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ABSTRACT

The feasibility of producing UF_6 by the catalysed reaction of UF_4 with oxygen (the Fluorox process) was investigated in a 150 mm diameter fluidised bed reactor and in supporting bench-scale experiments.

The rate of the Fluorox reaction in batch experiments was increased by an order of magnitude with 1 to 5 per cent catalyst (containing 3 to 4 per cent platinum on alumina). The maximum UF_6 production rate at 650°C was 0.9 kg h^{-1}. However, the platinum catalyst was completely poisoned after production of only 1 and 20 kg UF_6 per kg of catalyst when using respectively French and British UF_4 . Regeneration of the catalyst was demonstrated to be technically

(Continued)

feasible by washing with water or ammonium oxalate solution or treating with hydrogen and hydrogen fluoride at 350-650°C. However, since the very fast rate of poisoning would necessitate higher catalyst concentrations and/or frequent regeneration, the catalysed Fluorox process is unlikely to be economically competitive with the direct fluorination of UF_4.

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URANIUM HEXAFLUORIDE; PRODUCTION; FLUOROX PROCESS; CATALYSIS; PILOT PLANTS; BENCH-SCALE EXPERIMENTS; CATALYSTS; PLATINUM; FLUIDIZED BED REACTORS; URANIUM TETRAFLUORIDE; OXYGEN; CHEMICAL REACTION KINETICS

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1. INTRODUCTION

The Fluorox process produces uranium hexafluoride (UF_6) by reaction of uranium tetrafluoride (UF_4) with oxygen. Equimolar quantities of UF_6 and uranyl fluoride (UO_2F_2) are produced in the primary Fluorox reaction:

$$2UF_4\ (s) + O_2 \longrightarrow UO_2F_2\ (s) + UF_6\ (g) \qquad \Delta H_{298} = +\ 21\ kJ\ mol^{-1} \qquad (1)$$

The UO_2F_2 must be recycled by reduction and hydrofluorination to achieve complete conversion of uranium to UF_6:

$$UO_2F_2\ (s) + H_2 \xrightarrow{650°C} UO_2\ (s) + 2HF \qquad \Delta H_{298} = +\ 49\ kJ\ mol^{-1} \qquad (2)$$

$$UO_2\ (s) + 4HF \xrightarrow{250\text{-}550°C} UF_4\ (s) + 2H_2O \qquad \Delta H_{298} = -\ 181\ kJ\ mol^{-1} \qquad (3)$$

The uncatalysed Fluorox reaction requires temperatures of 800-850°C to achieve reasonable rates of UF_6 production. Two earlier pilot plant studies [Scott et al. 1960; Geertsma et al. 1965] revealed that sintering of UF_4 and corrosion of the reactors by UF_6 were major problems at these temperatures. Catalysis of the Fluorox reaction (and also the reduction reaction) by platinum and other transition metals was discovered at the Australian Atomic Energy Commission [Ekstrom and Batley 1973] and gave rise to the possibility of producing UF_6 by the Fluorox reaction at 600-650°C.

This report describes batch experiments carried out on the catalysed Fluorox reaction in a 150 mm diameter fluidised bed reactor. Such a reactor was chosen for the pilot plant primarily because of its good heat transfer characteristics which result in an even temperature distribution across the reactor and permit heating through the walls with only a moderate temperature gradient. These features should minimise corrosion and sintering in the reactor. It was also thought that the rapid mixing of particles in a fluidised bed reactor might be an advantage in increasing the effectiveness of the catalyst. In addition, transport of powders in fluidised bed reactor systems is fairly simple which makes them attractive for continuous processing of solids.

The catalysis of a gas/solid reaction by another solid is an uncommon phenomenon which had never before been investigated in a pilot plant. The

purpose of the pilot plant program was to establish the chemical and engineering feasibility of the catalysed Fluorox process on a significant engineering scale. In particular, information on catalyst life, product yield and operating characteristics was sought as a basis for an evaluation of the commercial prospects of the process. Some problems encountered in the pilot plant work were more conveniently investigated in smaller bench-scale equipment; these supporting experiments are also described.

A more fundamental study of the catalysed Fluorox reaction, carried out concurrently with the pilot plant development, is described in a companion report [Janov and Walls, in preparation]. The recycle reactions (2) and (3) are only dealt with briefly in the present report since a detailed study of them has been reported by LePage and Janov [1977].

2. LITERATURE REVIEW

The uncatalysed Fluorox reaction was discovered in the United States by Fried and Davidson [1945]. It was extensively investigated as a method of producing UF_6 without the use of elemental fluorine and culminated in the operation of a pilot plant at the Oak Ridge National Laboratory [Scott et al. 1960]. The South African Atomic Energy Board also investigated the process in a similar pilot plant [Geertsma et al. 1965].

This section briefly reviews the chemistry, kinetics and thermodynamics of the uncatalysed and catalysed Fluorox reactions and the results of the two pilot plant investigations.

2.1 Uncatalysed Fluorox Reaction

The Fluorox reaction is a gas/solid reaction with only a small heat of reaction (+ 21 kJ mol^{-1}) and an activation energy of 192 kJ mol^{-1}. The reaction rate is proportional to the surface area of the UF_4 and has an order of 0.4 with respect to oxygen pressure [Ferris 1959].

The Fluorox reaction is also accompanied by secondary reactions between unreacted UF_4 and product UF_6 which can give rise to α and β forms of UF_5, U_2F_9 and U_4F_{17}, the volatilities of which lie between those of UF_4 and UF_6 [Katz and Rabinowitch 1951]. The reactions proceed in a stepwise fashion and yield UF_5, U_2F_9 and U_4F_{17}, depending on the temperature and partial

pressure of UF_6 in the system. The overall reactions can be expressed as

$$UF_4 + UF_6 \rightleftharpoons 2UF_5 \quad (4)$$

$$3UF_4 + UF_6 \rightleftharpoons 2U_2F_9 \quad (5)$$

$$7UF_4 + UF_6 \rightleftharpoons 2U_4F_{17} \quad (6)$$

The rate at which equilibrium is attained is primarily dependent on the nature of the UF_4 and can be affected by sintering of UF_4 and the intermediate uranium fluorides. There are no reported values for their rates of formation or disproportionation. Figure 1 gives the disproportionation pressures of UF_6 over the intermediate uranium fluorides.

2.2 *Pilot Plant Investigations*

Oak Ridge National Laboratory Pilot Plant
[Scott et al. 1960]

Although some experiments were carried out in moving bed and flame reactors, the bulk of the development was in fluidised bed reactors. Initial experiments were in a 75 mm diameter batch-fed, fluidised bed reactor and later experiments were in a 100 mm diameter continuously-fed, fluidised bed reactor. The maximum UF_6 production rate (0.6 kg h^{-1}) was achieved at 815°C in an extended experiment over several days, but the total amount of UF_6 produced in the program was not reported. The reaction rates achieved in the continuously-fed, fluidised bed reactor were in good agreement with laboratory thermogravimetric studies. The reaction half-time was 15-20 minutes at 800-850°C with UF_4 powder of size 105-840 μm and surface area less than 0.2 m^2 g^{-1}. Good yields of UF_6 were reported in most experiments.

Scott et al. reported that reaction of UF_4 with UF_6 to form intermediate uranium fluorides was favoured by increasing temperature. To reduce the formation of intermediate uranium fluorides, it was necessary to operate the reactor with UF_4 diluted with at least four parts UO_2F_2. Sintering of UF_4 was also reduced by diluting the bed with UO_2F_2.

Off-gas filters were placed in the top of the reactor so that the small intermediate uranium fluoride and UF_4 particles which collected there could be returned to the reaction zone by periodically blowing them back off the

filters. Large quantities of intermediate uranium fluorides collected on the sintered metal filters but, provided that they were operated below 500°C, none could be detected past the filters.

The corrosion rate of the Inconel reactor was 0.4 to 2 μm h^{-1} when the bed was operated up to 860°C with wall temperatures of 50-150°C higher. In general, lower corrosion rates were obtained when operating conditions approached steady-state and there were no temperature fluctuations.

In the final evaluation of the uncatalysed Fluorox process, Scott et al. suggested that it should be considered as an alternative process for small plants with a throughput of less than 5000 t UF_6 per year, where fluorine production facilities do not already exist. However, they estimated that the economic benefits were likely to be small.

South African Pilot Plant
[Geertsma et al. 1965]

The central feature of the plant was a 100 mm diameter, continuously-fed, fluidised bed reactor similar to that used at the Oak Ridge National Laboratory (ORNL). It was made from Inconel and had a wall thickness of approximately 7 mm.

Considerable difficulty was encountered with sintering of UF_4 in the reactor; this may have been due partly to the large surface area of the UF_4 (1.5 m^2 g^{-1}) which was an order of magnitude greater than that of the UF_4 used at ORNL. In an effort to minimise sintering, the plant was operated with the highest possible gas velocity through the reactor which would not cause excessive elutriation of powder from the bed and blockage of filters. In addition, the concentration of UF_4 in the reactor was kept below 10 per cent.

Accumulation of significant quantities of intermediate uranium fluorides in the upper section of the reactor was also a problem. These were dislodged by using a vibrator and blowing back the filters; however, clogged filters still had to be removed for cleaning every 100 hours.

The plant was operated for a total of 700 hours and produced 114 kg of UF_6 before the reactor walls were significantly corroded. The corrosion rate was 12.7 μm h^{-1}. The maximum UF_6 production rate was 0.5 kg h^{-1} at 810°C.

2.3 Catalysed Fluorox Reaction

The reaction was studied in thermobalance and bench-scale fluidised bed reactor experiments by Batley et al. [1974] to determine its chemical reaction mechanism, the effect of catalyst type and concentration, and the suitability of fluidised bed reactors for this type of reaction.

In thermobalance experiments, the addition of 1 wt % of very fine catalyst powder (50% < 50 μm) increased the rate of the Fluorox reaction approximately tenfold at 640°C; higher concentrations of catalyst did not increase the rate further. The effectiveness of catalysts, which were typically 5 wt % platinum supported on alumina, was greatest for catalysts with high surface area and small particle size.

The ability of the catalyst to remain active was tested by cycling it five times through the sequence of three reactions (Equations 1, 2 and 3) of the complete process. The effectiveness of the catalyst in accelerating the oxidation reaction was not impaired by this treatment.

In the bench-scale fluidised bed reactor, Batley et al. [1974] found that the catalysed Fluorox reaction was faster than in the thermobalance; they attributed this to greater effectiveness of the catalyst particles as a result of their mobility in the fluidised bed. With 150-250 μm catalyst particles, the rate of the Fluorox reaction was increased sevenfold by the addition of 10 wt % catalyst to a 20 per cent UF_4/80 per cent UO_2F_2 mixture.

