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RESEARCH ESTABLISHMENT

LUCAS HEIGHTS

BENCH-SCALE STUDY OF THE REDUCTION AND HYDROFLUORINATION REACTIONS IN THE CATALYSED FLUOROX PROCESS

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ABSTRACT

The catalysed reduction of UO_2F_2 by hydrogen and the hydrofluorination of the UO_2 produced were investigated in separate and simultaneous reactions. The production of UO_2F_2 by hydrofluorination of UO_3 was also studied.

Some catalysed reduction of UO_2F_2 occurred at temperatures as low as 375°C. However, with particles of 100 to 300 μm diameter, only 50 per cent conversion was achieved at the catalysed rate for temperatures up to 460°C. Recombination of the active hydrogen atoms before they penetrated to the core of individual UO_2F_2 particles prevented the reduction from proceeding further at the catalysed rate.

Hydrofluorination of UO_2 produced from UO_2F_2 yielded 75 per cent conversion to UF_4 at 375°C and 50 per cent at 460°C, the low yields being due to sintering of the UF_4 which prevented further reaction.

(continued)

With UO_2F_2 particles of 100 to 300 μm diameter, the maximum conversion to UF_4 in simultaneous reduction and hydrofluorination experiments was 32 per cent at 365°C over 3 hours. The low yield was due to the size of the UO_2F_2 particles which limited the amount of catalysed reduction, and also to the sintering of UF_4.

Production of UO_2F_2 with a low surface area (1.6 $m^2\ g^{-1}$) was achieved by hydrofluorination between 300 and 400°C of denitrator UO_3 which was activated by vapour phase hydration over 10 per cent nitric acid.

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1. INTRODUCTION

The catalysed Fluorox process for the production of uranium hexafluoride (UF_6) involves the catalytic oxidation of uranium tetrafluoride (UF_4) to UF_6 and uranyl fluoride (UO_2F_2); the UO_2F_2 is then recycled by reduction with hydrogen to uranium dioxide (UO_2) and hydrofluorination to UF_4. In the plants proposed for the original uncatalysed Fluorox process, the reduction and hydrofluorination reactions were to be carried out separately [Scott *et al.* 1960]; however, Charlton [1975] showed that significant cost savings could be made if the two reactions were carried out in one reactor. (When the reactions are carried out together in one reactor, they will be referred to in this report as simultaneous reduction and hydrofluorination. The reactions actually take place consecutively as reduction must occur before hydrofluorination.)

Simultaneous reduction of UO_2F_2 and hydrofluorination to UF_4 may be possible, for it has been reported by Batley *et al.* [1974] that the catalyst for the oxidation of UF_4 also catalyses the reduction of UO_2F_2. This could have the effect of lowering the reduction temperature to that of the hydrofluorination, thus possibly allowing both reactions to take place in the one reactor. This report describes a bench-scale study of the important process variables in the recycle reactions using a fluidised bed reactor. In particular, the feasibility of carrying out the reactions simultaneously was investigated. In addition, the report describes the development of methods for producing UO_2F_2 by hydrofluorination of denitrator uranium trioxide (UO_3); this could be significant in the development of the Fluorox process because initial charges of UO_2F_2 may be required as a diluent in the oxidation reaction.

2. LITERATURE REVIEW

2.1 Hydrogen Reduction of UO_2F_2

This reaction is slightly endothermic with a heat of reaction of + 48.6 kJ mol^{-1} at 25°C, and + 44.5 kJ mol^{-1} at 600°C estimated from the thermochemical data of Rand & Kubaschewski [1963] and Perry [1973]. The products of the reaction are UO_2 and HF which can further react to form UF_4 and H_2O, a reaction which is reversible. This is a complex reaction in which the characteristics of the reduction reaction are difficult to isolate from the further reaction of the products.

Ferris & Gardner [1959] studied the reduction between 700 and 800°C and found little reaction between the products, presumably because of the unfavourable equilibrium position of the UO_2 + HF reaction at that temperature. Their data, however, show a significant dependence upon sample arrangement because the reaction is controlled by bed diffusion at these temperatures; the data are therefore specific to their apparatus and not generally applicable.

Kuhlman [1949] studied the reaction of UO_2F_2 produced from pot-denitrated UO_3 with a single particle size and sample arrangement between 450 and 700°C. Complete reduction was observed in about one hour at 600°C and 3 hours at 500°C.

Other workers have observed similar reaction times to those of Kuhlman with different solid arrangements. In thermobalance tests with pure hydrogen, Knudsen *et al.* [1961a] observed 97 per cent conversion over 85 minutes at 600°C, using UO_2F_2 derived from hydrolysis of UF_6, and Geertsma *et al.* [1965] showed almost complete reduction of a UO_2F_2 pellet in 4 hours at 550°C with hydrogen.

Recent work by Batley *et al.* [1974] showed that platinum and other metals are able to catalyse the hydrogen reduction of UO_2F_2 which was produced by hydrofluorination of denitrator UO_3. They found overall reaction times of about 23 minutes at 580°C with one per cent by weight of catalyst consisting of 5 wt % platinum on a support of gamma alumina. This compares with an overall reaction time of about one hour for the uncatalysed reduction at 580°C. It thus appears that reduction at temperatures below 550°C with practical reaction times is possible with the catalysed reaction.

Few quantitative data on the surface area or reactivity of the UO_2 produced by the reduction of UO_2F_2 have been reported. Both Belle [1961] and Katz & Rabinowitch [1951] stated qualitatively that the UO_2 was highly reactive. Knudsen *et al.* [1961b] reported surface areas of about 0.9 $m^2\ g^{-1}$ (stated incorrectly we think, as 'sq in/g') for UO_2 produced by the reduction at 650°C of a 3 kg bed of UO_2F_2 particles (400-800 μm size) derived from the hydrolysis of UF_6. Since this figure does not indicate a highly reactive UO_2, the nature of the UO_2 is unclear.

In summary, the scant published information suggests that this reaction is affected by diffusion and geometry at higher temperatures and further complicated by reaction between the products. The reduction

would appear practical at 600°C with conversion times of about one hour, and possibly below 550°C when the reaction is catalysed.

2.2 Hydrofluorination of UO_2

This reaction depends on the particular conditions under which it is carried out; there is extensive literature describing its characteristics. This review, therefore, only notes the general nature of the reaction and those characteristics which are directly relevant to the Fluorox process. The reaction is complicated by the high exothermic heat of reaction, its reversibility, and the sintering of the UF_4 product. The nature of the reactant UO_2, the temperature, and the physical situation of the reaction are thus important variables in determining how the reaction proceeds.

The heat of the reaction is -180 kJ mol^{-1} at 25°C and -172.9 kJ mol^{-1} at 600°C [Harrington & Ruehle 1959]. Sintering of the UF_4 product is complicated because of its dependence upon the type of UO_2 and its particle structure. Sintering of UF_4 has been observed by Lister & Gillies [1956] at temperatures as low as 200°C with material derived from ammonium diuranate, and at 450-500°C with material derived from thermally denitrator UO_3. This sintering process is particularly important, as the kinetics of the reaction are very dependent upon the surface area of the solid. However, no sintering characteristics of material derived from UO_2F_2 have been reported.

The reversibility of the reaction is evident from the equilibrium data of Petretic & Bertram [1953] and Briggs & Bonfer [1957] which show that there is a 1:1 weight ratio of UO_2 and UF_4 at about 650°C. The kinetics of the reaction are controlled not only by such factors as temperature and partial pressure of reactant gas, but also by the physical properties of the UO_2, the sintering characteristics of the resultant UF_4 and the interdependence of some of the variables. Thus, for example, an effect of particle size may be specific to a particular type of UO_2 in a given temperature range. No general expression of kinetic behaviour has been reported.

There is a marked effect of the type of UO_2 on the kinetics; also the effects of the origin of the UO_2 [Lister & Gillies 1956] and the temperature at which is has been reduced [Jonke & Levitz 1956] are important. These characteristics are related through the significance of surface area to both the initial reaction rate and sintering of the UF_4 product. The kinetics of the hydrofluorination of UO_2 derived from

UO_2F_2 are not described in detail although Geertsma *et al.* [1965] reported a reaction time (to 95 per cent conversion) of 2 hours at 400°C for UO_2 produced from UO_2F_2 at 550°C. This suggests that the hydrofluorination of UO_2 from UO_2F_2 was similar to that from fluidised bed denitrated material, which is not consistent with observations that UO_2 from UO_2F_2 is highly reactive [Belle 1961].

The effect of temperature on the kinetics is a combination of the temperature dependence of the equilibrium, the normal increase of rate with temperature, sintering of the UF_4 product and the interdependence of the type of UO_2. Because of sintering, the rate decreases markedly at temperatures of about 550°C for material derived from ammonium diuranate, whereas no decrease occurs below 740°C for material derived *via* thermal denitration [Lister & Gillies 1956]. No data are reported for the effect of temperature on hydrofluorination of UO_2 derived from UO_2F_2.

The effect of the partial pressure of HF has been found by most workers to be proportional to the difference between the actual partial pressure and the equilibrium partial pressure [Kuhlman 1948b; Smiley 1961; Tomlinson *et al.* 1961]. It is likely that the hydrofluorination of material derived from UO_2F_2 behaves in a similar manner.

