE SURFACE AREA OF ADU DECOMPOSITION PRODUCTS IN A ROTARY KILN FURNACE

(After Delmas and Holder 1963)

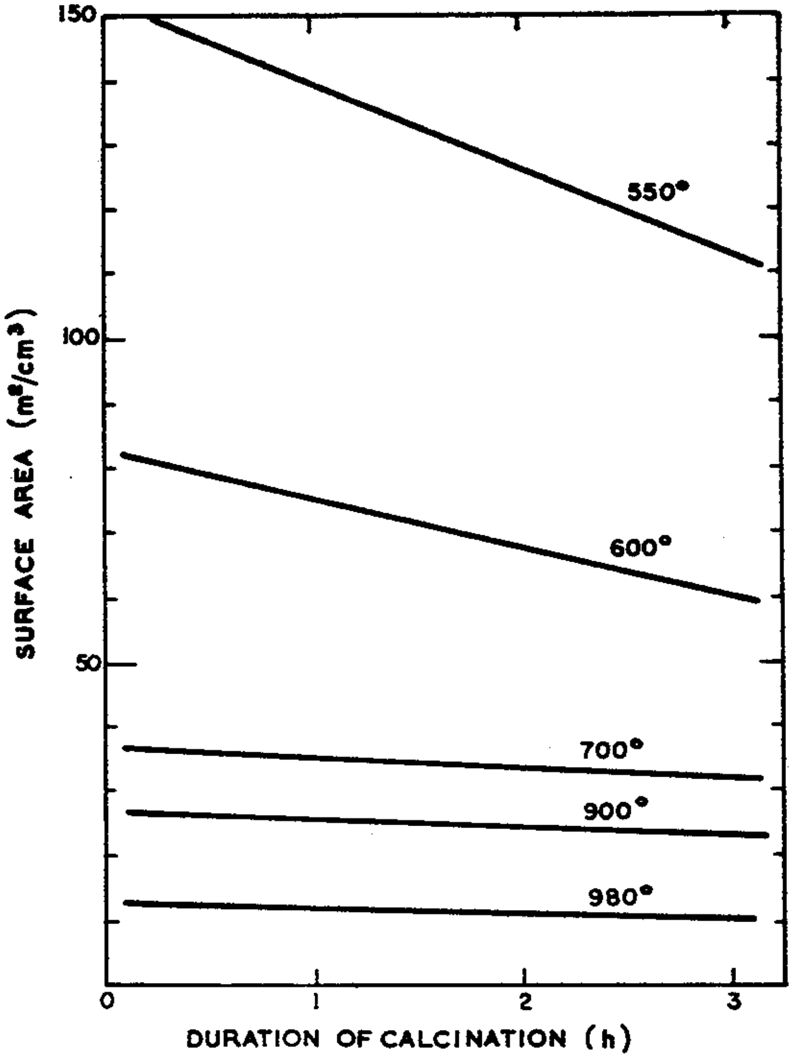


FIGURE 3 EFFECT OF CALCINATION DURATION ON THE SURFACE AREA OF ADU DECOMPOSITION PRODUCTS (After Delmas and Holder 1963)

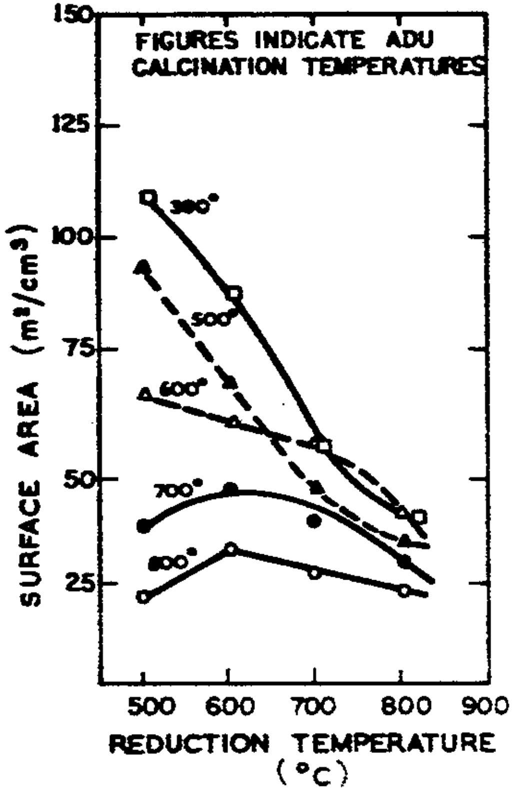


FIGURE 4 EFFECT OF REDUCTION TEMPERATURE ON THE SURFACE AREA OF $UO_2$ PRODUCED FROM VARIOUS ADU DECOMPOSITION PRODUCTS

(After Delmas and Holder 1963)