Batley et al. [1974] postulated that oxygen atoms or excited oxygen molecules are formed on the catalyst surface and move by surface migration and gas diffusion to the UF_4 particles where they enable the Fluorox reaction to proceed at an accelerated rate. The activation energies of the catalysed and uncatalysed reactions were the same; only the pre-exponential term in the rate constant was increased by the presence of catalyst.

3. PILOT PLANT EQUIPMENT AND PROCEDURES

3.1 Description of Pilot Plant

The plant consisted of two essentially independent parts; one was designed for the production of UF_6 by the catalysed Fluorox reaction and the

other for carrying out the recycle reactions, and for production of UF_4 from UO_2 and UO_2F_2 from UO_3. Each had a fluidised bed reactor and associated auxiliary equipment. A view of the overall plant is shown in Figure 2 and a flowsheet of the part for production of UF_6 is shown in Figure 3.

Uranium tetrafluoride was charged to the reactor through a top inlet valve (38 mm) and preheated oxygen was introduced through the bed support plate. The UF_6 and unreacted oxygen passed through the filters and along heated pipes to condensers in which the UF_6 was separated as a solid at -70°C. Residual UF_6 was removed by a chemical trap containing sodium fluoride pellets and then a caustic scrubber before the unreacted oxygen was discharged to the building ventilation system and vented through a 40 m high stack. The UF_6 was removed from the condensers, when they were off-line, by liquefying the UF_6 at 90°C and draining it into the UF_6 collection cylinder.

3.1.1 Fluidised bed reactor

The fluidised bed reactor was a Class I pressure vessel designed in accordance with ASME Boiler and Pressure Vessel Code - Section VIII, Division 1, 1971. The 1.1 m high reaction zone was fabricated from Inconel 600 pipe, 168 mm o.d. x 7 mm wall thickness. Above the reaction zone was an enlarged disengagement section which housed six filters for removal of solids from the exit gas. It was 400 mm diameter and fabricated from 13 mm thick Inconel 600 plate; the filters were made from sintered Inconel with a mean porosity of 10 μm. Automatic periodic blow-back was provided by means of a reverse flow of nitrogen through nozzles placed immediately downstream of each filter. Two filters at a time were blown back every 150 seconds with a 1.5 second pulse of nitrogen at 800 kPa to remove accumulated solids and return them to the reaction zone.

The gas distributor plate at the bottom of the reactor contained twenty equally spaced tuyeres (Figure 4) through which the gas entered. A 25 mm i.d. pipe inserted in the middle of the gas distributor allowed removal of solids from the fluidised bed reactor.

The reactor was heated by tubular heating elements bonded to the outside wall of the reactor by a layer of sprayed copper. Eleven kilowatts of heating was provided in four separately controlled horizontal sections along the reaction zone. An additional kilowatt was provided to heat the conical gas inlet section. To enable the reactor to be cooled rapidly, a 10 mm diameter

tube was also bonded to the outside of the reactor. Filtered compressed air was forced through this tube at the end of each experiment. The whole of the reactor including the filter section was insulated with a 75 mm thick layer of calcium silicate/mineral wool.

Thermocouples sheathed with Inconel tubing were inserted into the reaction zone through four horizontal branches located 150, 290, 540 and 820 mm above the gas distributor. Another sheathed thermocouple was inserted into the filter section of the reactor and several thermocouples were attached to the outside wall of the reactor. The pressure differences between the conical gas inlet section and the top of reactor, and across the off-gas filters, were measured by gauges, which were constructed from stainless steel and protected against corrosion by a purge of nitrogen (17 mL s^{-1}).

3.1.2 UF_6 collection system

Uranium hexafluoride was collected in two inverted U-tube phosphorised copper condensers similar in design to those used at Argonne National Laboratory [1962]. Each consisted of two 2.3 m high x 150 mm o.d legs which were connected near the top by a short piece of insulated 25 mm o.d. copper tube. The two condensers were used in series although in practice UF_6 was not collected in the second one.

Trichloroethylene cooled to -70°C in an external bath of dry ice was circulated through the condensers counter-current to the process gas. The trichloroethylene passed through 32 mm o.d. tubes positioned along the axis of each leg. To increase their heat transfer area, 16 longitudinal fins, each 50 mm wide, were attached radially around the refrigeration tube.

Each condenser could be heated by a 4 kW resistance element secured to the outside of the vessel by a 3 mm thick layer of heat transfer cement. During UF_6 collection operations, the walls of the condensers were maintained at 50°C to ensure that solid UF_6 did not completely block the vessels. During emptying operations, the non-condensible gas was first pumped out at -70°C and the UF_6 was then liquefied by heating the condensers to 90°C., The liquid UF_6 was drained through 25 mm o.d. copper tubes to a carbon steel cylinder (ERDA Model 12A). The interconnecting pipes were assembled with large radius curves so that the UF_6 condensers could be weighed with load cells to an accuracy of ± 2 kg. The UF_6 collection cylinder was weighed to ± 0.1 kg.

The chemical trap, which was fabricated from 1.5 m long x 170 mm o.d. Monel 400 pipe, contained 3 mm x 3 mm cylindrical sodium fluoride pellets. It was operated at 80°C when scavenging UF_6 from the reactor off-gases and UF_6 could be recovered by purging it with nitrogen at 400°C. The sodium fluoride pellets were prepared by heating sodium bifluoride pellets (obtained from Harshaw Chemical Company, USA) to 550°C.

The caustic scrubber, which was constructed from carbon steel lined with butyl rubber, consisted of a 1.3 m high x 168 mm o.d. tower on top of a tank of 270 L capacity. The scrubber tower was packed with 16 mm x 16 mm polypropylene Pall rings over which 20 wt % potassium hydroxide solution flowed at 0.35 L s^{-1}. In addition to treating the normal process gases, vent lines from bursting discs on the fluidised bed reactor, UF_6 condensers and chemical trap were routed to the base of the scrubber tower. Water cooling coils were provided in the catch tank in case of large accidental release of UF_6.

A 1.4 m long x 90 mm o.d. Monel vessel packed with 5 mm diameter alumina spheres (Alcoa H-151) provided additional protection for the vacuum pump.

3.1.3 Off-gas analysis system

Approximately 0.5 per cent (3.3 mL s^{-1}) of the gas leaving the reactor was diverted through a thermal conductivity cell so that the UF_6 concentration could be continuously monitored. The Gow Mac Model 24-104 cell with nickel filaments gave a linear response of 0.6 mV per one per cent UF_6 in the gas at a cell current of 80 mA. The cell was operated at 135-150 kPa and 100°C.

The UF_6 that passed through the thermal conductivity cell was collected in a small condenser (180 mm x 55 mm o.d.) immersed in a bath of dry ice and trichloroethylene and weighed at the end of each experiment; the total gas flow through the thermal conductivity cell was also metered. This allowed the calibration of the thermal conductivity cell to be checked. Since the quantity of UF_6 produced in single experiments was too small to be measured by weighing the main UF_6 condensers, the weight collected in the small condenser was also used to calculate the total UF_6 production.

3.2 Materials

Table 1 summarises the surface area, determined by nitrogen adsorption, and bulk density of the materials used. Figure 5 shows the as-received size distributions.

Uranium tetrafluoride

Uranium tetrafluoride powders from two sources were used in the pilot plant work. They were significantly different in appearance, in physical behaviour and in chemical reactivity as measured in thermobalance experiments [Janov and Walls 1981].

The 650 kg of UF_4 purchased from British Nuclear Fuels Ltd (BNFL) was produced via the thermal denitration of uranyl nitrate route. Individual UF_4 particles were spherical and their surfaces had a non-porous appearance (Figure 6a). The powder flowed freely and fluidised well.

The 500 kg of UF_4 purchased from Commissariat à l'Energie Atomique (CEA) was produced via the ammonium diuranate precipitation route and individual particles had a coral-like appearance (Figure 6b). This material did not fluidise nor flow as well as the British UF_4.

The particle size distributions of the as-received powders were similar. The British UF_4 was used in the as-received form but the size distribution of the French UF_4 was modified by isostatic pressing at 276 MPa followed by crushing in an attempt to improve the fluidisation characteristics of the powder. The size of French UF_4 used in different experiments is given in the results.

Catalyst

The catalyst was purchased from Engelhard Industries Pty Ltd in two separate batches. The first contained 4.2 per cent platinum supported on γ-alumina and the second contained 2.9 per cent. Both batches of catalyst had a surface area of 120 $m^2\ g^{-1}$ but this was reduced on contact with UF_6 (see Section 6.1).

The first batch of catalyst had 10 wt % of particles less than 89 μm diameter (98% < 250 μm) and was used as-received, primarily with British UF_4.

The second batch was finer and had 20 wt % of particles less than 89 μm. For the batch-continuous experiment, the -89 μm fraction was removed as it was likely to segregate from the coarser particles in the fluidised bed.

Uranyl fluoride

About 70 kg of UO_2F_2 was produced for this work by reacting UO_3 powder with hydrogen fluoride (diluted with nitrogen) at 300-400°C in the second 150 mm diameter fluidised bed reactor. The UO_3, which had been produced by thermal denitration of uranyl nitrate [Fane et al. 1974], was initially unreactive. However, after hydration over dilute nitric acid for 10 days at 60°C, essentially complete conversion to UO_2F_2 was obtained. The UO_2F_2 was very hygroscopic, so it was handled, as far as possible, in an enclosed glove-box in which the relative humidity was reduced to 20-40 per cent.

Alumina

Low surface area alumina of the type commonly used in uranium fluorination experiments [Anastasia et al. 1968] was substituted for uranyl fluoride in several experiments. The alumina (Alcoa Grade T61) was crushed and sieved and the 150-300 μm size fraction used.

Process gases

The oxygen was medical grade dry oxygen supplied by Commonwealth Industrial Gases Ltd. Nitrogen was obtained by vaporisation of liquid nitrogen. Moisture in both gases was less than 10 μg g^{-1} when entering the plant, consequently drying columns were not used.

3.3 Procedures

3.3.1 Commissioning

All process vessels were hydrostatically pressure-tested before installation. The assembled plant was leak-tested by measuring the rate of pressure decrease and by helium leak detectors. The overall leak-tightness of the plant was about 6×10^{-2} kPa L s^{-1} with nitrogen at 260 kPa and that of the UF_6 condensers was better than 1×10^{-2} kPa L s^{-1}.