Effects such as particle size and bed diffusion have often been considered significant [Kuhlman & Swinehart 1958; Hawthorn *et al.* 1960], but these effects have not been reported for the reaction of material derived from UO_2F_2. Similarly, the variation of rate with conversion is very dependent on the type of UO_2 and the reaction conditions [Harrington & Ruehle 1959], but no data have been reported for the behaviour of UO_2 derived from UO_2F_2. In general, the reaction rate deviates significantly from zero-order except with the faster reacting types of UO_2, for example, UO_2 from ammonium diuranate [Jonke & Levitz 1956].

Many different reaction systems have been employed to carry out this reaction on a production scale, the suitability of each being dependent on the type of UO_2 used. Each of the systems was aimed at maximising the overall conversion and reaction rate and limiting sintering. Fluidised beds have been employed to facilitate the removal of heat [Smiley & Brater 1958], and packed beds have been used to allow a gradation of temperature to limit the early sintering and control the

reaction [Huet 1960]. Fluidised beds have been applied in batch operation and in two-stage (two different temperatures) continuous operation [Hawthorn *et al.* 1960] for UO_2 produced *via* thermal denitration. However, Smiley [1961] reported failure to achieve high conversion with higher activity UO_2 (pot-calcined material) in fluidised beds because of sintering. A moving bed system with a pelletised feed was proposed by Geertsma *et al.* [1965] for hydrofluorination of UO_2 derived from UO_2F_2. No details of systems for other UO_2F_2 materials are available.

2.3 Simultaneous Reduction of UO_2F_2 and Hydrofluorination to UF_4

This has been studied on a laboratory scale by Bernhardt *et al.* [1949] who reported no success with hydrogen and hydrogen fluoride reactants. They observed conversions to UF_4 no greater than 40 per cent, thereby illustrating the difficulty in simultaneous hydrofluorination, which is best performed between about 400 and 500°C, and reduction, which requires temperatures in the range 600 to 650°C.

Higher conversions from simultaneous reactions have been obtained with other reductants such as ammonia [Bernhardt *et al.* 1949], starch [Eister 1956] and carbon tetrachloride [Bernhardt *et al.* 1949]. However, these reductants present serious practical difficulties on a production scale [Bernhardt *et al.* 1949; Eister 1955].

As discussed above, the simultaneous reaction may be possible with hydrogen as a reductant if the reaction is catalysed. The results of Batley *et al.* [1974] indicate that catalysed reduction might be practical below 550°C making possible the simultaneous reaction with hydrogen and hydrogen fluoride.

2.4 Activation of Denitrator UO_3

The hydrofluorination of denitrator UO_3 was found to be difficult without prior activation (see Section 4.2), but no reference to activation towards this reaction has been found. However, the need for activation before the reduction of denitrator UO_3 is well known. Three basic methods have been employed: hydration of the UO_3; fine crushing; and the addition of sulphate ions to the uranyl nitrate before denitration to give a sulphated UO_3.

Activation by vapour and liquid phase hydration has been reported by several workers [Orrick 1953; Morrow *et al.* 1961; Dell & Wheeler 1963] and increases in reduction rates of more than a factor of five have been obtained [Taylor & Dell 1965]. Taylor & Dell suggested that

hydration beyond about $UO_3.0.8\ H_2O$ does not greatly increase the activation further, and gives an activity almost the same as the stable dihydrate. Vapour phase hydration to $UO_3.0.8\ H_2O$ took about nine days in their experiments. The mechanism of activation by hydration has been considered in detail by Dell & Wheeler [1963] who concluded that hydration leads to a substantial volume expansion which is retained on subsequent dehydration, leaving the UO_3 in an expanded porous form. It is, therefore, likely that this means of activation is applicable to the hydrofluorination reaction as well. Recent communications from British Nuclear Fuels Limited [BNFL 1974] indicate that they propose to employ a hydration step using weak nitric acid for activation of UO_3 in future conversion plants.

Activation by fine crushing was reported by Taylor & Dell [1965] and improvements in hydrogen reduction rates by up to a factor of three were obtained. The surface area of the UO_3 increased by about the same order of magnitude. Morrow *et al.* [1965] found the same amount of activation (factor of about three) when they crushed 200 μm particles to 50 μm size. This method of activation is employed by Kerr-McGee [1972] at their Sequoyah plant.

Increase in activity by sulphate ion addition during denitration is well established. The data were reviewed by Harrington & Ruehle [1959] who showed increases in hydrogen reduction rates by up to a factor of two with sulphate ion concentrations up to about 700 $\mu g\ g^{-1}$. This method of activation is employed by British Nuclear Fuels Limited [Rogan 1972] in their production plant at Springfields, but it may be undesirable in a catalysed process because addition of an impurity could poison the catalyst.

2.5 Hydrofluorination of UO_3

The hydrofluorination of UO_3 to produce UO_2F_2 is an exothermic reversible reaction. The heat of reaction is $-124.8\ kJ\ mol^{-1}$ at 25°C and $-123.9\ kJ\ mol^{-1}$ at 600°C [Harrington & Ruehle 1959]; however, that calculated from the equilibrium data of Kuhlman [1948a] is only $-79.5\ kJ\ mol^{-1}$. These equilibrium data show about a 10 per cent UO_3 fraction in the solid at 540°C with an increasing fraction above that temperature. The slow rate of the reverse reaction introduces difficulties in observing the true equilibrium conditions [Kuhlman 1948a] and this could have caused the discrepancy in heats of reaction.

Moore [1954] has shown that the rate of hydrofluorination is almost independent of temperature and Kuhlman [1948a] observed an activation energy for the reaction of only 4.6 kJ mol^{-1}. Kuhlman [1948a] also showed that the rate of reaction is about first order dependent on the solids conversion and gas composition.

To limit the reverse reaction and prevent the spontaneous decomposition of UO_3 to U_3O_8 above 550°C, which would lead to a proportion of UF_4 in the product, it is desirable to carry out the reaction at lower temperatures since there is no great decrease in reaction rate. Thus investigators such as Ferris & Gardner [1959] carried out the hydrofluorination reaction at only 300°C to give a 93 per cent UO_2F_2 product.

3. EXPERIMENTAL

3.1 Apparatus

The equipment, which was located in a fume hood, is shown schematically in Figure 1. The fluidised bed reactor was supplied with mixtures of the reactant gases (H_2 and HF) and nitrogen which were metered through rotameters and preheated to the reactor temperature. The preheater was a 40 mm diameter nickel tube, 0.3 m long, packed with nickel rings (6 mm diameter x 6 mm long) and mounted in a manually controlled, electrically heated furnace of 2 kW capacity. A similar furnace, controlled to ± 2°C by a three-term controller, was used to heat the reactor. The reactor was made of 42 mm diameter nickel pipe, 0.5 m long; it was fitted with a bed support plate (gas distributor) and an off-gas filter made of nickel Rigimesh.

The reactor exit gases were scrubbed with 20 wt % potassium hydroxide (KOH) solution and vented to the building air extract system. Copper tubing was used throughout the apparatus; Monel compression tube fittings enabled vessels to be readily disconnected. The line carrying HF was insulated and trace-heated to 100°C with Pyrotenax heating cable. Pressure connections were purged with nitrogen to prevent the back diffusion of HF.

Hydrogen fluoride was supplied from a 300 g capacity cylinder of liquid HF which was warmed by a surrounding coil of copper tube carrying warm water from a temperature-controlled water bath. A pressure switch on the HF vapour line switched off the heaters in the event of the pressure rising above 250 kPa (g).

3.2 Off-gas Analysers

Thermal conductivity and infrared gas analysers were used to analyse the off-gas from the fluidised bed reactor. A small sample of the off-gas was bled through the analysers by adjusting the rate of bubbling in a secondary KOH scrubber. The thermal conductivity cell was used to show the progress of the reduction reaction by following the change in the hydrogen concentration in the off-gas. Similarly, the infrared gas analyser was used to study the hydrofluorination reaction by following the change in the HF concentration.

The thermal conductivity analyser was a GOW-MAC 24-454 instrument fitted with a nickel block and filaments. It was operated with a bridge current of 90 mA, cell temperature of 100°C and gas flows (reference and sample) of 6 $\ell\ h^{-1}$. Operating under these conditions the instrument gave a response as shown in Figure 2(a).

The infrared gas analyser was a Wilks variable filter Miran I instrument fitted with a 50 mm flow-through gas cell. The cell had sapphire windows and an electric heater to maintain the cell at 100°C. The instrument was operated at a wave number of 3975 cm^{-1} with a band width of about 50 cm^{-1} and gave a response as shown in Figure 2(b). Tests with samples containing up to 30 vol.% water vapour showed that no significant interference by water vapour occurred at this wave number. A sample gas flow of about 6 $\ell\ h^{-1}$ was used and the instrument performed satisfactorily at these settings throughout the study provided the cell and windows were kept free of foreign matter.

3.3 Feed Materials

As discussed in Section 4.1, denitrator UO_3 was used as the starting raw material in this study since it gave rise to UO_2F_2 similar to that produced in the oxidation stage of the Fluorox process. The UO_3 was produced in a fluidised bed thermal denitrator as described by Fane *et al.* [1974]. Various batches of UO_3 were used in this study and their characteristics are described in Table 1.

The catalyst used in the experimental runs was 5 wt % platinum supported on Alcoa H-151 alumina crushed to a particle size between 400 and 600 μm.