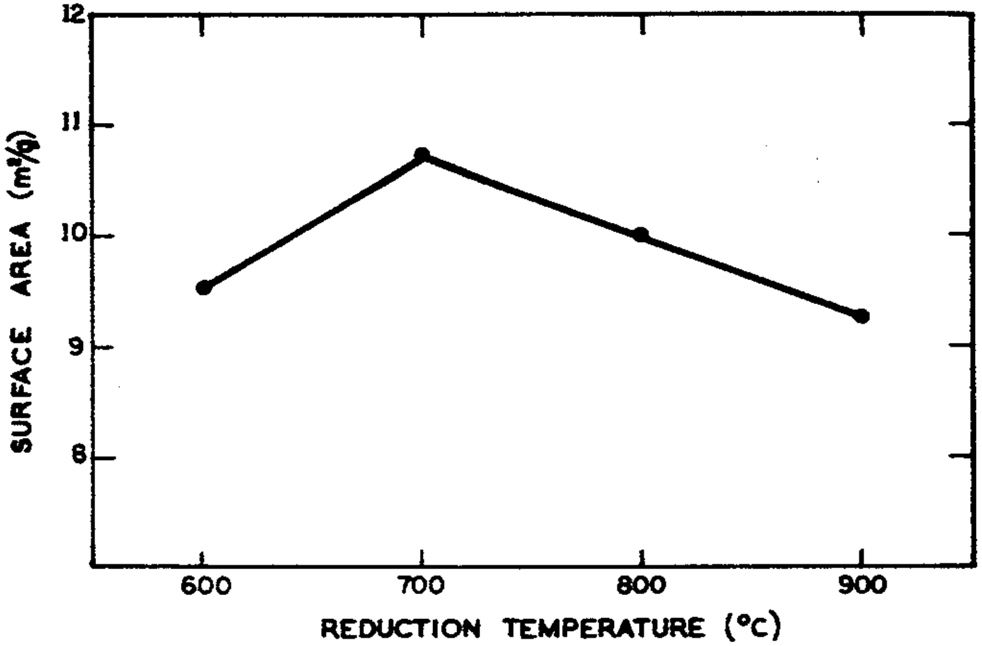


FIGURE 5. SURFACE AREA OF $UO_2$ REDUCED DIRECTLY FROM ADU

(After Jokes and Landsporsky 1964)