Parts of the plant which came into contact with UF_6 were chemically degreased by circulating trichloroethylene, water and methanol through them and then purging dry with nitrogen. Before commencement of the experimental program, the vessels were conditioned with fluorine at atmospheric pressure and room temperature. The vessels were fluorinated several times during the experimental program, for instance, after uranium had been washed from the reactor with water and aluminium nitrate solution.

To enable the rate of corrosion to be determined at a later stage, the thickness of the walls and the inside diameter of the reactor were measured accurately.

3.3.2 Batch experiments

All but one experiment was carried out in the batch mode of operation at a reaction temperature of 650°C. In a typical experiment, half of the inert material (UO_2F_2 or alumina) was loaded into the reactor at room temperature followed by UF_4 (mixed with catalyst) and the remainder of the inert material. This loading sequence was adopted to facilitate mixing in the reactor during fluidisation and to prevent UF_4 from lodging in the drain pipe or between the tuyeres of the gas distributor where it would have been stagnant and likely to sinter. In experiments in which no inert material was used, the catalyst was pre-mixed with about 20 per cent of the UF_4 which was added to the reactor midway through the loading. In most experiments, a close fitting Inconel bar was inserted in the drain pipe between the gas distributor and bottom valve to limit the amount of stagnant powder in the reactor.

The quantity of material loaded into the reactor varied from 14 to 29 kg which corresponded to static bed heights of 370 to 780 mm and bed height to diameter ratios of 2.5 to 5.2. Thus there were always two thermocouples in the bed at heights of 150 and 290 mm above the gas distributor. The concentration of UF_4 in the feed powder was varied from 5 to 100 per cent and the concentration of catalyst from 0 to 6.8 per cent.

Moisture was very undesirable in the plant since it reacts with ten times its weight of UF_6. It also reacts with UF_4 at temperatures above 350°C to form UO_2 and with UO_2F_2 to form U_3O_8 and these react with UF_6. For this reason, the UF_4, catalyst and inert alumina were dried in an oven at 150°C before loading into the reactor. The UO_2F_2, which absorbs moisture very quickly, was stored in sealed jars in the glove-box from whence it could be

transferred directly into the reactor to minimise its handling in ambient air. Final drying took place in the reactor during heating.

The powder was fluidised with nitrogen at 1.67 L s^{-1} at room temperature before heating to 650°C at approximately 300°C per hour. During heating, the UF_6 condensers and chemical trap were by-passed so that moisture from the reactor was carried along heated pipes to the scrubber. The temperature of the top of the reactor rose to 200-250°C when the reaction zone was at 650°C. The UF_6 condensers, chemical trap, gas preheater and blow-back chamber were also brought to their operating temperatures while the reactor was heating.

As the temperature in the reactor rose, the flow rate of nitrogen was gradually reduced to 0.75 L s^{-1}. This corresponded to four to seven times the minimum fluidisation velocity for the powder at 650°C and was selected to give good mixing of components in the reactor. At a gas flow rate of 0.75 L s^{-1}, the temperature was within ± 2°C of 650°C throughout most of the bed but decreased rapidly over the bottom 90 mm to 560°C at the gas distributor. When the fluidised bed had stabilised at the operating temperature, the UF_6 condensers and chemical trap were brought on-stream and the fluidising gas changed gradually from nitrogen to oxygen over a period of about 10 minutes.

On completion of the experiment, the oxygen was replaced with nitrogen, the UF_6 condensers by-passed and evacuated (at -70°C), and the plant cooled to room temperature.

3.3.3 Batch-continuous experiment

This experiment was designed to investigate the catalyst poisoning more rapidly. In addition, lower concentrations of more closely sized UF_4 were used and the catalyst was pretreated with UF_6.

The catalyst (particle size 90-300 μm) was pretreated with UF_6 in batches at 650 and 250°C in an attempt to increase the yield of UF_6. The intention was to treat all of the catalyst at 650°C but, because of experimental difficulties, 60 per cent had to be treated at the lower temperature. Consequently, the catalyst was only partially inert to UF_6 during the batch-continuous experiment. As described in Section 6.1, treatment of the catalyst with UF_6 does not decrease its effectiveness in promoting the Fluorox reaction.

At the start of the experiment (Run 65), 19.2 kg of UO_2F_2 mixed with 1.4 kg of catalyst was heated to 650°C while being fluidised with nitrogen. The fluidisation was interrupted briefly while one kilogram of French UF_4 (particle size 124-251 μm) was charged to the bed through the top of the reactor; good mixing of the components was ensured by fluidising the bed with nitrogen for five minutes before it was replaced with oxygen. The progress of the Fluorox reaction was then monitored by measuring the amount of UF_6 in the product gas and then allowing the UF_4 to react to completion before the next batch of UF_4 was charged to the reactor. Four separate one kilogram batches of UF_4 were charged to the bed of UO_2F_2 at 650°C using the same procedure. The rate of reaction in this experiment was calculated from the rate of UF_6 production.

At the end of the experiment, the vertical distributions of catalyst and unreacted UF_4 were determined to check that there had been no undesirable segregation of powders. This was done by stopping the fluidisation while the reactor was still hot, cooling the reactor to room temperature, and then sectioning the bed by vacuuming successive layers of powder from the top of the bed.

3.3.4 Calculation of reaction rates

The extent and rate of reaction in batch experiments were calculated from the amount of UF_4 left in the reactor. Representative samples of the powder from the reactor were chemically analysed by selective dissolution methods described in Appendix A.

Determination of the amount of UF_4 left at the end of experiments was difficult because only about 95 per cent of the powder was recovered from the reactor. The remainder stuck to the walls of the reactor or was retained in the filter section. As the composition of this material had to be estimated, this led to uncertainty in calculating the results. The maximum and minimum values given in Tables 4, 6 and 7 assume that the unrecovered material was either all diluent (UO_2F_2 or Al_2O_3) or UF_4. The arithmetic average of these is used in the remainder of the report even though it probably underestimates the amount of UF_4 converted and hence the rate of reaction.

The alternative method (used in the batch-continuous experiment) for determining the rate of reaction would have been to base the calculations on UF_6 production. However, UF_6 was consumed in several secondary reactions with

alumina, unreacted UF_4 and walls of the vessels and, therefore, its rate of production was not satisfactory for determining the rate of the primary Fluorox reaction.

The reaction rates are reported as apparent reaction rate constants, R (h^{-1}), given by the expression:

$$(1-x)^{1/3} = 1-Rt \qquad (7)$$

where x = weight fraction of converted or reacted UF_4, and
t = reaction time (h)

This expression applies strictly to particles of one size in which the reaction proceeds at the surface of a shrinking core [Levenspiel 1972]. In thermobalance tests with UF_4 of the size distribution used in the pilot plant, the expression closely fitted the progress of the reaction and was, therefore, used to calculate an apparent reaction rate constant, R. The time to complete half of the reaction, $t_{½}$, is given by the expression

$$t_{½} = \frac{0.693}{R} \qquad (8)$$

Figure 7 shows a family of calculated reaction curves for R = 0.001, 0.01, 0.1 and 1.0 h^{-1} based on Equation 7.

4. PILOT PLANT RESULTS AND DISCUSSION

Although previous pilot plant experience at temperatures above 800°C [Scott et al. 1960; Geertsma et al. 1965] indicated the desirability of operating with UF_4 which had been diluted with at least four parts of inert UO_2F_2, only limited quantities of UO_2F_2 were available when this project commenced. Consequently, a number of experiments were carried out to check whether a diluent was necessary at the lower temperatures (650°C) used for the catalysed Fluorox reaction and in an attempt to make more UO_2F_2.

Subsequently, many experiments were carried out with low surface area alumina as a substitute for UO_2F_2. This alumina was not completely inert to UF_6 and the yield* of UF_6 in these experiments was low, particularly when

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* UF_6 yield (%) = $\frac{\text{Weight } UF_6 \text{ produced}}{\text{Weight } UF_4 \text{ converted}} \times \frac{628}{352} \times 100$

+ UF_6 produced = UF_6 collected or measured by thermal conductivity cell

alumina was used for the first time. These experiments, therefore, were useful for measuring the rate of conversion of UF_4 but not the quantity of UF_6 produced+.

The available UO_2F_2 feedstock was used only after preliminary experience had been gained with the alumina diluent.

4.1 General Operating Experience

4.1.1 Build-up of uranium in reactor

It was usual to have a small discrepancy in the uranium balance. On average, 4.8 per cent of the uranium in the feed could not be accounted for in the UF_6 or solid residues removed from the reactor. This uranium either stuck to the inside of the reactor, or the off-gas filters, or lodged in the expanded upper section of the reactor.

In 53 batch experiments in which 199 kg of UF_4 and 461 kg of UO_2F_2 were used, 32 kg of uranium compounds was held up in the reactor. This accumulation of uranium compounds caused a gradual increase in both the pressure drop across the off-gas filters and the resistance to heat transfer across the walls of the reactor. The temperature difference across these walls had to be raised from 20 to 100°C to maintain the temperature of the bed at 650°C. The pressure drop across the filters rose from 5 to 110 kPa.

In the production plant, the accumulated uranium compounds on the walls of the reactor would not be a problem and, indeed, would act as a protective layer against corrosion. Temperature differences across the walls of the reactor as great as 150°C were used by Scott et al. [1960] without any apparent problem. In the present work, however, the hold-up of uranium introduced uncertainties in the determination of reaction rates and also necessitated operation at the design limits of the reactor and heaters. Twice during the operation the build-up made it necessary to wash the reactor after approximately 14 kg had accumulated. The reactor was filled with water and then aluminium nitrate solution at 60°C. Approximately 75 per cent of the accumulated material was recovered from the reaction zone; 78 per cent was soluble in water (UO_2F_2) while the remainder was UF_4. The balance of the accumulated material was in the upper section of the reactor and on the filters.

The filters could only be cleaned effectively by removing them from the reactor. They were covered with a 3 mm thick layer of very fine grey powder which slowly turned green on exposure to ambient air. Chemical analysis of the grey powder indicated that it contained 17.7% U(IV), 52.3% U(VI) and 14.4% F^-, but X-ray diffraction analysis failed to identify any of the intermediate uranium fluorides. The grey powder was removed by scraping but this only reduced the pressure drop across the filters by 25 per cent; they had to be soaked in aluminium nitrate solution at 60°C to remove the remainder of the blockage which was held in the pores of the sintered metal filters.

4.1.2 UF_6 collection

The quantity of UF_6 produced in the experiments was limited because it reacted with the alumina diluent in some experiments, the catalyst support and small quantities of oxides of uranium in the uranyl fluoride.