3.4 Procedure

The experiments were designed to investigate the kinetics of the reactions, and hence batch sizes, gas flow rates and reactant gas dilutions were chosen so as not to control the rate of reaction. The batch

sizes were further limited to give fluidised bed height to diameter ratios (unexpanded) between two and three, and total gas flow rates were controlled to give gas velocities between three and five times the minimum fluidising velocity at the reaction temperature. The composition of the reactant gases was set giving consideration to the sensitivity of the analysers in following the reaction through changes in the off-gas composition. The detailed procedure for each run varied according to the particular experiment; however, the same basic procedures were used in all experiments.

At the start of each run, the solids (typically 300 g) were loaded into the reactor, the reactor was sealed and connected into the system, and the equipment was thoroughly purged with nitrogen. The line heating, HF vaporiser (if required), preheater and off-gas analysers were then heated to the operating temperatures with a fluidising flow of nitrogen (20 $m\ell\ s^{-1}$) passing to the reactor. The flow of nitrogen through the pressure connections was set at 1 $m\ell\ s^{-1}$. When the fluidised bed reactor and other equipment had reached the required temperatures, the reactant gases were introduced at the flow rate and concentration for the particular experiment. The reaction was then followed by noting the temperature in the reactor and the outputs of the off-gas analysers. System pressures and temperatures were constantly watched throughout the operation.

When the reaction was completed, as indicated by the analysers and reactor temperatures, the reactant gases (H_2, HF) were turned off and the system was allowed to cool to ambient temperature while a fluidising flow of nitrogen was maintained. The system was thoroughly purged with nitrogen at ambient temperature before the solids were removed from the reactor for analysis.

3.5 Analytical Methods

The solid product from each experiment was analysed to determine the conversion achieved. This conversion was also compared with the integration of the outputs from the off-gas analysers over the duration of the experiment to check the calibrations of the analysers. The methods for analysing products from the different reactions are given below.

3.5.1 Conversion of UO_3 to UO_2F_2

The fraction of UO_2F_2 in UO_3 was determined by dissolving the UO_2F_2 in water and weighing the residual UO_3 after drying it at 350°C.

This method was tested with prepared samples and shown to give results accurate to ± 3 per cent. Samples were thoroughly crushed before the solubility determination.

3.5.2 Conversion of UO_2F_2 to UO_2 and UF_4

The reaction product could contain various proportions of UO_2F_2, UO_3, UO_2, UF_4, U_3O_8 and catalyst, although the majority of the catalyst was removed by sieving before analysis. It should be noted that the catalyst support may have been converted to AlF_3. The analysis of the product was carried out in two ways after finely grinding the sample.

Method A The proportion of UO_2F_2 was determined by dissolving the UO_2F_2 in demineralised water and weighing the residue. The fraction of UF_4 in the water-insoluble residue was determined by dissolving it in aluminium nitrate solution (2 g of $Al(NO_3)_3$ per gram of sample) and weighing the residue. A fresh portion of sample was completely dissolved in phosphoric acid and total U and U(IV) were determined to give the conversion of the reduction reaction (U(VI)/U(IV) ratio) and the approximate proportion of catalyst by difference (the proportion of catalyst was small and may have dissolved during analysis depending upon the extent of its fluorination during reaction).

Method B The fraction of UO_2F_2 was determined by dissolving it in demineralised water and weighing the residue. The UF_4 proportion was determined by sintering a fresh sample with sodium peroxide, dissolving it in weak nitric acid, then carrying out fluoride ion analysis using a specific fluoride ion electrode. The UF_4 concentration was computed from the fraction of UO_2F_2 and an approximate figure for the catalyst concentration (small) which was found subsequently. A fresh sample was completely dissolved in phosphoric acid and total U and U(IV) were determined to give the conversion of the reduction reaction (U(VI)/U(IV) ratio) and the approximate proportion of catalyst by difference.

Both of these methods were used and, provided that the samples were very finely ground, good agreement was obtained between them. It was further shown that the catalyst was largely removed from the samples before analysis and little interference was caused by it.

3.5.3 Hydration of UO_3

The water content of activated UO_3 was determined gravimetrically by dehydrating a small sample at 350°C.

3.6 Measurement of Powder Surface Areas

The surface areas were measured using a continuous flow method developed by Nelsen & Eggertsen [1958]; in this method, nitrogen is adsorbed by the sample at liquid nitrogen temperatures from a stream of nitrogen and helium and subsequently eluted by warming. The amount of nitrogen adsorbed was determined by thermal conductivity analysis of the gas stream. Before nitrogen adsorption, the solid was conditioned by heating to 300°C in a stream of helium for 18 hours.

4. RESULTS AND DISCUSSION

4.1 Comparison of UO_2F_2 Starting Material and UO_2F_2 Produced in the Fluorox Reaction

The surface area and other characteristics of the UO_2F_2 are obviously significant in determining the rates of reaction and conversion in the reduction and hydrofluorination reactions. It would, therefore, have been desirable to study the reactions with UO_2F_2 derived specifically from the catalysed Fluorox reaction. However, bench-scale experiments with the catalysed Fluorox reaction at 600 to 650°C in a fluidised bed reactor failed to yield a product with a high proportion of UO_2F_2 when starting with a charge of UF_4 [Batley *et al.* 1974].

It was necessary, therefore, to produce quantities of UO_2F_2 with properties similar to those of the UO_2F_2 produced in the Fluorox reaction. The surface area of the UO_2F_2 produced in the catalysed Fluorox reaction was first determined by carrying out the catalysed Fluorox reaction at 650°C in a tube furnace for 24 hours to give a high conversion. The catalyst for this reaction was present in the form of the platinum metal boat, and 5% wt Pt on alumina pellets (4 g) placed around the UF_4 solid (5 g). The arrangement of the catalyst ensured that the UO_2F_2 product was not contaminated with any high surface area catalyst support. The UO_2F_2 thus produced had a surface area of 1.8 $m^2 g^{-1}$.

Preparation of UO_2F_2 by calcination of ADU at 400°C and hydrofluorination at 350°C gave a surface area of 9 $m^2 g^{-1}$. A lower surface area material was produced by using a lower reactivity starting material (with a lower surface area), namely UO_3 produced by thermally denitrating uranyl nitrate solution at 300°C (Table 1). Production of kilogram quantities of the starting UO_2F_2 from this UO_3 is described in Section 4.2.

The small quantity of UO_2F_2 produced *via* the Fluorox reaction was reduced to UO_2 in hydrogen at 600°C in order that a comparison could be

made between its surface area and those quoted in other reports. The surface area of our material was 2.6 m^2 g^{-1} for UO_2 produced from UO_2F_2 and was lower than expected from the comments of Belle [1961] and Katz & Rabinowitch [1951], but greater than the 0.9 m^2 g^{-1} reported by Knudsen *et al.* [1961b]

4.2 Production of UO_2F_2 by Hydrofluorination of Denitrator UO_3

A large number of UO_3 activation and hydrofluorination experiments were carried out to produce a satisfactory UO_2F_2 and these are summarised in Table 2.

Complete hydrofluorination of denitrator UO_3 which had not been activated by pretreatment was unsuccessful, with conversions to UO_2F_2 of no greater than 41 per cent. Hydrofluorination temperatures up to 500°C, HF inputs to five times the stoichiometric requirement and reaction times up to three hours were unsuccessful in obtaining high conversion.

The low conversions in all experiments were attributed to the unreactive nature of the denitrator UO_3 which had a surface area of about 0.15 m^2 g^{-1} and particles of a smooth non-porous appearance (Figure 3). Activation of the UO_3 was therefore attempted and activation by hydration was chosen in preference to crushing the UO_3 or adding sulphate ion. Crushing would have resulted in the production of fine particles which are undesirable in a fluidised bed reactor and addition of sulphate ions could poison the platinum catalyst in subsequent reaction steps.

Vapour phase hydration at 60°C for nine days over demineralised water to give $UO_3.0.8\ H_2O$ was successful in obtaining high conversions to UO_2F_2 with UO_3 from Batch A (Table 2, Runs P4 and P7); however, hydration to less than $UO_3.0.8\ H_2O$ did not give sufficient activation to yield high conversions (Table 2, Run P5). This means of activation was not successful with all types of UO_3 as Runs P9 to P13 show in Table 2. Hydration to 0.8 H_2O over 10 per cent nitric acid was found effective in activating the remaining batches of UO_3 (Table 2, Runs P16 and P17) and this was adopted as the standard activation technique. Direct liquid phase hydration in demineralised water and 10 per cent nitric acid was attempted but was unsuccessful (Table 2, Runs P14 and P15).

The vapour phase hydration to $UO_3.0.8\ H_2O$ over nitric acid took about nine days at 60°C and required frequent stirring in a static

humidifier to obtain a uniform product which would give high conversions to UO_2F_2 (Table 2, Run P16). The hydrated UO_3 produced in this manner was dehydrated during heating before hydrofluorination, with the water being lost at about 250°C.

The material produced by hydration showed an increase in surface area from about 0.15 to 0.8 $m^2\ g^{-1}$ resulting from surface cracking of the particles during hydration (Figure 4). The surface area of the UO_2F_2 produced from the activated UO_3 was about 1.7 $m^2\ g^{-1}$ (Table 2); this is close to the 1.8 $m^2\ g^{-1}$ surface area of the UO_2F_2 produced from the Fluorox reaction. The UO_2F_2 produced from this hydrated UO_3 was, therefore, a comparable material for the reaction studies.

The conversion of UO_3 to UO_2F_2 was approximately first order with respect to unconverted solid (Figure 5) and had an activation energy of 5 kJ mol^{-1}, in close agreement with the results of Kuhlman [1948b] using pot-calcined UO_3.