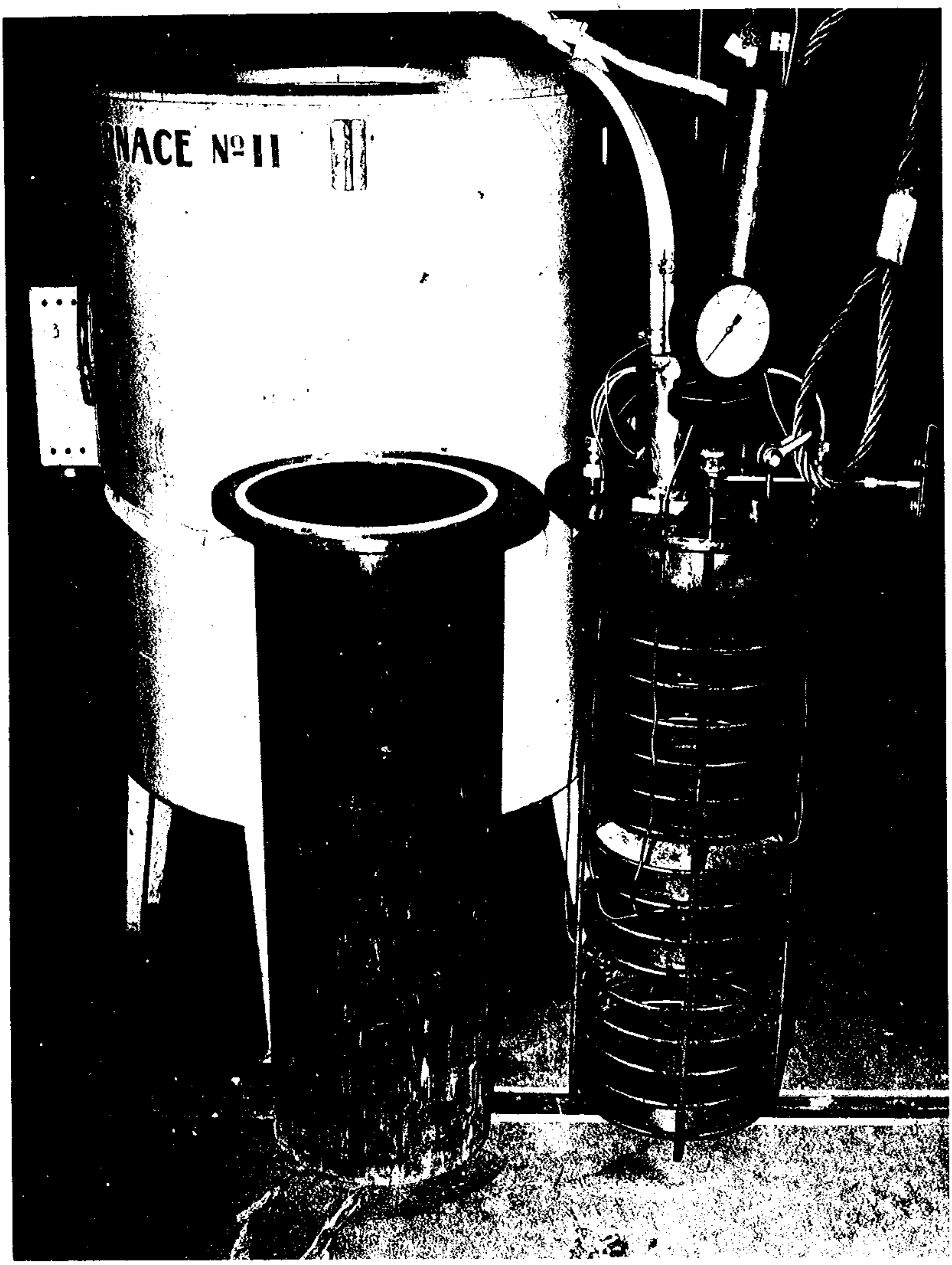