The total quantity of UF_6 collected in the product cylinder was only 15.2 kg although it was estimated, from analysis of the product gas, that 30 kg left the reactor. Some of the balance reacted with the walls of the UF_6 condensers and a fine layer of UO_2F_2 (possibly formed by reaction of UF_6 with metal oxides) was observed on some of the internal surfaces. The majority of the discrepancy occurred in the early part of the project.

The greatest quantity of UF_6 collected in a single experiment was 1.9 kg in the batch-continuous experiment (Table 8, Run 65) at an overall yield of 84 per cent, based on the amount of UF_4 converted. In catalysed experiments in which British UF_4 feed was diluted with UO_2F_2 (Table 6), an average of one kilogram of UF_6 was produced in each of six experiments with yields ranging from 64 to 89 per cent.

The UF_6 condensers functioned satisfactorily and nearly all the UF_6 was collected in the first. Transfer of UF_6 from the condenser to the product cylinder was straightforward although it took about seven hours to heat the UF_6 above its triple point. This was due to the low gas density in the condenser at the start of heating which resulted in poor heat transfer from the outside walls to the finned condenser in the middle of the vessel. A better method of melting the UF_6 would have been to circulate hot fluid through the finned condenser tube.

+ UF_6 produced = UF_6 collected or measured by thermal conductivity cell

4.1.3 Corrosion

Only a minor amount of corrosion was detected in the reactor after 380 hours of operation at 650°C. Ultrasonic measurements at two locations in the reaction zone indicated that the metal thickness of the wall was reduced by less than 130 μm. The Inconel sheath of a thermocouple extracted from the reaction zone had also decreased in radius by 130 μm. Thus the corrosion rate in the reactor was approximately 0.3 μm h^{-1}. However, insufficient UF_6 was produced to prove that corrosion of the reactor in a catalysed Fluorox plant operating at 650°C would be insignificant.

4.2 Experiments with 100 per cent UF_4 Feed

Six experiments, summarised in Table 2, were carried out with 100 per cent British UF_4 feed. The aim was to produce, for subsequent experiments, UO_2F_2 which was of the same size and derived from the UF_4 feed powder. It was thought that this might be feasible because four-hour tests had shown that British UF_4 powder did not sinter into lumps in an inert atmosphere at 650°C. Furthermore, 60 per cent conversion of undiluted UF_4 to UO_2F_2 had been achieved fairly rapidly in earlier catalysed tests in a 50 mm diameter fluidised bed reactor [Batley et al. 1974].

In the pilot plant, however, it was impossible to achieve complete conversion to UO_2F_2 because the uncatalysed reaction was impracticably slow; also, in catalysed reactions the UF_4 sintered badly, forming a solid mass in the upper part of the fluidised bed. In an endeavour to prevent sintering, the gas flow rate was increased to stir the bed more vigorously and the oxygen partial pressure was increased gradually to slowly produce an outer shell of UO_2F_2 before the onset of a more rapid reaction; both measures were unsuccessful. Experiments with 100 per cent French UF_4 feed were not attempted as it had a higher surface area and would have been more likely to sinter.

With British UF_4, the reaction rate was increased significantly by the addition of fresh catalyst. In uncatalysed experiments, the average apparent reaction rate constant was 0.0025 h^{-1} and increased seven- and sixteen-fold with the addition of 0.5 and 1.0 per cent fresh catalyst respectively. The yield of UF_6 based on quantity of UF_4 converted was good (> 83 per cent) in the first three experiments. The yield in the second three was low, however, because the reactor had to be washed between experiments to remove the

sintered UF_4, and the metal surfaces exposed during the washing were not re-passivated by fluorination.

The relative increases in reaction rate were greater than had been observed in thermobalance tests using 30 mg samples of this material. However, the absolute values of the apparent reaction rate constants were very much lower than those measured in thermobalance tests with the same UF_4 and catalyst (Table 3). The difference in apparent reaction rate constants was largest for the uncatalysed Fluorox reactions. When UF_4 residues from the uncatalysed pilot plant experiments were re-tested in the thermobalance, they reacted 50 per cent more slowly than fresh UF_4. This decrease was proportional to the reduction in UF_4 surface area because they had had six hours of microsintering in the pilot plant reactor. Even so, the UF_4 reacted much faster in the thermobalance than in the pilot plant.

The slower rates of reaction in the pilot plant, although not completely understood, are related to the larger mass of UF_4 present. It is postulated that intermediate uranium fluoride species formed by reaction of UF_6 with UF_4 retards the overall rate of the Fluorox reaction, particularly the uncatalysed reaction. In the pilot plant the UF_6 was in contact with the UF_4 for a longer time, thereby favouring the formation of intermediate uranium fluorides and causing the overall rate of reaction to be decreased. Further results supporting this theory are given in Sections 4.3 and 6.3.

4.3 Uncatalysed Experiments with Diluted UF_4 Feed

Dilution of UF_4 feed with UO_2F_2 or alumina increased the rate of the uncatalysed Fluorox reaction by up to two orders of magnitude. When 21 per cent British UF_4 in UO_2F_2 was used instead of 100 per cent UF_4 feed, the apparent reaction rate constant increased from 0.0025 to 0.019 h^{-1}. When 20 per cent British UF_4 in fresh alumina was used, the apparent reaction rate constant increased further to 0.10 h^{-1} and was of the same order as that determined in the thermobalance with very small undiluted samples (Table 3). The variation in apparent reaction rate constant with concentration of British UF_4 in fresh alumina feed over the range 5 to 100 per cent is shown in Figure 8 and Table 4.

Dilution of UF_4 seemed to decrease the rate of formation of intermediate uranium fluorides and increase the overall rate of reaction. When fresh alumina diluent was used the additional increase was due to the complete

absorption of UF_6 by the alumina particles very close to the source of UF_6 generation. Hence the UF_6 was unable to contact other UF_4 particles in the reaction zone and the formation of intermediate uranium fluorides was minimised.

In another series of uncatalysed experiments with French UF_4 and alumina diluent, the apparent reaction rate constant decreased by as much as an order of magnitude when the alumina was re-used with fresh UF_4. The re-used alumina did not react as readily with UF_6 (shown by increased yield of UF_6) and hence more of it was available to take part in the formation of intermediate uranium fluorides.

The effect of diluting the UF_4 feed on the uncatalysed reaction rate was also observed in thermobalance experiments by Janov and Walls [1981] and in bench-scale experiments described in Section 6.3. Unfortunately, no evidence of the intermediate uranium fluorides in the reaction zone was found in any of this work. This was probably due to the fact that intermediate uranium fluorides disproportionate at 650°C and were only present in small quantities during the Fluorox reaction. When the oxidation of UF_4 stopped, the intermediate uranium fluorides decomposed and, therefore, were not found in the powder at the end of experiments.

French UF_4 was more reactive than British UF_4; with 20 per cent UF_4 in UO_2F_2 the apparent reaction rate constants were 0.079 and 0.019 h^{-1} respectively. They were proportional to the surface areas of the UF_4 powders.

4.4 Catalysed Experiments with Diluted UF_4 Feed

The results in this section refer only to experiments using fresh catalyst in which the UF_4 feed was diluted with UO_2F_2. Table 5 summarises the apparent reaction rate constants for these experiments for both British and French UF_4. Uncatalysed reaction rate constants from experiments with 20 per cent UF_4 feed are included for comparison.

The reaction rate with British UF_4 was higher than that with French UF_4 with the same amount of catalyst. With 20 per cent UF_4 in the feed, a seven-fold increase in apparent reaction rate constant was achieved with 1 per cent catalyst and British UF_4, but 5 per cent catalyst was required to achieve a similar increase with French UF_4.

The effect of UF_4 concentration on the catalysed reaction rate was not investigated systematically in the pilot plant. There was some evidence that it was not as important as for the uncatalysed reaction. For instance, with 20 and 100 per cent British UF_4 feed, the ratio of apparent reaction rate constants was 7.6 without catalyst and 3.3 with 1 per cent catalyst. With French UF_4 and approximately 5 per cent catalyst, the ratio of apparent reaction rate constants for feed containing 5 and 19 per cent UF_4 was less than 1.5.

The smaller influence of UF_4 concentration on the catalysed reaction rate was also observed in both bench-scale fluidised bed tests [Batley et al. 1974] and thermobalance tests [Janov and Walls 1981]. This suggests that, in the presence of a catalyst, the reaction proceeds in a different manner. The uncatalysed Fluorox reaction takes place simultaneously throughout individual UF_4 particles and there is still some green UF_4 visible on the outside surfaces of particles which have been mostly converted to UO_2F_2. The catalysed Fluorox reaction, on the other hand, commences on the outside of the UF_4 particles and proceeds inwards; the outside surfaces consist only of UO_2F_2 soon after the reaction commences. Thus there is less opportunity for the UF_6 to react with unreacted UF_4 in neighbouring particles and the overall catalysed reaction rate is not dependent on the concentration and amount of UF_4 in the feed.

4.5 Catalyst Poisoning

Although the rate of the Fluorox reaction was increased by an order of magnitude when fresh catalyst was used, the catalyst lost its effectiveness quite rapidly with continued use. This was demonstrated in four series of experiments:

(i) Batch experiments with British UF_4/UO_2F_2.

(ii) Batch experiments with British UF_4/alumina.

(iii) Batch experiments with French UF_4/UO_2F_2.

(iv) Batch-continuous experiment with French UF_4/UO_2F_2.

In these series of experiments, the powder residue containing some unreacted UF_4 and catalyst from one experiment was re-used in the next.

Sufficient UF_4 was added before each experiment to ensure that the starting concentration of UF_4 remained approximately constant. However, owing to the production of UO_2F_2, the concentration of catalyst could either be allowed to gradually decrease or, alternatively, a small amount of fresh catalyst could be added to maintain its original concentration. Both approaches were used but had obvious problems for accurate determination of rate of catalyst poisoning.

4.5.1 Batch experiments with British UF_4/UO_2F_2 feed

Table 6 summarises the details of these experiments and Figure 9 shows the decrease in apparent reaction rate constant against amount of UF_6 produced and UF_4 converted. A steady decrease in catalyst effectiveness was observed throughout the series of experiments even though small amounts (0.1 and 0.2 per cent) of fresh catalyst were added in some experiments to maintain a constant catalyst concentration. The catalyst was completely poisoned after conversion of approximately 11 kg UF_4 and production of 4.5 kg UF_6 which is equivalent to the production of 19.6 kg UF_6 per kg of catalyst. In a final experiment (Table 6, Run 47), 1.1 per cent of fresh catalyst was added to the completely poisoned catalyst. The catalytic activity was restored, showing that the decrease in reaction rate had been due to poisoning and not to some other effect.