4.3 Catalysed Reduction of UO_2F_2

A series of experiments on the catalysed reduction of UO_2F_2 with hydrogen was carried out using UO_2F_2 produced as described in Section 4.2 (Table 3). These experiments were performed below 500°C, which was lower than the temperatures previously studied by Batley *et al.* [1974], and in the region in which isothermal, simultaneous hydrofluorination and reduction may be practical. A 5 wt % concentration of catalyst was used in all experiments as Batley *et al.* [1974] found near-maximum enhancement of the reaction at this concentration.

All the experiments showed an initial fast rate of reaction to about 40-50 per cent conversion, followed by a slower rate of reaction (Figure 6), similar to those of Batley *et al.* [1974] at 530°C. The initial reduction is considerably faster than the rate observed by Kuhlman [1949]; however, the subsequent slower rate is similar. This suggests that the initial reaction is probably catalysed, whereas the latter is not, thus giving the discontinuity shown in Figure 6. It is interesting to note that the initial fast rate of reduction was observed at a temperature as low as 375°C.

Microscopic examination of sectioned particles that had only been reduced about 50 per cent showed an outer UO_2 layer surrounding an inner unconverted UO_2F_2 core (Figure 7). This indicates that catalysis is only effective in reducing the outer layer, which is penetrated to a finite distance by the active species of the reactant gas; conversely, the

inner core reacts at the uncatalysed rate.

In an effort to reduce all of the UO_2F_2 at the catalysed rate, Run R4 (Table 3) was carried out with the UO_2F_2 crushed to a particle size between 120 and 180 μm. Since the active species produced on the catalyst surface might penetrate only a fixed distance below the outer surface of the UO_2F_2 particle, a finer particle size material could give a higher conversion during the fast initial reduction phase. The results in Table 3 show that there was no significant increase in conversion. Further, the reaction rate was the same as with the uncrushed particles. This is explained by the appearance of the uncrushed UO_2F_2 particles (Figure 8) which had an open-cracked structure. Thus, the result of Run R4 indicates that the crushing did not expose a significantly greater amount of the UO_2F_2 to the active species produced on the catalyst surface, but rather fractured the UO_2F_2 particles along existing fissures. Some reduction was evident along cracks in the larger particles, supporting this explanation. Further, analysis of the fine particles (< 120 μm) from Run R2 (Table 3) showed greater than 95 per cent conversion, whereas less than 40 per cent of the coarse particles (> 250 μm) were converted. This strongly supports the premise that the active reactant gas species can only penetrate a finite distance into the UO_2F_2 particle before they are deactivated. Batley *et al.* [1974] observed that the proximity of the catalyst particles to the reacting particles was significant, and pointed out that the active species probably consist of hydrogen atoms. Thus, recombination of hydrogen atoms during diffusion through the pores of the UO_2F_2 particles would be likely. Batley *et al.* [1974] also observed that the rate of the catalysed reduction with particles smaller than about 200 μm was about twice as fast as with particles greater than about 300 μm.

The reduction of UO_2F_2 yields HF as a product which can then react with the UO_2 produced to give UF_4. The maximum possible extent of this reaction is 50 per cent conversion to UF_4, the actual extent being determined by the particular conditions of the reduction reaction. The conversions to UF_4 for the various reduction reactions in this study are given in Table 3, which shows that little of the released HF reacted with the UO_2 product and only about 10 per cent of the possible hydrofluorination took place. This compares with up to 20 per cent observed by Kuhlman [1949] in static bed experiments. The fluidised bed reaction

system would more effectively sweep the HF produced away from the solids before further reaction could take place than would the static system.

4.4 Hydrofluorination of UO_2 Derived from UO_2F_2

Hydrofluorination experiments were carried out at 460 and 375°C (Table 4; Figure 9). At both temperatures, the rate of reaction decreased with time and the total conversion was less than 100 per cent. The conversion observed at 375°C was about 75 per cent which was higher than that observed at 460°C (about 50 per cent). The decreasing rate of reaction with conversion is typical [Harrington & Ruehle 1959] of the hydrofluorination reaction. However, the total conversions are lower than those noted by Harrington & Ruehle, who also reported no decrease in the amount of conversion with increasing temperature.

Lister & Gillies [1956] showed that final conversions for hydrofluorination of ADU and U_3O_8-derived UO_2 increased with temperature up to about 480°C. For denitrator-derived UO_3, they showed conversions increasing with temperature below 600°C. They also showed that UF_4 derived from both ADU and U_3O_8 sintered significantly in the temperature range 350 to 500°C. The UO_2 from UO_2F_2 used in this study would generally not appear to have behaved as those described by Lister & Gillies and there seems to have been substantial sintering at 460°C. Smiley [1961] also reported low conversions in fluidised bed reactors and sintering was suggested as one of the problems, particularly at high temperatures using UO_2 derived from pot-calcined material.

Microscopic examination of the products of these hydrofluorination experiments did not show any layering, as unreacted UO_2 remained finely divided throughout the particles. Therefore, any sintering of the UF_4 product to limit the conversion took place on a sub-particle scale, and this is possible with the open structure of the initial UO_2 material.

4.5 Simultaneous Catalysed Reduction of UO_2F_2 and Hydrofluorination to UF_4

Four runs were carried out between 365 and 460°C with both HF and hydrogen being present (Table 5). The progress of the reduction and hydrofluorination reaction at 365°C is illustrated by the conversion curves in Figure 10. Table 5 shows that complete conversion to UF_4 was not obtained, the reasons being low conversion to UO_2 in the reduction reaction at low temperatures, and low conversions to UF_4 in the hydrofluorination reaction at higher temperatures. Figure 10 further shows that all the UO_2F_2 does not have to be reduced to UO_2 before hydrofluorination begins.

That reduction was the limiting factor at the lower temperatures was expected from the data discussed in Section 4.3 and a low overall conversion resulted. The limiting influence of the hydrofluorination reaction on the overall reaction at higher temperatures might also be expected from the data discussed in Section 4.4. Microscopic examination of the solid products from the simultaneous reactions showed interesting features. The material produced at higher temperatures (Run RH1, Table 5) showed a predominance of green UF_4 and blackish UO_2 as the conversions would suggest. The UO_2 was distributed throughout the particles (some UO_2 at the centre of the particle) and this supports the view expressed in Section 4.4 that UF_4 sintering takes place at a sub-particle level and not only on the outside layers of the particle. The distribution of UO_2F_2 in the particles which were reacted at low temperatures was difficult to discern with the microscope because of the translucence of the UO_2F_2 and UF_4 and the strong lighting required. However, sectioned particles produced at 365°C, showed the lighter coloured, unreacted UO_2F_2 at the centre of the particle, as expected from the nature of the limited catalysed reduction at this temperature.

It appears that high conversions in the simultaneous reaction under isothermal conditions, with the UO_2F_2 (100-300 μm) used in this study, might be obtained over extended periods (>> 3 hours) at temperatures below 375°C. This would allow the reduction reaction to go to completion without the hydrofluorination being greatly limited. Alternatively, as was suggested in Section 4.3, a fine particle size (< 120 μm) might allow a high conversion of the catalysed reduction at 375°C and thus give high overall conversion to UF_4 in shorter times. This could not be attempted in the present study because the reactor had no provision for dislodging accumulated fine powder from the off-gas filters, but it will be investigated in subsequent pilot plant experiments.

5. CONCLUSIONS

UO_2F_2 with a low surface area (1.6 $m^2\ g^{-1}$) was produced by hydrofluorinating denitrator UO_3 which was activated by vapour phase hydration over 10 per cent nitric acid solution. Activation for nine days at 60°C yielded a product of composition $UO_3.0.8\ H_2O$ which could be dehydrated below 300°C. Hydrofluorination between 300 and 400°C using 40 vol.% HF in nitrogen gave a product containing > 98% UO_2F_2 in one hour.

In the temperature range 375 to 460°C, with 100 to 300 μm diameter UO_2F_2 particles, reduction with hydrogen was only catalysed for the

initial 50 per cent of conversion; the balance of reaction was at an uncatalysed rate. Analysis of particles greater than 250 μm diameter showed that, at this transition in reaction rates, they were 40 per cent converted whereas particles less than 120 μm diameter were 95 per cent converted. Microscopic examination of the larger particles showed an outer UO_2 layer surrounding an inner core of unconverted UO_2F_2, indicating that the active hydrogen atoms produced on the catalyst surface can only penetrate a finite distance into the UO_2F_2 particles.

The hydrofluorination of UO_2 produced by hydrogen reduction of UO_2F_2 did not proceed to completion because of sintering of the UF_4 product. The maximum attainable conversion of UO_2 to UF_4 decreased with increasing temperature for reactions at 375 and 460°C. At 375°C, the final conversion was about 75 per cent but at 460°C it was about 50 per cent.

With 100 to 300 μm diameter UO_2F_2 particles, simultaneous reduction and hydrofluorination to UF_4 gave a maximum yield of only 32 per cent in experiments between 365 and 460°C because only about 50 per cent of the UO_2F_2 was reduced at the catalysed rate and the conversion to UF_4 was incomplete owing to sintering. It appears that successful simultaneous reduction of UO_2F_2 and hydrofluorination to UF_4 may only be carried out isothermally in less than three hours at temperatures below 375°C and with particles of < 120 μm diameter.