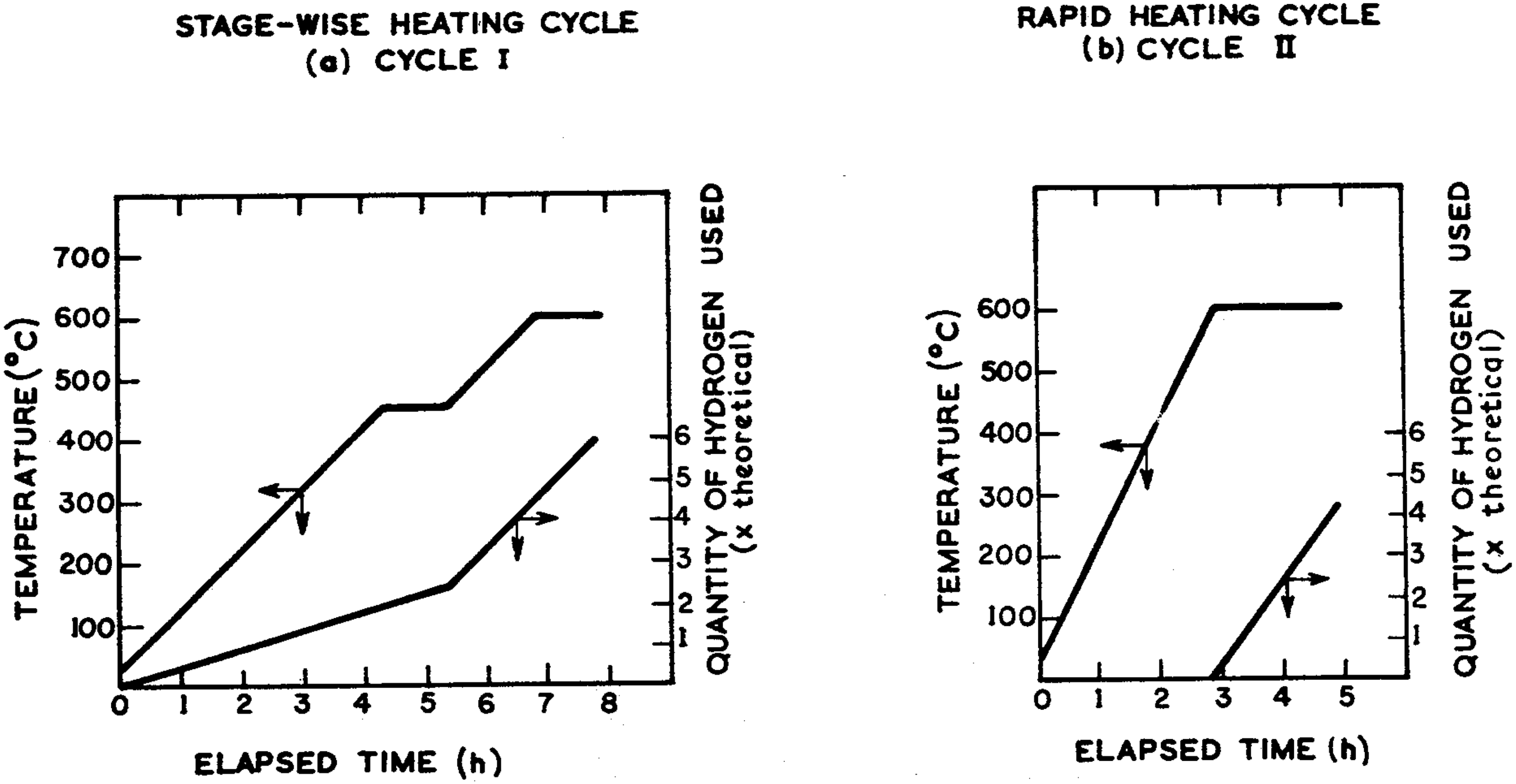