The concentration of catalyst in the reactor was checked at the end of each experiment by measuring the amount of platinum in representative samples of the powder. This showed that catalyst had not been lost from the reactor. Representative samples containing poisoned catalyst were also tested in the thermobalance and found to be inactive.

The UF_6 yield in this series of experiments was reasonably good and ranged from 65 to 89 per cent. With fresh catalyst, the initial rate of UF_6 production was 0.6 kg per hour.

4.5.2 Batch experiments with British UF_4/alumina feed

The decrease in apparent reaction rate constant was slight in the first four experiments in which the UF_6 yield was low (Table 7). The UF_6 yield increased in the fifth and sixth experiments and, significantly, the apparent reaction rate constant decreased simultaneously. A total of 21.9 kg UF_4 was converted before the apparent reaction rate constant decreased by an order of

magnitude, but only 3.1 kg UF_6 was produced. This is equivalent to production of approximately 15 kg UF_6 per kg catalyst which is similar to the rate of catalyst poisoning obtained with British UF_4/UO_2F_2 feed.

4.5.3 Batch experiments with French UF_4/UO_2F_2 feed

These experiments were carried out with approximately 20 per cent French UF_4/UO_2F_2 feed to which 5 per cent catalyst was added; the UF_4 was -500 μm in size (39 wt % < 90 μm).

Because of experimental difficulties, the results of the early experiments were unreliable, but in the last three experiments there was a steady decrease in apparent reaction rate constant from 0.17 to 0.054 h^{-1}. The apparent reaction rate constant for the uncatalysed reaction had been measured previously as 0.079 h^{-1}.

The surprising feature of these experiments was that the catalyst was poisoned very much more quickly than in experiments with British UF_4. Only 8.3 kg UF_4 was converted and 1.4 kg UF_6 produced before the catalyst was completely poisoned, even though the quantity of catalyst in the reactor was 3 to 5 times greater than in the previous two series. Only 1 kg UF_6 was produced per kg catalyst before it was rendered ineffective.

4.5.4 Batch-continuous experiment with French UF_4/UO_2F_2 feed

The UF_4 and catalyst were sized more closely than in previous experiments to eliminate any possibility of UF_4/catalyst segregation which might decrease the rate of reaction. That this was effective was demonstrated by two separate determinations of their vertical distribution in the reactor. Before Run 64, the distribution of 20 per cent UF_4 in UO_2F_2 was measured after fluidisation at 650°C in nitrogen. At the end of Run 65/4, the catalyst (and unreacted UF_4) distributions were measured. All were very evenly distributed throughout the reactor.

This series of experiments was actually carried out as a single batch experiment (Run 64) followed by the batch-continuous experiment (Run 65/1 to 65/4), as it was decided to interrupt the experiment and examine the powder product when no UF_6 was detected in the off-gas in Run 64. The details of these experiments are summarised in Table 8 and the concentration of UF_6 in the product gas in Run 65/1 to 65/4 is shown in Figure 10.

A progressive decrease in the catalyst effectiveness is evident from the decrease in peak UF_6 concentration and in the increasing length of time needed to complete each reaction. The maximum UF_6 production rate was 0.8 kg UF_6 per hour.

The uncatalysed rate of reaction of 5 per cent French UF_4 in UO_2F_2 was not measured in the pilot plant. However, the powder residue from Run 65/4 was tested in the bench-scale fluidised bed reactor (see Section 6) and the catalyst in it was shown to be completely ineffective. Thus, the catalyst had been completely poisoned after converting 7.8 kg UF_4 and producing 1.86 kg UF_6; that is, after production of about 1.3 kg UF_6 per kg catalyst. This rate of catalyst poisoning was similar to that found in batch experiments with French UF_4 but more than an order of magnitude faster than with British UF_4.

When tested in the bench-scale fluidised bed reactor, the effectiveness of the catalyst after Run 64 was found to be unimpaired. Thus the catalyst poisoning all occurred in the batch-continuous experiment in which UF_6 was produced.

4.5.5 Possible causes for catalyst poisoning

A number of possible causes for the poisoning of the catalyst were considered. None, however, was positively identified as the sole or prime cause.

Uranium hexafluoride reacted with the high surface area alumina on which the platinum was supported and reduced the surface area of the catalyst from about 120 to 20 $m^2\ g^{-1}$. However, the effectiveness of the catalyst was not decreased by exposure to UF_6 alone. This was demonstrated in bench-scale and thermobalance tests (see Section 6) in which the catalyst was treated with UF_6 for extended periods at 650°C before it was used in Fluorox reactions.

In the pilot plant, however, the catalyst was exposed to intermediate uranium fluorides as well as UF_6 and these may have poisoned the catalyst. Examination of the poisoned catalyst particles by optical microscope showed them to be a lustrous black colour (with some inclusions of white UO_2F_2) which seemed to be coated with a thin layer of clear material; it appeared as if a clear viscous liquid had been applied to them and allowed to dry leaving a smooth surface finish, similar to epoxy resin. The UO_2F_2 particles from the pilot plant also appeared to have a glazed surface finish when viewed through

the optical microscope. In contrast, the fresh catalyst and catalyst treated with UF_6 had a matt appearance with a coral-like surface texture. These differences are not as apparent in the black and white photographs (Figure 11a-c) which were taken in a scanning electron microscope. The poisoned catalyst was successfully regenerated by two methods in bench-scale tests described in Section 6. The regenerated catalyst was free of the epoxy resin-like coating and had the coral-like texture of the unpoisoned catalyst (Figure 11d).

The rates of catalyst poisoning differed by more than an order of magnitude in experiments with British and French UF_4. The UF_4 powders were not prepared by the same method and the surface area of the French UF_4 was four times that of British UF_4. Hence the UF_4 materials were of unequal reactivities and this may have resulted in different concentrations and rates of formation of intermediate uranium fluorides in the reactor. However, the intermediate uranium fluorides are reported to disproportionate at temperatures well below 650°C (Figure 1), so a mechanism by which the intermediate uranium fluorides could cause the poisoning is difficult to postulate.

Another possible reason for the catalyst poisoning and the difference in the rates of poisoning was that the feed materials contained significant and varying amounts of sulphur. It is generally known that sulphur poisons platinum catalyst [Fischer and Kelemen 1978]. The British and French UF_4 contained 52 and 3.5 $\mu g\ g^{-1}$ sulphur respectively. The UO_2F_2 and alumina diluents used in experiments with British UF_4 were essentially free of sulphur, whereas the UO_2F_2 used in experiments with French UF_4 contained 430-850 $\mu g\ g^{-1}$ of sulphur. Analysis of the mixed powder at the end of experiments showed that the sulphur was released during the Fluorox reaction, as it generally contained less than 5 $\mu g\ g^{-1}$ sulphur. However, there was no sign of foreign elements, particularly sulphur, on the surface of the poisoned catalyst from Run 65/4 when it was examined by electron probe analysis using a scanning electron microscope. More conventional methods of analysing for sulphur could not be used as it was difficult to separate more than a few particles of catalyst from the UO_2F_2. Thus, although poisoning of the catalyst by sulphur is conceivable, no direct evidence for it could be found.

Segregation of catalyst from the UF_4 was also considered as a possible reason for the decrease in the rate of the Fluorox reaction. This was shown to be unimportant by careful measurement of the catalyst distribution in the

reactor. Furthermore, any segregation of particles in a fluidised bed usually occurrs within a few minutes, whereas the catalyst was poisoned over a period of several hours.

5. BENCH-SCALE EQUIPMENT AND PROCEDURES

Supporting bench-scale experiments were carried out in the following equipment:

- a 50 mm diameter vertical reactor,
- a 38 mm diameter horizontal reactor, and
- a thermobalance with 200 mg capacity.

5.1 50 mm Diameter Vertical Reactor

This reactor was used to confirm rates of reaction observed in the pilot plant, investigate the effect of UF_4 concentration, quantity, and bed geometry on the rate of the uncatalysed Fluorox reaction, and carry out recycle reactions on product from pilot plant oxidation experiments which contained poisoned catalyst.

The reactor could be operated as either a fixed or fluidised bed. Figure 12 shows the layout of associated equipment when the reactor was operated as a fluidised bed. When it was operated as a fixed bed, the reactant gases were introduced through the top of the reactor and withdrawn through the bottom. The reactor, which was made from a 0.5 m length of 50 mm diameter nickel tube, was fitted with a gas distributor and off-gas filter made from porous sintered nickel plate to which a fine nickel mesh was bonded. In fixed bed experiments, the powder rested on the bottom plate, but in fluidised bed experiments the gas entered through the bottom plate and suspended the powder.

Reactant gas mixtures were metered through rotameters and preheated to the reaction temperature in a 0.3 m long x 40 mm diameter nickel vessel packed with 6 mm x 6 mm nickel Raschig rings. The preheater and reactor were both heated in electrical furnaces of 2 kW capacity which were controlled to ±2°C. Hydrogen fluoride was supplied from 300 g capacity liquid HF cylinders which were warmed by a surrounding copper coil carrying water from a temperature

controlled bath. A pressure switch on the HF vapour line switched off the heaters in the event of the pressure rising above 350 kPa.

The exit gases from reduction and hydrofluorination experiments passed through a scrubber containing 20 wt % KOH solution, and exit gases from Fluorox experiments passed through a trap immersed in dry ice to collect UF_6. Approximately 3.3 mL s^{-1} of exit gas was diverted through a thermal conductivity cell (see Section 3.1.3) for analysis of UF_6.

Fluidised bed experiments were typically carried out with 300 g of powder and a gas flow rate of 83 mL s^{-1} (NTP). Fixed bed experiments were generally carried out with smaller quantities of feed material and gas flow rates varying from 3.3 to 20 mL s^{-1} (NTP). Undiluted oxygen was used in Fluorox experiments and 30 per cent hydrogen/nitrogen and 30 per cent hydrogen fluoride/nitrogen were used in the reduction and hydrofluorination experiments, respectively.

At the start of each experiment, the solids were loaded into the reactor, then the reactor was sealed, connected into the system and thoroughly purged with nitrogen. When the reactor had reached the operating temperature, the reactant gases were introduced; the reaction was followed by monitoring the temperature in the reactor and the output of the thermal conductivity cell. Fluorox experiments were carried out at 650°C, reduction at 650°C and hydrofluorination at 250-550°C.

When the reaction was complete, as indicated by the thermal conductivity cell and/or reactor temperatures, the reactant gases were turned off and the system allowed to cool to ambient temperature while being purged with nitrogen. The solids were then removed for analysis.