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NOTES

TABLE 1

CHARACTERISTICS OF UO_3 FEED MATERIALS

UO_3 Batch No.	Particle Size Distribution				Surface Area ($m^2\ g^{-1}$)	Water Content $\frac{H_2O}{U}$ mol ratio	Nitrate Content $\frac{NO_3}{U}$ mol ratio	Pour Density ($g\ cm^{-3}$)	Tap Density ($g\ cm^{-3}$)	Reactivity to H_2 Reduction. Maximum Rate of H_2 Reduction at 600°C with 30% H_2/N_2 ($\%\ s^{-1}$)
	< 100 µm (%)	< 200 µm > 100 µm (%)	< 300 µm > 200 µm (%)	> 300 µm (%)						
A	5	30	50	15	0.16	0.05	~ 0.03	4.0	4.3	-
B	5	35	50	10	0.10	0.1	~ 0.03	4.1	4.4	~ 0.07
C	5	25	55	15	0.10	0.1	~ 0.03	3.9	4.3	~ 0.07

Reactivity of UO_3 to hydrogen reduction determined by Fane et al. [1974]

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TABLE 2

SUMMARY OF UO_3 HYDROFLUORINATION EXPERIMENTS

Run No.	UO_3 Feed Material: UO_3 Batch No.	UO_3 Feed Material: Pretreatment of UO_3 Feed	UO_3 Feed Material: Surface Area of Treated UO_3 ($m^2\ g^{-1}$)	Temperature (°C)	Gas Flow Rate ($m^3\ h^{-1}$)	Conc'n of HF (%)	HF Supplied (% of stoichiometric requirement)	Duration (h)	Final Conversion (%)	Surface Area of Product ($m^2\ g^{-1}$)
P1	A	none	n.a.	370	0.18	40	5	3	10	
P2	A	none	n.a.	350	0.30	40	4	1.5	32	
P3	A	none	n.a.	500	0.30	40	4	1.5	41	
P4	A	Vapour phase hydration with frequent stirring to give a uniform 0.8 H_2O	0.6	450	0.30	40	1.6	0.6	95	1.7
P5	A	Vapour phase hydration with frequent stirring to give a uniform 0.6 H_2O		450	0.30	40	4	1.5	64	
P6	A	Vapour phase hydration without stirring giving non-uniform hydrate of 0.8 H_2O mean		450	0.30	40	4	1.5	60	
P7	A	Vapour phase hydration with stirring giving uniform 0.8 H_2O product	0.8	430	0.48	40	2.5	0.6	95	1.8
P8	A	"		400	0.48	40	2.5	0.6	95	
P9	B	"		400	0.48	40	6.5	1.5	55	
P10	B	"		400	0.48	40	6.5	1.5	50	
P11	B	"		250-400	0.48	40	6.5	1.5	60	
P12	C	"		400	0.48	40	6.5	1.5	50	
P13	C	"		250-400	0.48	40	6.5	1.5	55	
P14	C	Liquid phase hydration - direct washing in 10% HNO_3 giving about 1.0 H_2O		400	0.48	40				
P15	C	Liquid phase hydration - direct washing in demineralised H_2O giving about 1.0 H_2O		400	0.48	40	6.5	1.5	79	
P16	C	Vapour phase hydration over 10% HNO_3 with stirring giving uniform 0.8 H_2O	0.85	400	0.48	40	2.5	0.6	98	1.6
P17	C	"	0.8	300	0.48	40	2.5	0.6	98	

TABLE 3

SUMMARY OF EXPERIMENTS ON THE CATALYSED* REDUCTION OF UO_2F_2

Run No.	Temperature (°C)	Particle Size of Solids (μm)	Gas Flow Rate ($m^3\ h^{-1}$)	Conc'n of H_2 (%)	Duration (h)	Conversion of U(VI) to U(IV) (%)	Conversion to UF_4 (% of UO_2 product reacted to UF_4)
R1	460 ± 5	~ 100-300	0.30	30	8.0	95	4
R2	425 ± 3	~ 100-300	0.30	30	1.5	45	5
R3	375 ± 3	~ 100-300	0.30	30	5.0	50	5
R4	425 ± 3	~ 120-180	0.30	30	1.5	48	5

All runs carried out with 5 wt % concentration of catalyst.

TABLE 4

SUMMARY OF UO_2 HYDROFLUORINATION EXPERIMENTS

Run No.	Feed Material		Temperature of Reduction (°C)	Temperature of Hydro-fluorination (°C)	Gas Flow Rate ($m^3\ h^{-1}$)	Conc'n of HF in Gas (vol.%)	Duration (h)	Conversion of UO_2 to UF_4 (% UO_2 in feed converted to UF_4)
	Produced from Reduction Run No.	Conc'n of UO_2 in Feed (%)						
H1	R1	95	460 ± 5	450-470	0.48	30	3	50
H2	R3	50	375 ± 3	370-380	0.48	30	3	75

Catalyst present in reduction product largely sieved out of material before hydrofluorination.

TABLE 5

SUMMARY OF SIMULTANEOUS UO_2F_2 REDUCTION AND HYDROFLUORINATION EXPERIMENTS

Run No.	Temperature (°C)	Gas Flow Rate ($m^3\ h^{-1}$)	Concentration of H_2 in reactant gas (vol.%)	Concentration of HF in reactant gas (vol.%)	Duration (h)	Conversion of U(VI) to U(IV) (%)	Conversion UO_2 to UF_4 (% UO_2 product converted to UF_4)
RH1	460 ± 10	0.48	30	20-40	4	75	35
RH2	430 ± 10	0.48	30	20-40	4	60	35
RH3	400 ± 10	0.48	30	20-40	3	40	40
RH4	365 ± 5	0.48	30	20-40	3	35	90

All runs carried out with 5 wt % concentration of catalyst.

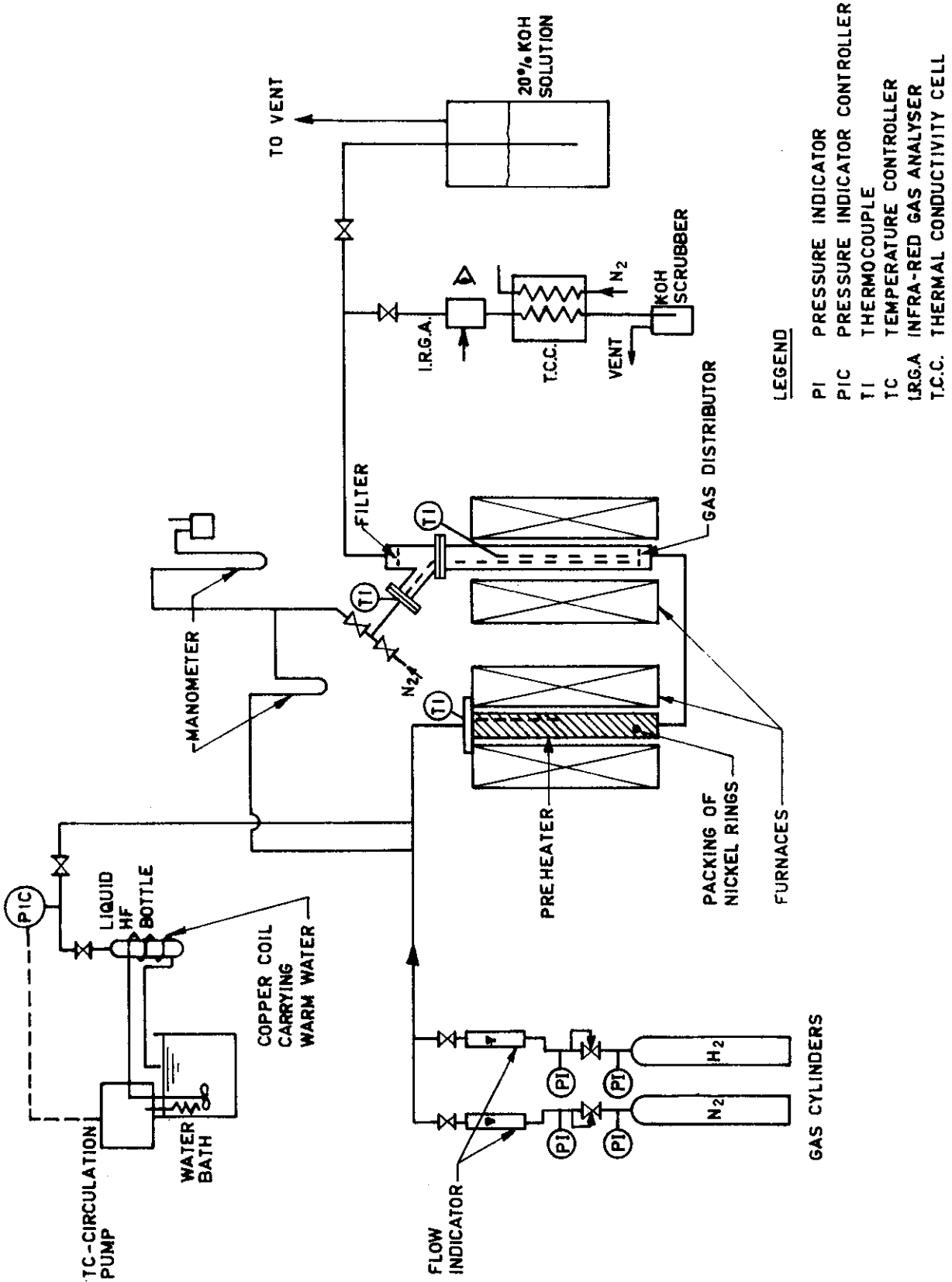
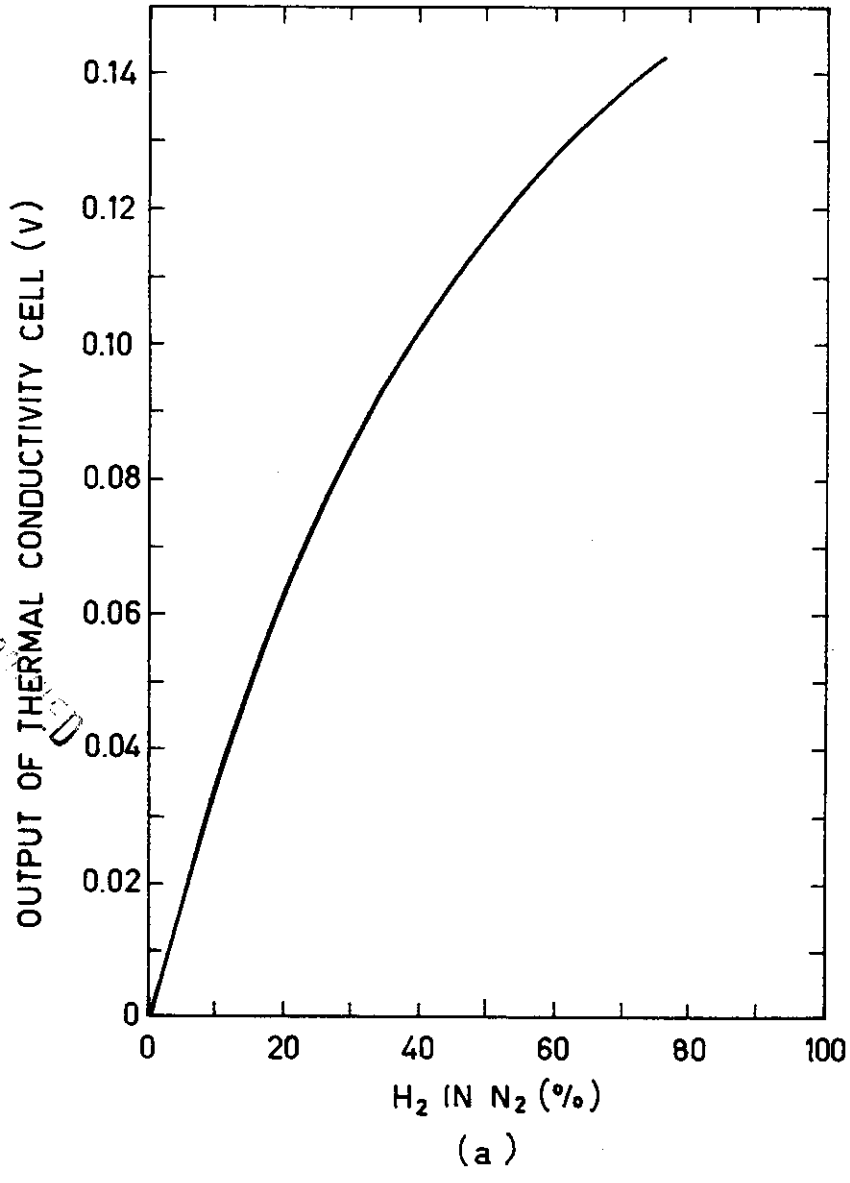