FIGURE 6. BATCH-TRAY CALCINATION-REDUCTION FURNACE



STAGE-WISE HEATING CYCLE
(a) CYCLE I

RAPID HEATING CYCLE
(b) CYCLE II

FIGURE 7. BASIC HEATING CYCLES

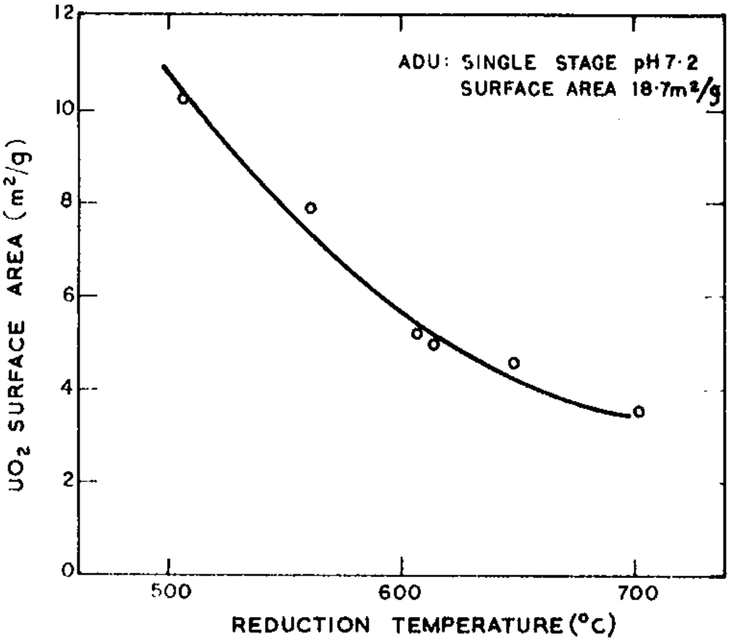


FIGURE 8. EFFECT OF REDUCTION TEMPERATURE ON UC$_2$ SURFACE AREA

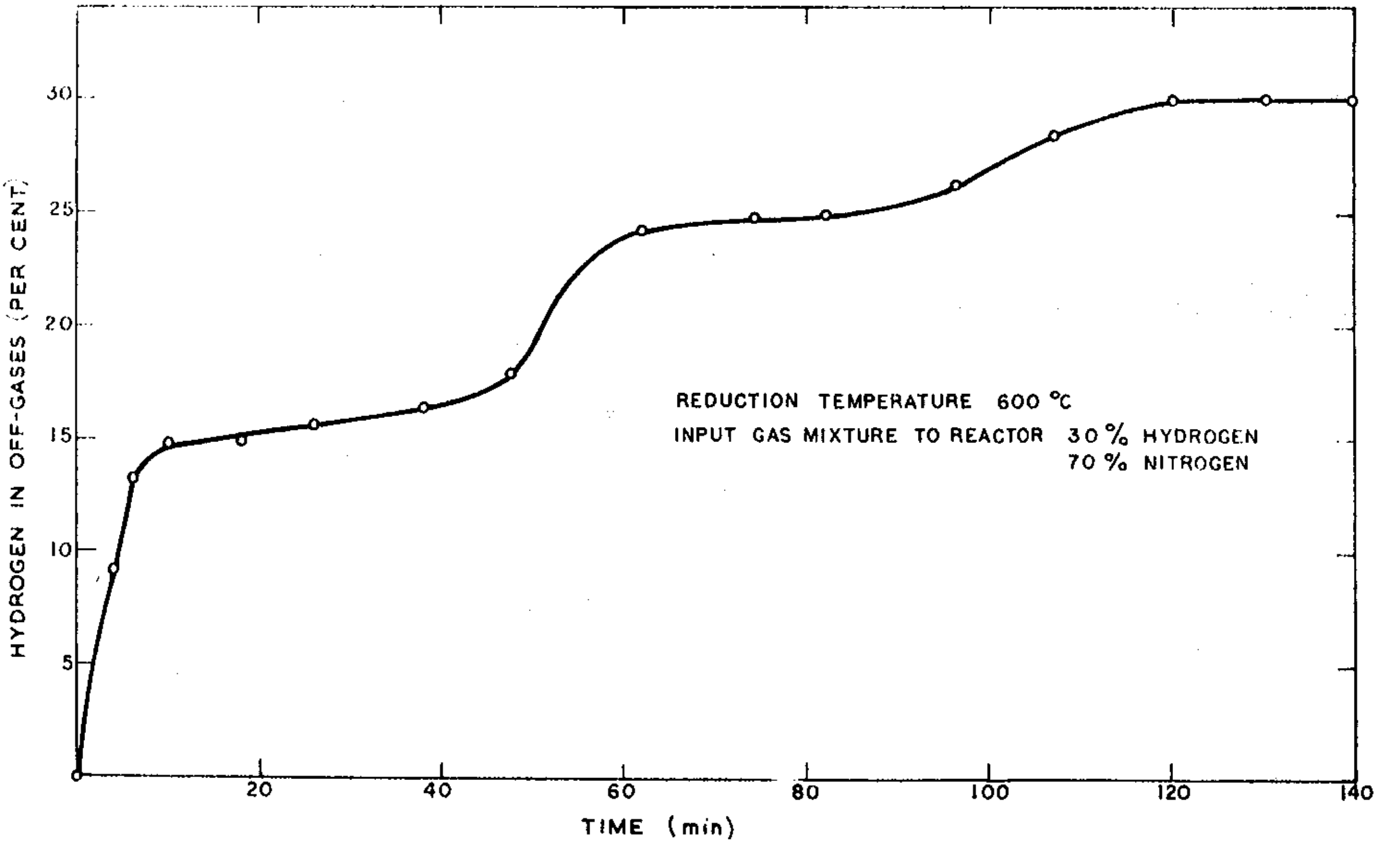