5.2 38 mm Diameter Horizontal Reactor

This apparatus was used for treating small catalyst samples (up to 5 g) with UF_6, hydrogen fluoride, and hydrogen at temperatures up to 650°C. The samples were placed in a small platinum boat in the nickel reactor and the various gas streams were passed over them for periods ranging from two to eight hours. The treated catalysts were tested for changes in weight, surface area and effectiveness in promoting the Fluorox reaction. The latter were mostly carried out in the thermobalance but some checks were made in the 50 mm diameter fluidised bed reactor.

The hydrogen fluoride supply and collection systems were the same as those for the 50 mm diameter vertical reactor. The UF_6 was obtained from small 50 mm diameter UF_6 cylinders by passing a stream of carrier gas (10 mL s^{-1}) through them at room temperature. The cylinders contained approximately 100 g of pure, solid UF_6 located at the bottom of the cylinders. The stream of carrier gas was directed onto the top surface of the UF_6 and became loaded with approximately 3 vol % UF_6 before leaving the cylinders and passing through the horizontal reactor. Thus, approximately 10 g of UF_6 per hour was passed over the catalysts which were contacted by 4 to 16 times their own weight of UF_6. Uranium hexafluoride leaving the reactor was collected in a trap immersed in dry ice.

5.3 Thermobalance

Fluorox reaction rates were measured in the thermobalance with 20-200 mg samples to check pilot plant and bench-scale results and test the effectiveness of catalysts after various treatments including regeneration of poisoned catalysts. The equipment and procedures for these measurements have been described by Janov and Walls [1981].

6. BENCH-SCALE RESULTS AND DISCUSSION

6.1 Catalyst Development and Testing

Catalyst treated at simulated Fluorox process conditions

The platinum/alumina catalyst underwent significant changes when contacted by gases in the Fluorox process. Table 9 shows the changes in weight, surface area and appearance which occurred when the catalyst was treated with UF_6, hydrogen and hydrogen fluoride in the 38 mm diameter horizontal reactor at conditions simulating those in the Fluorox process.

Treatment with UF_6 at 650°C increased the weight of the catalyst by 90 per cent and decreased its surface area from 120 to 20 m^2g^{-1}. The increase in weight was shown by chemical analysis to be due partly to the conversion of the alumina support material to aluminium fluoride and partly to the deposition of uranium compounds in the pores of the catalyst.

$$2\ Al_2O_3 + 3\ UF_6 \longrightarrow 4\ AlF_3 + 3\ UO_2F_2 \quad (8)$$

$$2\ Al_2O_3 + 6\ UF_6 \longrightarrow 4\ AlF_3 + 6\ UF_4 + 3\ O_2 \quad (9)$$

When the UF_6 treatment was carried out in nitrogen (Table 9, Run 1) significant quantities of green UF_4 could be seen in the pores of the catalyst indicating that Reaction 9 had occurred. When the UF_6 treatment was in oxygen (Table 9, Run 4) white UO_2F_2 was deposited in the pores of the catalyst. Complete conversion of the alumina to aluminium fluoride would increase its weight 64 per cent; complete conversion with deposition of UF_4 or UO_2F_2 would increase its weight approximately 520 per cent. Thus in the experiments summarised in Table 9, if it is assumed that the uranium deposited in the pores of the catalyst, only 17 per cent of the alumina reacted with UF_6.

The amount of conversion varied, however, with the size of the catalyst particles. Catalyst which was -45 μm increased in weight by 220 per cent when treated with UF_6 in oxygen, while that which was 125-180 μm increased only 50 per cent. The -45 μm catalyst has a higher external area per weight and it seems that the UF_6 only reacted with the outer shell of the catalyst before the reaction stopped. Catalyst was treated with UF_6 for up to 8 hours but very little additional conversion occurred after 2 hours, indicating that formation of UO_2F_2 and aluminium fluoride in the outer shell of the catalyst hinders further reaction in its core.

When catalyst which had been extensively treated with UF_6 was exposed to hydrogen at 650°C for 4 hours (Table 9, Run 5), the UO_2 inclusions were converted to a brown colour (UO_2) and there was a 3 per cent decrease in weight, and its surface area was slightly decreased. When this catalyst was further treated with hydrogen fluoride, the uranium inclusions were converted to green UF_4 and there was an 18 per cent increase in weight; this was more than twice that expected from the conversion of the UO_2 to UF_4 and indicates that some more alumina was converted to aluminium fluoride. There was also a substantial decrease in surface area to 2 $m^2\ g^{-1}$.

Finally, the same catalyst was oxidised at 650°C for 6 hours to simulate the beginning of its second cycle in a Fluorox plant. Its weight only decreased 5.3 per cent whereas approximately 20 per cent could have been expected from complete conversion of the UF_4 inclusions to UO_2F_2 and UF_6.

Surprisingly, the effectiveness of the catalyst was not significantly altered by these changes to its surface area and structure. Figures 13 and 14 show the rate of weight loss, during the Fluorox reaction, of samples containing fresh catalyst and catalyst treated by UF_6 and then hydrogen, hydrogen fluoride and oxygen. For the -45 μm catalyst, the rate of weight loss was actually slightly higher with the treated catalyst than with fresh catalyst because the latter reacted with some of the UF_6.

The effectiveness of catalyst treated with UF_6 in oxygen was also unaltered in bench-scale fluidised bed experiments with 20 wt % UF_4 in UO_2F_2.

Pre-treatment of catalyst with hydrogen fluoride

Treatment of fresh platinum/alumina catalyst with hydrogen fluoride rendered it inert to UF_6. However, the resulting aluminium fluoride substrate was very friable and unsuitable for use in the pilot plant.

Exposure to 30 per cent of hydrogen fluoride in nitrogen for three hours at a temperature increasing from 250 to 550°C increased the weight of catalyst by 43 to 50 per cent for sizes ranging from -45 μm to 124-180 μm. This corresponded to 63 to 74 per cent conversion of alumina to aluminium fluoride. The surface area of the catalyst was reduced to 4-6 $m^2\ g^{-1}$ but, as is shown in Figure 14, its effectiveness was not altered. When the treated catalyst was exposed to UF_6 at 650°C its weight increased by only 2-3 per cent.

Calcium fluoride substrates

Catalysts were prepared by coating 5 wt % platinum on crystalline calcium fluoride (104-124 μm) which is inert to UF_6. The surface area of this material was only 0.5 $m^2\ g^{-1}$ and its effectiveness in promoting the Fluorox reaction was low. Addition of three parts of catalyst to one part of French UF_4 only increased the apparent reaction rate constant six times whereas platinum on alumina catalyst increased it about 100 times [Janov and Walls 1981]. Indeed, the sixfold increase would almost be expected in uncatalysed samples diluted by that amount of inert material (see Section 6.3).

Precipitated calcium fluoride had a surface area of 15 $m^2\ g^{-1}$ but unfortunately its particle size was too small for use in a fluidised bed.

6.2 Catalyst Regeneration

Complete regeneration of poisoned catalyst was achieved fairly simply by two different methods - washing with water or ammonium oxalate solution followed by drying at 650°C, or treatment with hydrogen and hydrogen fluoride at conditions normally used in the recycle reactions of the Fluorox process. The second method was suggested by earlier thermobalance results [Batley et al. 1974] in which the catalyst was not poisoned throughout five complete cycles of the Fluorox process.

The poisoned catalyst could not be separated physically from the UO_2F_2 with which it was mixed and substantial quantities of UO_2 had to be treated with the catalyst. In the first method, the UO_2F_2 was dissolved, but in the second it was converted to UF_4. As there would have been insufficient stocks of UO_2F_2 feed to embark on further pilot plant experiments with 20 per cent UF_4/UO_2F_2 feed, regeneration was not tested in the pilot plant. Instead the two methods were demonstrated in thermobalance and bench-scale experiments.

Regeneration by washing

Catalyst which had been completely poisoned in pilot plant Run 65/4 was washed with ammonium oxalate solution and water. The surface area of the regenerated catalyst was 12 $m^2\ g^{-1}$ compared with 120 $m^2\ g^{-1}$ for fresh catalyst. Thermobalance experiments showed that it was equally as effective as fresh catalyst.

Unfortunately, this method of regeneration would be impracticable in a Fluorox plant unless a simple physical method could be found for separating the catalyst from the uranium-bearing powder.

Regeneration by reduction and hydrofluorination

Two sets of experiments were devised to demonstrate the regeneration of poisoned catalyst by reduction and hydrofluorination. The first was carried out with gram quantities of material; reduction and hydrofluorination were done in the horizontal reactor and the final tests of the catalysts were in the thermobalance. The second was carried out exclusively in the vertical 50 mm diameter fluidised bed reactor with 200 g batches of powder.

In the small-scale tests, catalyst/UO_2F_2 from Run 65/4 and UO_2F_2 used as diluent in the pilot plant were reduced (at 650°C) and hydrofluorinated (at 250-550°C) and then mixed with samples that had not been recycled to give samples containing no catalyst, poisoned catalyst and recycled catalyst in otherwise similar UF_4/UO_2F_2 mixtures. The recycled catalyst had a matt coral-like appearance. Figure 15 shows the rate of reaction, measured in the thermobalance, when these samples were oxidised at 650°C. It is clear that the recycle reactions have increased the effectiveness of the catalyst substantially.

In the fluidised bed experiments, powder from Run 65/4 was reduced, oxidised to U_3O_8 and hydrofluorinated in the 50 mm diameter fluidised bed reactor to give a mixture containing 38 per cent UF_4, 4.3 per cent catalyst and 57.7 per cent UO_2F_2. This material was then reacted with oxygen at 650°C (Table 10, Run 30) until all the UF_4 was consumed. In subsequent experiments, approximately 20 per cent French UF_4 of known quality was added to the regenerated catalyst/UO_2F_2 mixture. Runs 31 to 34 show that the effectiveness of the catalyst was substantially restored. The apparent reaction rate constant varied from 0.39 to 0.51 h^{-1} in these experiments compared to 0.08 h^{-1} for poisoned catalyst.

Indeed, when account is taken of the decreasing catalyst concentration in Runs 31 to 36, there is no evidence that the regenerated catalyst was poisoned in these experiments in which 16.8 kg UF_6 was produced per kg catalyst.

6.3 Effect of UF_4 Concentration and Quantity on the Rate of the Uncatalysed Fluorox Reaction

A series of experiments was carried out in the 50 mm diameter vertical reactor to investigate the reasons for the very large difference in the rates of the uncatalysed Fluorox reaction observed in the pilot plant and thermobalance.