FIGURE 1. BENCH-SCALE FLUIDISED BED EQUIPMENT



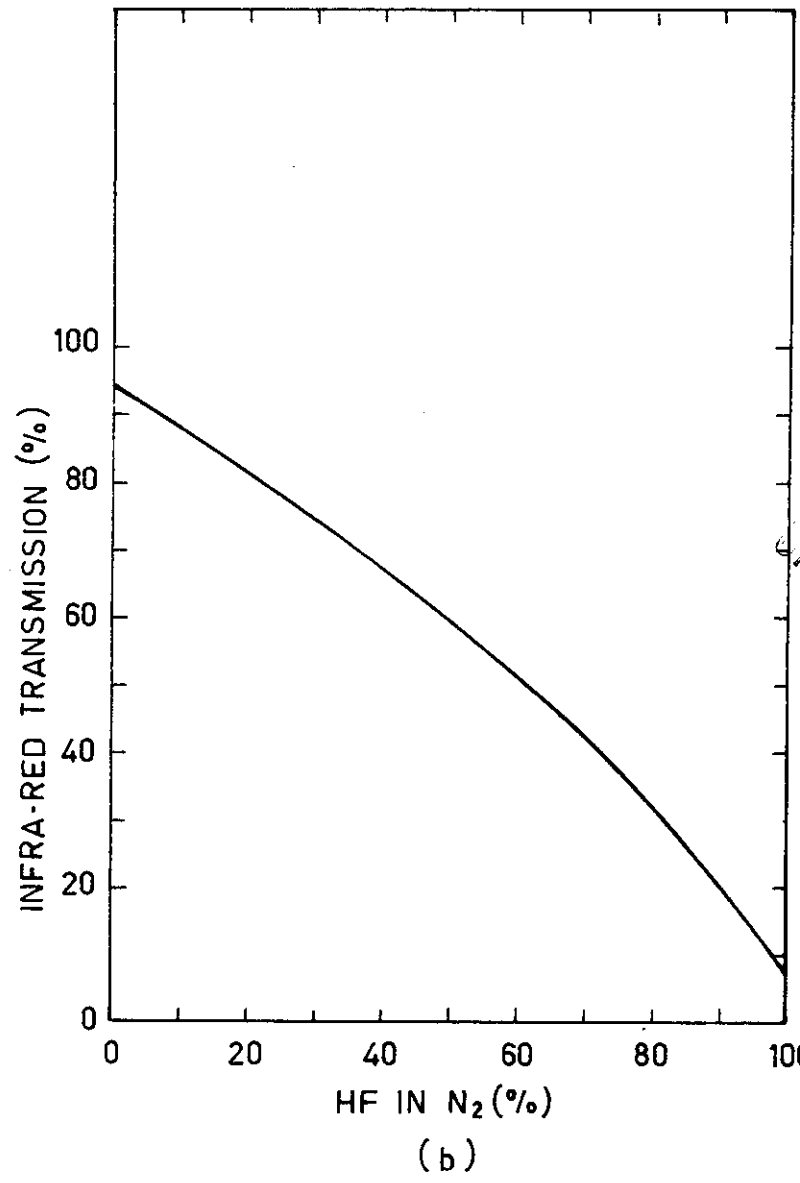


FIGURE 2. CALIBRATION CURVES OF THE OFF-GAS ANALYSERS

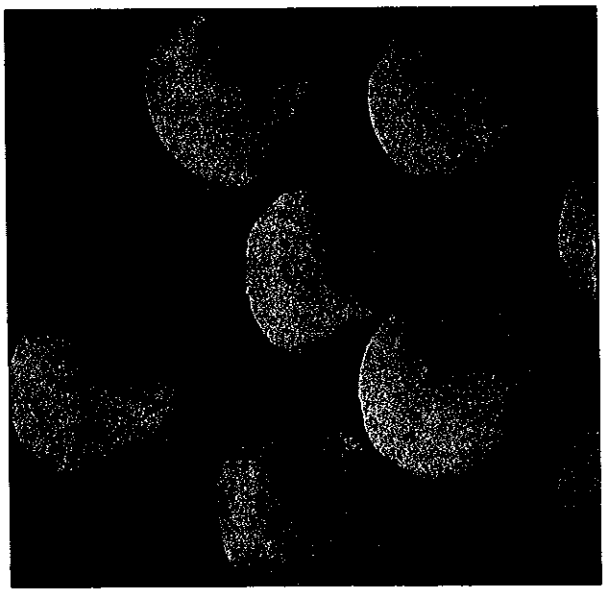


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FIGURE 3. UNHYDRATED UO_3

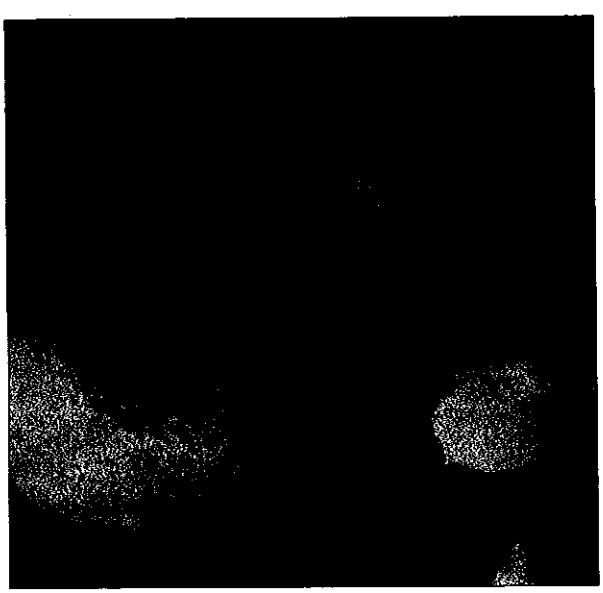

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FIGURE 4. UO_3 HYDRATED TO UO_3.0.8 H_2O