FIGURE 9. PERCENTAGE HYDROGEN IN OFF-GASES DURING REDUCTION REACTION

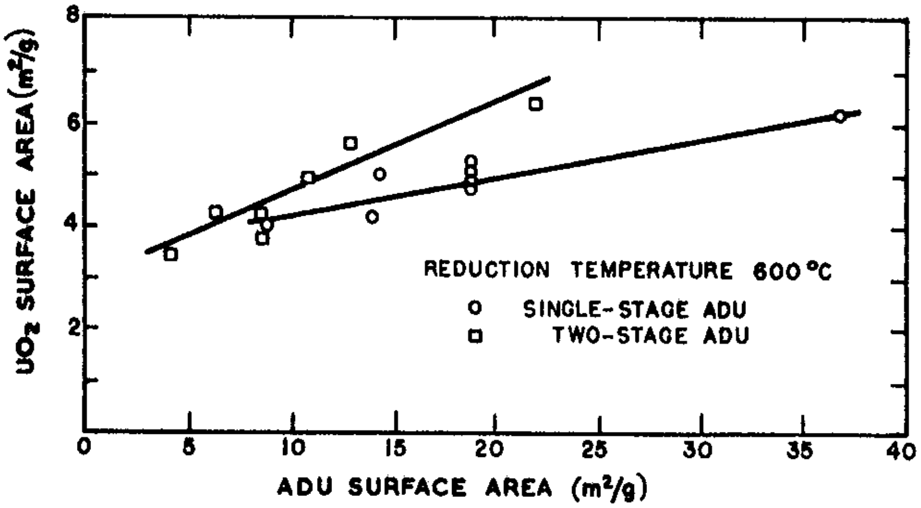


FIGURE 10 EFFECT OF ADU SURFACE AREA ON UO$_2$ SURFACE AREA

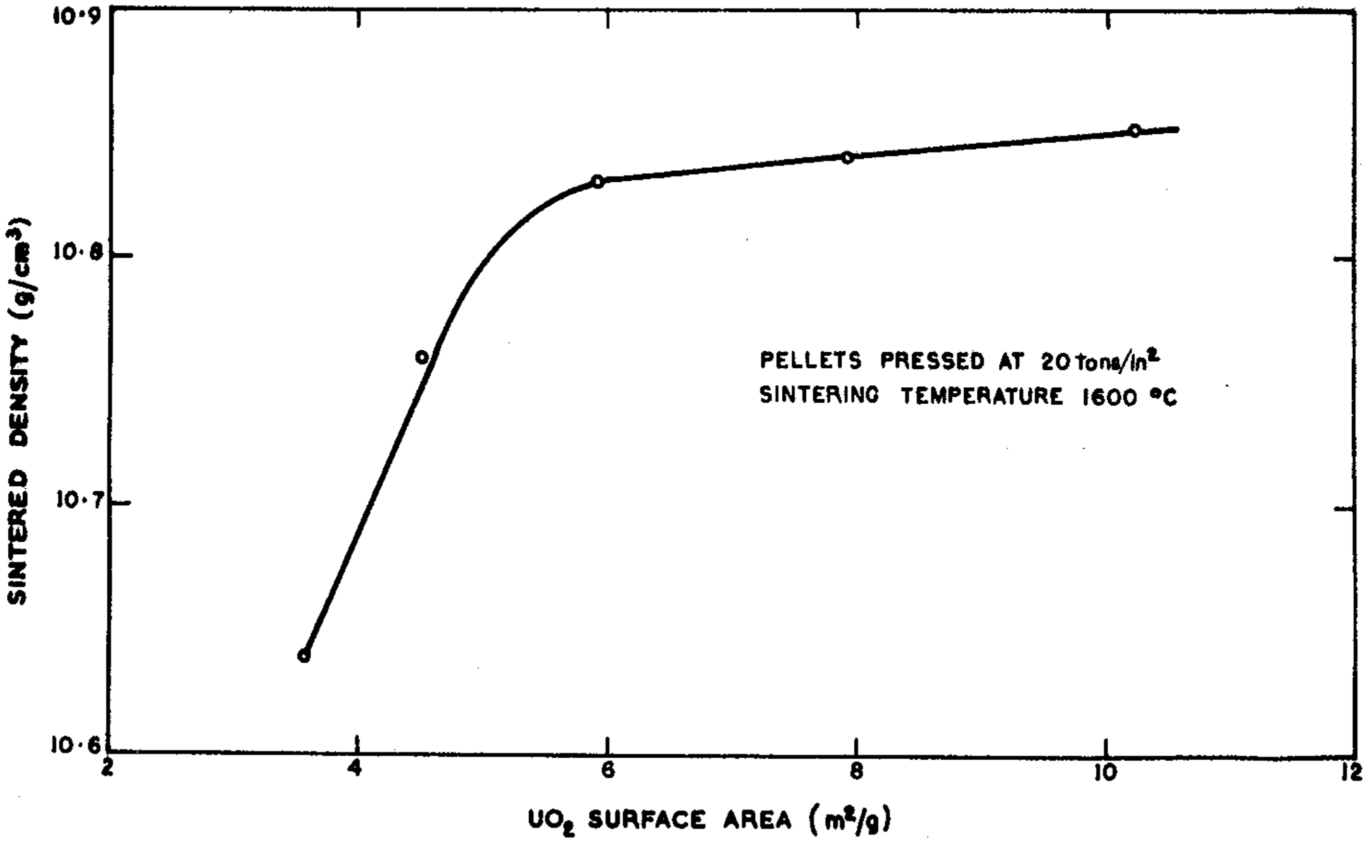


FIGURE 11. EFFECT OF UO$_2$ POWDER SURFACE AREA ON THE DENSITY OF SINTERED PELLETS