Static beds of 100 per cent British UF_4 were reacted at 650°C with oxygen passing downward through the powder at 32 mm s^{-1}. With increasing bed height from 13 to 100 mm, the apparent reaction rate constant decreased only slightly from 0.017 to 0.011 h^{-1}. These rate constants were between those measured in the pilot plant ($R = 0.0025\ h^{-1}$) and thermobalance ($R = 0.074\ h^{-1}$) with 100 per cent British UF_4 feed. It was observed, however, that UF_4 was not uniformly distributed in the static bed. The top 1-2 mm of powder was almost

completely converted to a soluble white compound, presumably UO_2F_2, which formed a smooth skin suggesting that it had melted during the reaction. Below this top layer the conversion of UF_4 decreased rapidly as shown in Table 11. When the direction of oxygen flow was reversed through the static bed, the overall reaction rate was the same but the top layer was only slightly converted. However, the bottom layer could not be examined because it was disturbed during the sectioning of the bed.

Rates of reaction comparable to those observed in the thermobalance were achieved in the 50 mm diameter reactor with very small and thinly spread samples. For example, when 1.5 g of British UF_4 was placed in a heap in the reactor, it reacted slowly at a rate corresponding to $R = 0.011\ h^{-1}$. When 2 g of the same material was spread in a thin layer, however, it reacted much faster at a rate corresponding to $R = 0.029\ h^{-1}$. When even smaller samples (200 mg) were placed in nickel and gold pans inside the 50 mm diameter reactor, they reacted at rates corresponding to $R = 0.039\ h^{-1}$. By comparison, the apparent reaction rate constant in the thermobalance was $R = 0.074\ h^{-1}$ with even smaller samples (30 mg).

Thus it is clear that the overall rate of the uncatalysed Fluorox reaction is strongly dependent on the quantity and geometrical configuration of UF_4 being reacted. Thinly spread small samples and leading surfaces of larger samples react very much faster than UF_4 which is surrounded by other UF_4 particles. It is postulated that the UF_6 product undergoes secondary reactions with unreacted UF_4 particles and these decrease the overall rate of reaction.

The overall reaction rate in a static bed was also dependent on the oxygen flow rate through it. Table 12 shows that a threefold increase in the apparent reaction rate constant occurred when the flow rate was increased from 1.7 to 25.5 mm s^{-1} in static beds. At the higher flow rate, the concentration of UF_6 in the gas was lower and seems to have decreased the rate of the secondary reaction between UF_6 and unreacted UF_4.

The dependence of the uncatalysed Fluorox reaction rate on the concentration of UF_4 in the feed was also confirmed in the 50 mm reactor using fluidised and static beds of material. For a given amount of UF_4 feed, the concentrations of UF_6 and UF_4 are less in a dilute bed thus decreasing the rate of the secondary reaction between UF_6 and unreacted UF_4.

7. SUMMARY OF RESULTS

(a) At 650°C, the catalysed Fluorox reaction cannot be carried out with more than 30 per cent UF_4 in the reactor, as sintering occurs at higher concentrations.

(b) With 20 per cent UF_4 in UO_2F_2, the rate of the Fluorox reaction was increased by an order of magnitude by the addition of fresh catalyst containing 3-4 per cent platinum on alumina. This was obtained in pilot plant experiments with 1 per cent catalyst using British UF_4 and 5 per cent catalyst using French UF_4.

(c) The highest rate of UF_6 production achieved in the 150 mm diameter fluidised bed reactor at 650°C was 0.9 kg h^{-1}.

(d) The catalyst was poisoned rapidly with continued use in the pilot plant, but the rates of poisoning were significantly different when using British and French UF_4. With British UF_4, the catalyst was completely poisoned after production of approximately 20 kg UF_6 per kg catalyst, whereas with French UF_4 this occurred after production of only 1 kg UF_6 per kg catalyst.

(e) The catalyst was not poisoned by exposure to pure UF_6 at 650°C. In bench-scale tests, the effectiveness of the catalyst was not altered even though its surface area was reduced from 120 to 20 m^2 s^{-1}.

(f) Fresh catalyst and catalyst treated with pure UF_6 had a porous, coral-like appearance, whereas poisoned catalyst had a smooth, lustrous appearance. The poisoning is thought to be caused by intermediate uranium fluorides which coat the catalyst particles.

(g) The poisoned catalyst could be regenerated by

  (i) washing with water or ammonium oxalate solution, and

  (ii) treating with hydrogen and hydrogen fluoride at the conditions used for recycling UO_2F_2 in the Fluorox process.

(h) The rate of the uncatalysed Fluorox reaction is very dependent on the amount and concentration of UF_4 in the reactor. This is thought to be due to competing reactions involving intermediate uranium fluorides.

(i) High UF_6 yields (> 90 per cent) were achieved when UO_2F_2 diluent was used and the catalyst and reaction vessels had been passivated towards UF_6.

(j) Only a small amount of corrosion (< 130 μm) was detected in the reactor after 380 hours of operation at 650°C in which 30 kg of UF_6 were produced.

8. EVALUATION OF THE CATALYSED FLUOROX PROCESS

Production of UF_6 by the method recommended by Batley et al. [1974] for the catalysed Fluorox process was considered to be only marginally cheaper than by the fluorination of UF_4 [Charlton 1975]. The pilot plant experiments, however, showed that there were significant technical problems which would not allow the process to be operated in this way. Consequently, the catalysed Fluorox process is likely to be uncompetitive with the established method of UF_6 production.

The main technical problems were low reaction rates at 650°C and rapid poisoning of the catalyst. To compensate for the latter, the process could be operated with greater concentrations or more frequent regeneration of the catalyst than was originally envisaged.

If the quantity of UF_6 produced before catalyst poisoning increases linearly with concentration of catalyst, then calculations in Appendix A show that to maintain a reasonable rate of reaction, 2.9 per cent catalyst would need to be used with British UF_4 and 93 per cent with French UF_4. This scheme would seem feasible with British UF_4 but with French UF_4 the cost of the additional catalyst would make it unattractive. However, the premise that the amount of UF_6 production at the catalysed rate increases linearly with concentration of catalyst was not tested.

In the alternative scheme, the catalyst concentration could be kept low by more frequent regeneration via the recycle reactions. However, to prevent

the UF_4 concentration increasing in the process, part of the UO_2F_2 would need to be replaced with an inert powder such as calcium fluoride. About 60 per cent inert powder would be needed with British UF_4 and 88 per cent with French UF_4 (Appendix A). Thus, the recycle reactors would have to be substantially larger and would be more costly to operate.

The peak UF_6 production rate demonstrated in this work was 0.9 kg h^{-1} UF_6 and compares unfavourably with production of 15 kg h^{-1} UF_6 by reaction of UF_4 with fluorine in the same reactor. The catalysed Fluorox reaction rate could be increased by operation above 650°C but the rate of corrosion of the reactor would increase unacceptably [Scott et al. 1960]. The catalysed Fluorox reaction rate could possibly be increased by using a higher concentration of catalyst at 650°C. Thermobalance tests have shown that a higher concentration of catalyst significantly increases the rate of reaction with French UF_4 but not, however, with British UF_4 [Janov and Walls 1981]. Catalyst with a smaller particle size than was used in the pilot plant is also known to be more effective.

However, fluidised bed reactors are unsuitable for powders with particles less than about 50 μm diameter. It is possible that an alternative design of reactor, such as a rotary kiln, could be used. As well as being suitable for use with small diameter catalyst particles, the rotary kiln would accept a wider range of particle sizes in the uranium feed powder without segregation or elutriation. This would be particularly important in a full Fluorox plant in which the UF_4 particles would be expected to disintegrate after several cycles in each of which they lose 50 per cent of their weight.

However, two very important technical aspects of this catalysed Fluorox process need more investigation: catalyst poisoning and behaviour of the intermediate uranium fluorides. These investigations were not pursued because the slow rate of UF_6 production and the rapid rate of catalyst poisoning did not warrant further effort on the development of the process.

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TABLE 1

BULK DENSITIES AND SURFACE AREAS OF POWDERS USED IN FLUIDISED BED REACTORS

Property	British UF_4	French UF_4	Alumina	UO_2F_2	Catalyst
Bulk Density ($kg\ m^{-3}$)	3700	2600	2040	2700	1000-1500
Surface Area ($m^2\ g^{-1}$)	0.35	1.45	<1	1.8	120

TABLE 2

BATCH EXPERIMENTS IN PILOT PLANT WITH 100% UF_4 FEED

Temperature: 650°C UF_4 Type: British

Catalyst Conc. (%)	Weight of UF_4 in Feed (kg)	Process Gas Flow Rate ($L\ min^{-1}$)	Reaction Time (h)	UF_4 Conversion (%)	Apparent Reaction Rate Constant, R (h^{-1})	$t_{\frac{1}{2}}$ (h)	UF_6 Recovery (%)
0	16.5	14	6.0	4.7	0.003	69	83
0	19.0	31	5.5	3.2	0.002	100	~100
0.5	19.0	42	5.0	25	0.018	11	~100
0.5	19.0	15-40	4.25	20	0.017	12	31
1.0	19.0	30 and 40	4.25 (O_2 partial pressure increased slowly)	33	0.029	7.1	32
1.0	19.0	30	1.83 (O_2 partial pressure increased slowly)	27	0.054	3.8	22

TABLE 3

COMPARISON OF APPARENT REACTION RATE CONSTANTS IN PILOT PLANT AND THERMOBALANCE EXPERIMENTS WITH 100% UF_4 FEED

Temperature: 650°C UF_4 Type: British
Catalyst: Fresh

Catalyst Concentration (%)	Apparent Reaction Rate Constant, R (h^{-1})	
	Thermobalance	Pilot Plant
0	0.074	0.0025
0.5	0.25	0.0175
1.0	0.19	0.0415

TABLE 4

UNCATALYSED BATCH EXPERIMENTS IN PILOT PLANT WITH VARYING UF_4 CONCENTRATION

Temperature: 650°C Process Gas Flow Rate: 0.75 L s^{-1}
UF_4 Type: British Diluent: Alumina (150-300 μm)
Weight of Feed: 13.5 - 16.0 kg

UF_4 Conc. (%)	Reaction Time (h)	UF_4 Conversion (%)	Apparent Reaction Rate Constant, R (h^{-1})	$t_{½}$ (h)	UF_6 Yield (%)
4.8	1.5	86 ± 14	0.32	0.64	0
9.5	3.0	94 ± 6	0.20	1.0	0
19.0	3.0	76 ± 11	0.13	1.6	0
30.6	7.0	50 ± 9	0.029	7.0	10
100	~6.0	~4.0 (a)	0.0025 (a)	~80 (a)	~80 (a)

(a) Average values from Table 2.