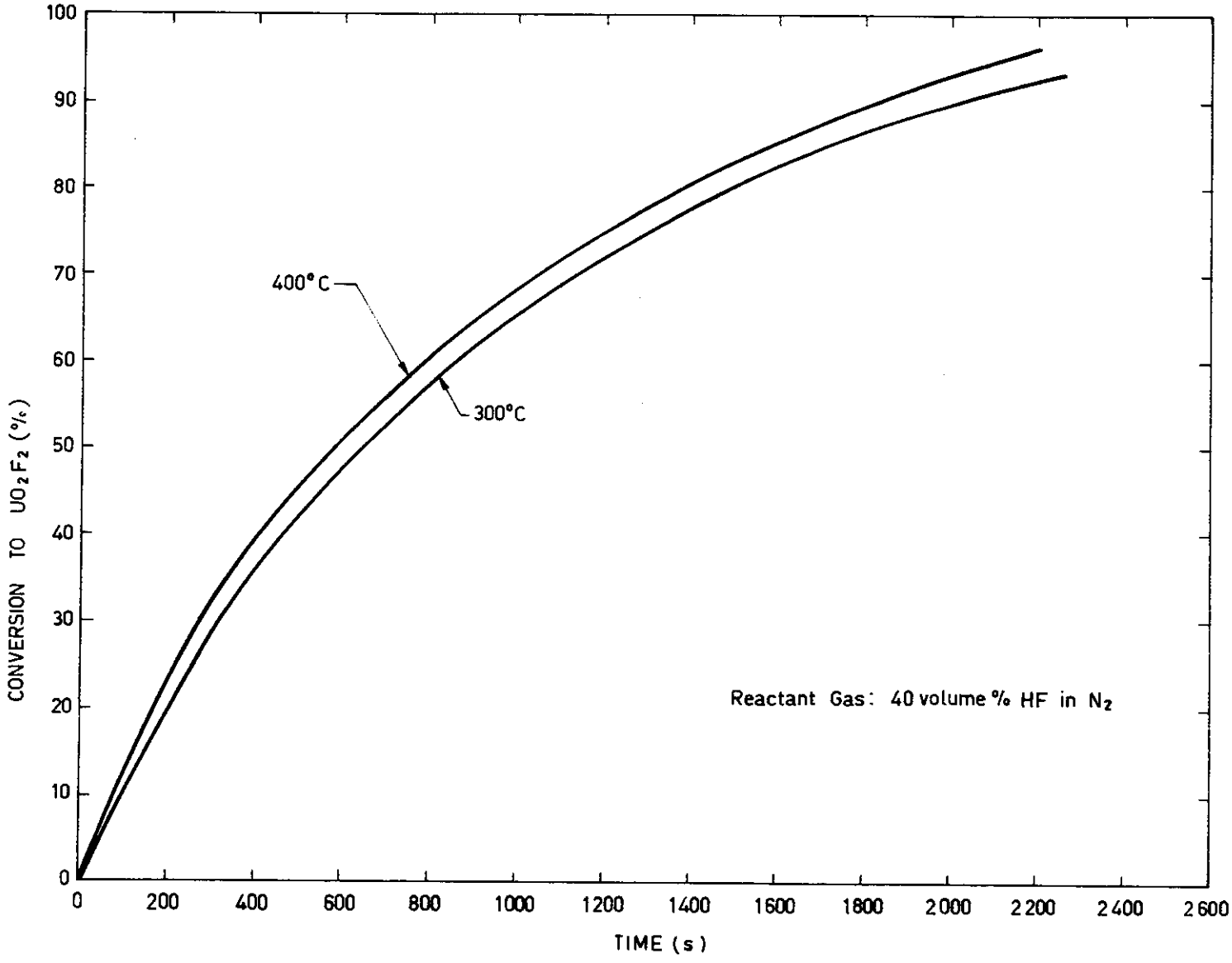

FIGURE 5. CONVERSION-TIME CURVES FOR HYDROFLUORINATION OF HYDRATED UO_3

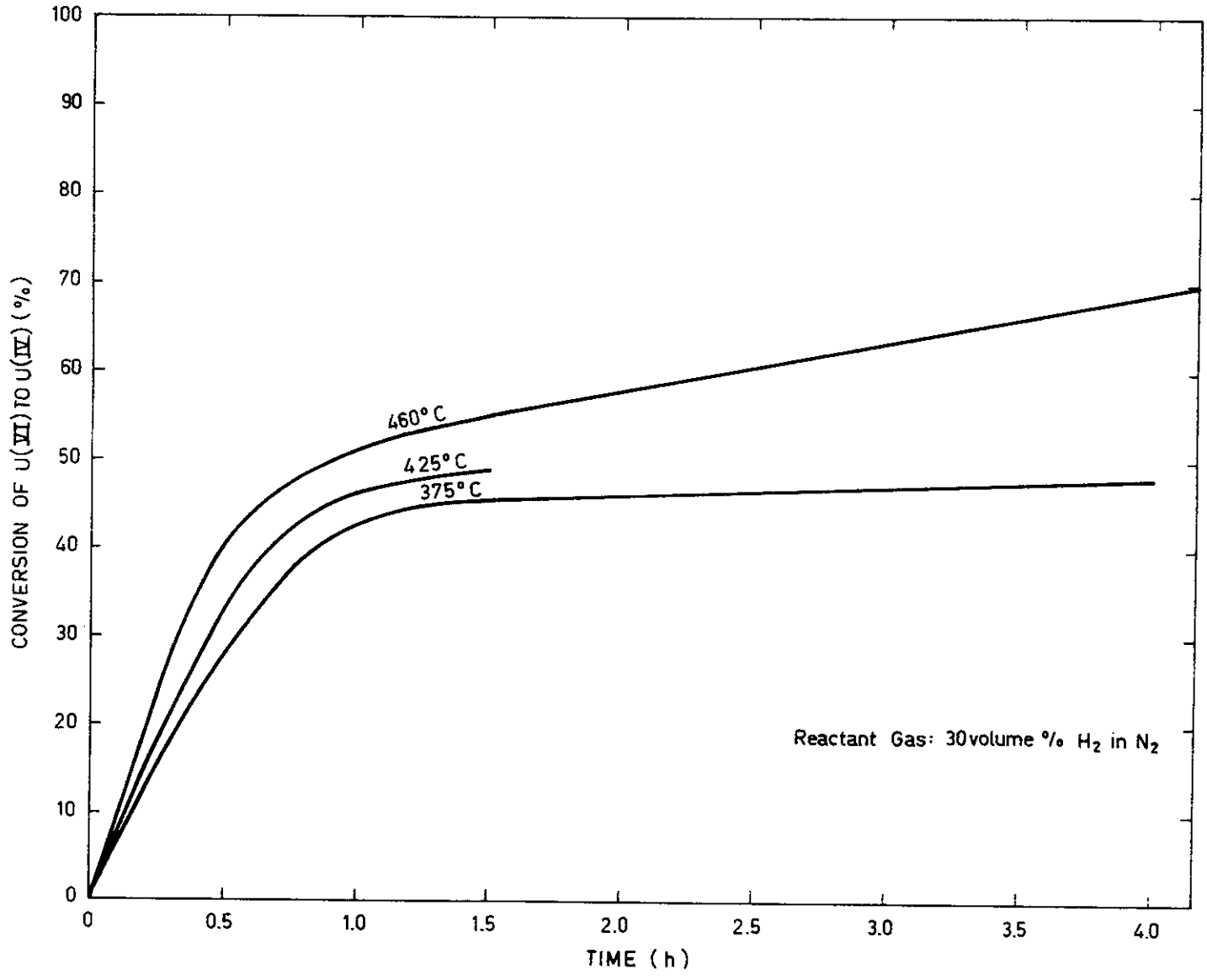

FIGURE 6. CONVERSION-TIME CURVES FOR REDUCTION OF UO_2F_2

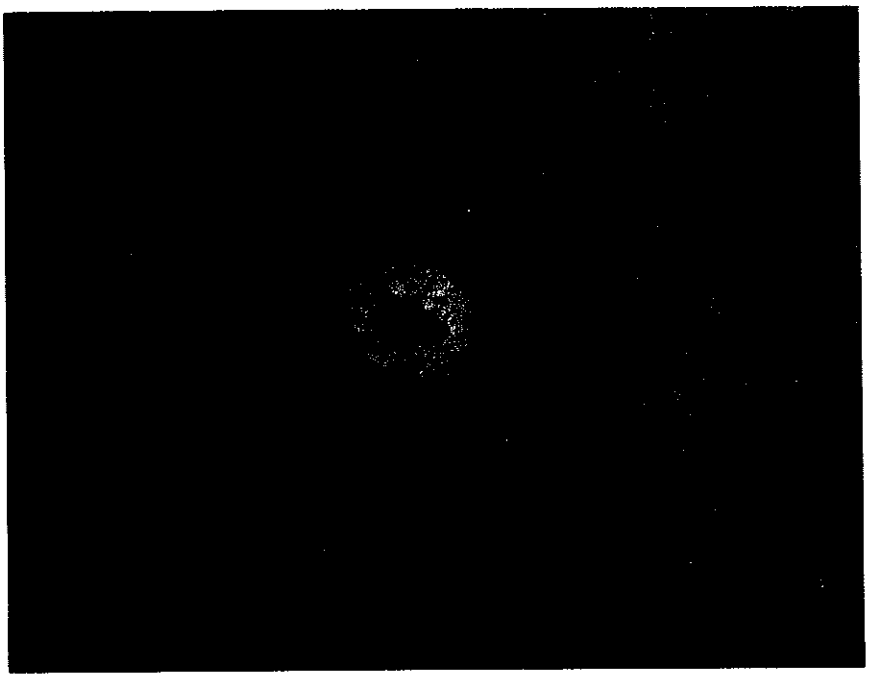

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FIGURE 7. SECTIONED PARTICLE OF UO_2F_2 REDUCED IN 30 VOL. % HYDROGEN IN NITROGEN AT 425 °C FOR 1.5 h

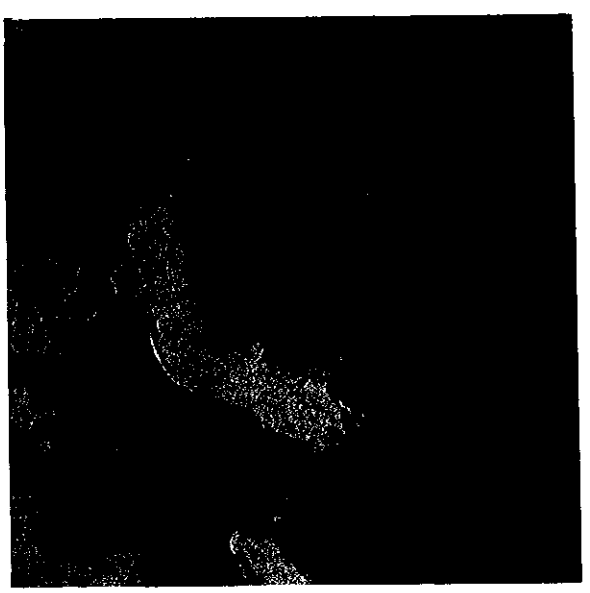

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FIGURE 8. PARTICLES OF UO_2F_2 PRODUCED BY HYDROFLUORINATION OF HYDRATED DENITRATOR UO_3

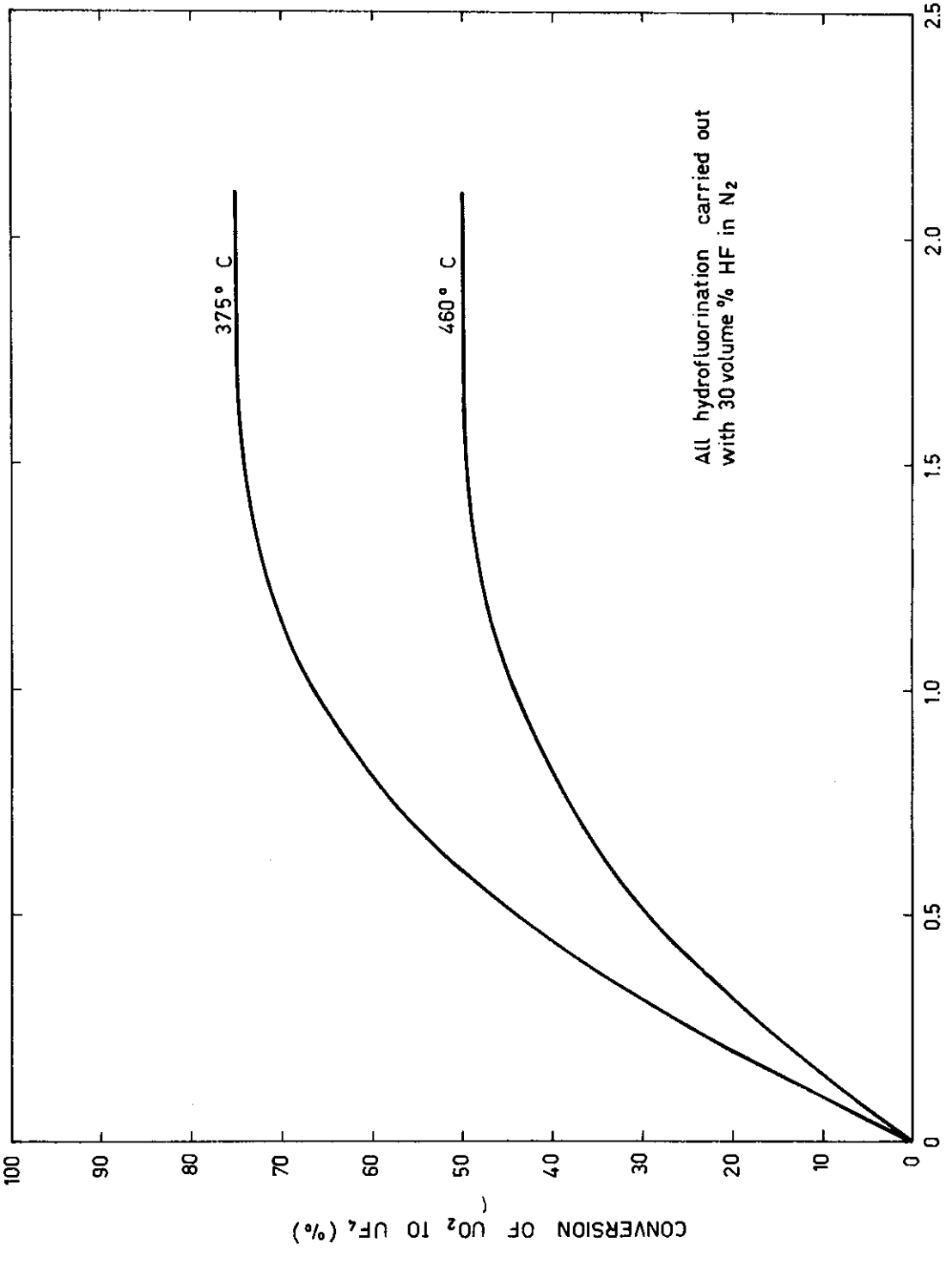

FIGURE 9. CONVERSION-TIME CURVES FOR HYDROFLUORINATION OF UO_2 DERIVED FROM UO_2F_2

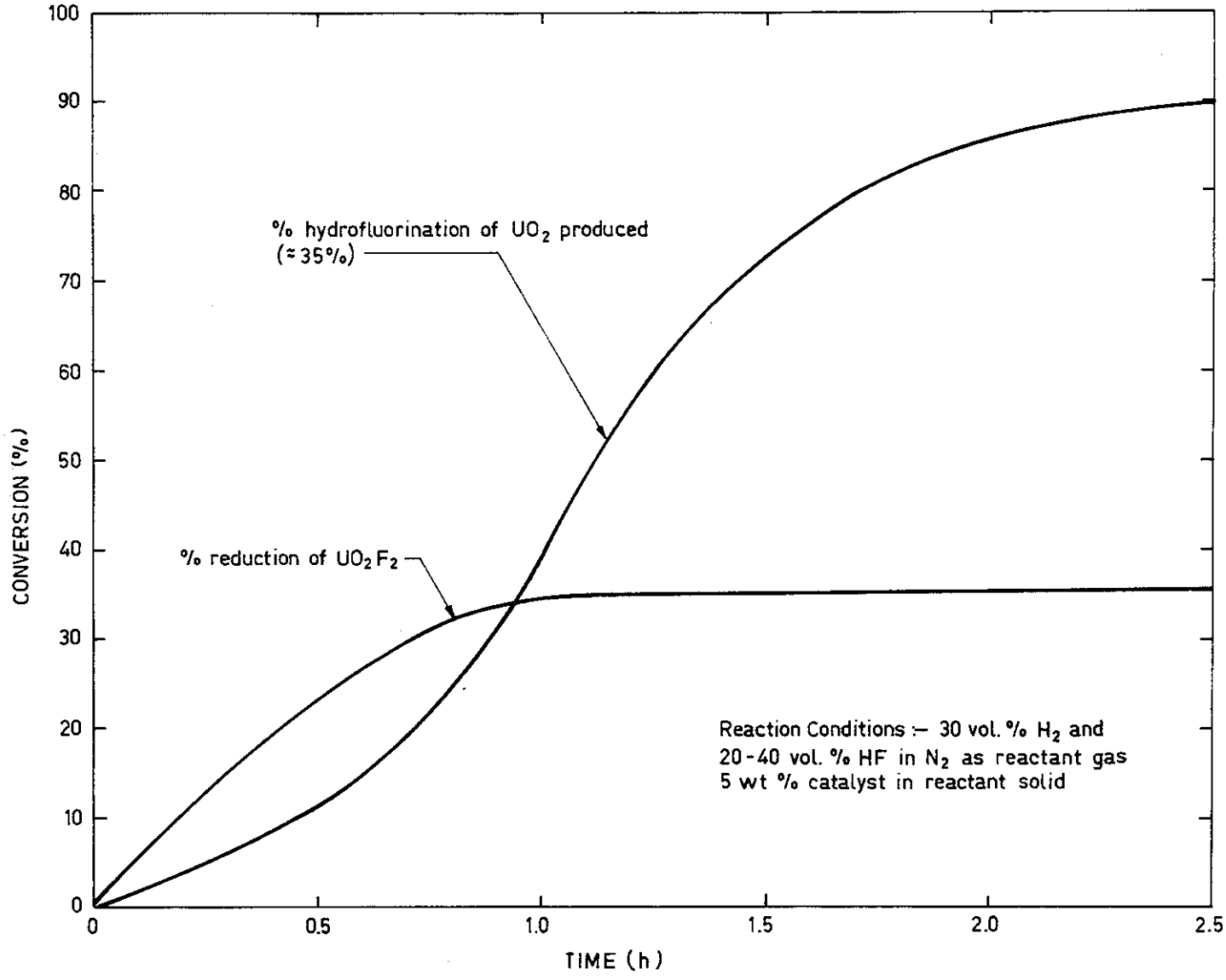

FIGURE 10. CONVERSION CURVES FOR THE REDUCTION OF UO_2F_2 AND SIMULTANEOUS HYDROFLUORINATION TO UF_4 AT 365°C