TABLE 5

APPARENT REACTION RATE CONSTANTS IN PILOT PLANT

EXPERIMENTS USING FRESH CATALYST AND UF_4/UO_2F_2 FEED

Catalyst Conc. (%)	UF_4 Conc. (%)	Apparent Reaction Rate Constant, R (h^{-1})
British UF_4		
0	20	0.019
1.2	20	0.14
French UF_4		
0	20	0.079
1.0	20	0.079
5.1	5.5	0.78
6.8	19	≥0.55

TABLE 6

CATALYSED BATCH EXPERIMENTS IN PILOT PLANT

WITH BRITISH UF_4/UO_2F_2 FEED

Temperature: 650°C Process Gas Flow Rate: 0.75 L s^{-1}

UO_2F_2 and catalyst in Runs 46/2 to 47 were from preceding experiments

Run No.	Composition of Feed (%)			Weight of Feed Powder	Reaction Time	UF_4 conversion	Apparent Reaction Rate Constant, R	$t_{½}$	UF_6 Yield
	UF_4	UO_2F_2	Catalyst	(kg)	(h)	(%)	(h^{-1})	(h)	(%)
46/1	20.1	78.7	1.2	19.88	3.75	89 ± 9	0.14	1.5	75
46/2	17.8	81.0	1.2[a]	20.04	5.5	75 ± 8	0.067	3.1	89
46/3	19.0	79.8	1.2[b]	18.88	5.0	71 ± 21	0.067	3.1	71
46/4	18.1	79.3	1.2	17.62	10	67 ± 19	0.031	6.7	64
46/5	16.2	81.6	1.2	15.01	21	63 ± 36	0.013	15.8	68
47	21.5	77.4	2.3[c]	15.99	5.5	984 ± 16	0.083	2.5	65

(a) 0.1 per cent } fresh catalyst added to maintain constant

(b) 0.2 per cent } concentration of catalyst

(c) Includes 1.1 per cent fresh catalyst and 1.2 per cent poisoned catalyst from Run 46/5

TABLE 7

CATALYSED BATCH EXPERIMENTS IN PILOT PLANT WITH

BRITISH UF_4/ALUMINA FEED

Temperature: 650°C Process Gas Flow Rate: 0.75 L s^{-1}

Alumina, UO_2F_2 and catalyst in Runs 29/2 to 29/6 were from preceding experiments

Run No.	Composition of Feed (%)				Weight of Feed Powder	Reaction Time	UF_4 Conversion	Apparent Reaction Rate Constant, R	$t_{1/2}$	UF_6 Yield
	UF_4	Al_2O_3	UO_2F_2	Catalyst	(kg)	(h)	(%)	(h^{-1})	(h)	(%)
29/1	31.9	66.7	-	1.4	17.24	2.5	85	0.19	1.1	0
29/2	26.2	52.6	20.1	1.05	22.34	2.5	65 ± 16	0.12	1.75	0
29/3	24.4	48.3	26.4	0.84	27.00	2.0	66 ± 19	0.15	1.35	27
29/4	26.4	42.0	31.0	0.65	23.50	3.42	85 ± 8	0.14	1.50	37
29/5	24.8	29.4	45.0	0.82[a]	23.55	5.5	60 ± 25	0.048	4.3	58
29/6	26.4	28.4	44.6	0.63	23.51	6.0	22 ± 9	0.013	15.8	58

(a) · 0.22 per cent fresh catalyst added

TABLE 8

CATALYSED BATCH-CONTINUOUS EXPERIMENT IN PILOT PLANT WITH FRENCH UF_4/UO_2F_2 FEED

Temperature: 650°C Process Gas Flow Rate: 0.75 L s^{-1}

UF_4 Size: 124-251 μm Catalyst Size: 90-300 μm

Run No.	Composition of Feed (%)			Weight of Feed Powder	Reaction Time	UF_4 conversion	Apparent Reaction Rate Constant, R	$t_{½}$	UF_6 Yield
	UF_4	UO_2F_2	Catalyst	(kg)	(h)	(%)	(h^{-1})	(h)	(%)
64	17.3	76.1	6.6	22.09	1.75	91 ± 8	0.32[a]	0.64	0
65/1	4.6	88.9	6.5	21.67	0.67	~100	>0.55[b]	<0.38	42
65/2	~4.5	~89.2	~6.4	~22.4	0.83	~100	0.55	0.38	91
65/3	~4.4	~89.4	~6.2	~22.9	1.2	~100	0.38	0.54	93
65/4	~4.3	~89.7	~6.0	~23.4	2.25	~100	0.29	0.71	106

(a) Run 64 was a batch experiment and R was calculated from the analysis of the powder residue

(b) Runs 65/1 to 65/4 were batch-continuous and R was calculated from UF_6 production. Owing to the low yield of UF_6 in Runs 65/1 an accurate value for R could not be calculated.

TABLE 9

CHANGES IN CATALYST PROPERTIES PRODUCED BY TREATMENT WITH UF_6, HYDROGEN, HYDROGEN FLUORIDE AND OXYGEN

Fresh Catalyst: 2.9 per cent platinum on alumina

Surface Area: 120 m^2 g^{-1}

Run No.	Feed	Treatment	Surface Area (m^2 g^{-1})	Weight Change (%)	Colour of Material Deposited in Pores of Catalyst
1	Fresh catalyst	3.2 vol % UF_6/N_2, 650°C, 2 h	24.2	+92	Green
2	Fresh catalyst	1.7 vol % UF_6/N_2, 650°C, 6 h	24.1	+87	Green
4	Fresh catalyst	3 vol % UF_6/O_2, 650°C, 6 h	20.2	+90	White
5	Product from Run 4	100% H_2, 650°C, 4h	15.0	- 3	Brown
6	Product from Run 5	20 vol % HF/N_2, 250-550°C, 3 h	2.0	+18	Green
8	Product from Run 6	100% O_2, 650°C, 6 h	1.6	-5.3	White

TABLE 10

FLUIDISED BED EXPERIMENTS IN 50 mm DIAMETER VERTICAL REACTOR

DEMONSTRATING REGENERATION OF CATALYST BY RECYCLE REACTIONS

Temperature: 650°C French UF_4: 124 -251 μm

Run No.	UF_4 Conc. (%)	Catalyst Conc. (%)	Reaction Time (min)	UF_4 Conversion (%)	Apparent Reaction Rate Constant, R (h^{-1})	t (h)	UF_6 Yield (%)	UF_6 UF_5 [a] (%)	Notes
				Uncatalysed and Fresh Catalyst					
15	20	0	60	31	0.12	1.8	15	10.2	
14	17.6	6.5	36	79.2	0.68	0.30	52	19.5	
				Poisoned Catalyst from Run 65/4					
23	20	3.5	36	15.1	0.088	2.3	10	3	
37	19	3.5	36	13.5	0.079	2.6	0	10	
				Regenerated Catalyst					
30	38	4.3	120	98	n.d.	n.d.	30 [b]	10	Recycled via U_3O_8
31	19.8	3.7	35	65	0.51	0.41	40	19	French UF_4 added
32	21.0	3.2	35	54	0.39	0.53	27	14	French UF_4 added
33	20.0	2.6	36	66	0.50	0.41	41	18	French UF_4 added
34	21.0	2.1	35	54	0.39	0.53	27	16	French UF_4 added
35A	39	1.4	35	18	0.11	1.9	18	3	Rate slow due to high UF_4 conc.
35B			180	96	n.d.	n.d.	48 [b]	19	Continuation of Run 35A
36	20	1.25	36	28	0.23	0.90	19	5	

(a) Calculated from weight of material on filter (assumed to be UF_5).

(b) Some UF_6 lost due to leaks in equipment.

TABLE 11

VARIATION OF UNCATALYSED REACTION RATE WITH

POSITION IN 50 mm DIAMETER VERTICAL REACTOR

Temperature: 650°C UF_4 Type: British

Oxygen Flow Rate: 32 mm s^{-1} Static Bed Height: 25 mm

Direction of Gas Flow: Downward Duration of Reaction: 6 hours

Position	Weight Fraction of Bed (%)	Conversion (%)
Top	7	95
Next	31	18
Next	37	16
Bottom	25	17

TABLE 12

VARIATION OF UNCATALYSED REACTION RATE WITH

OXYGEN FLOW RATE IN 50 mm DIAMETER VERTICAL REACTOR

Temperature: 650°C UF_4 Type: British

Static Bed Height: 25 mm Direction of Gas Flow: Downward

Oxygen Flow Rate (mm s^{-1})	Apparent Reaction Rate Constant, R (h^{-1})
5.3	0.0081
16	0.0088
32	0.016
79	0.023

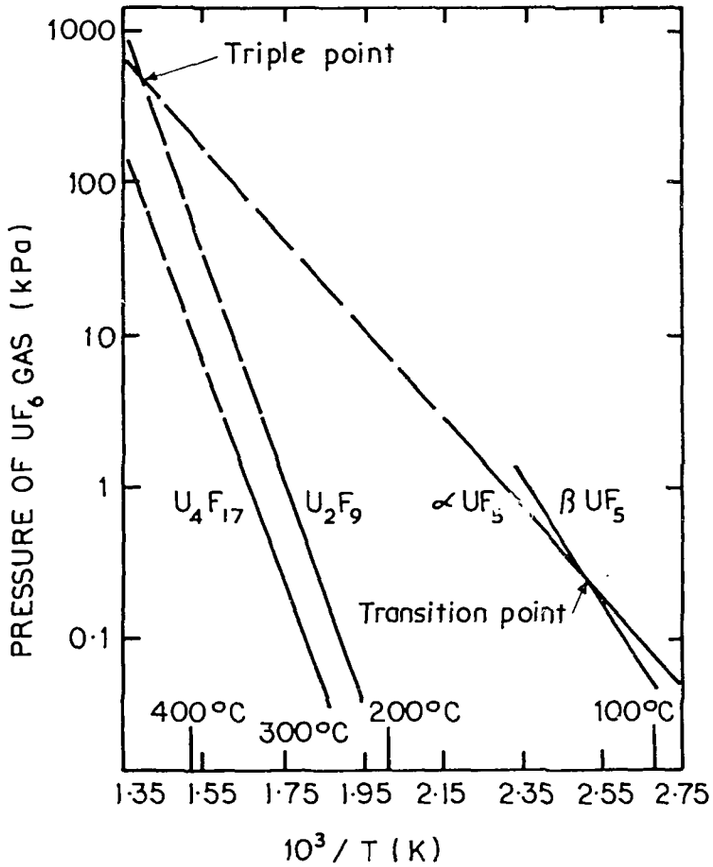


FIGURE 1. DISPROPORTIONATION PRESSURES OF U_4F_{17}, U_2F_9, α UF_5 AND β UF_5
(After Katz and Rabinowitch 1951)

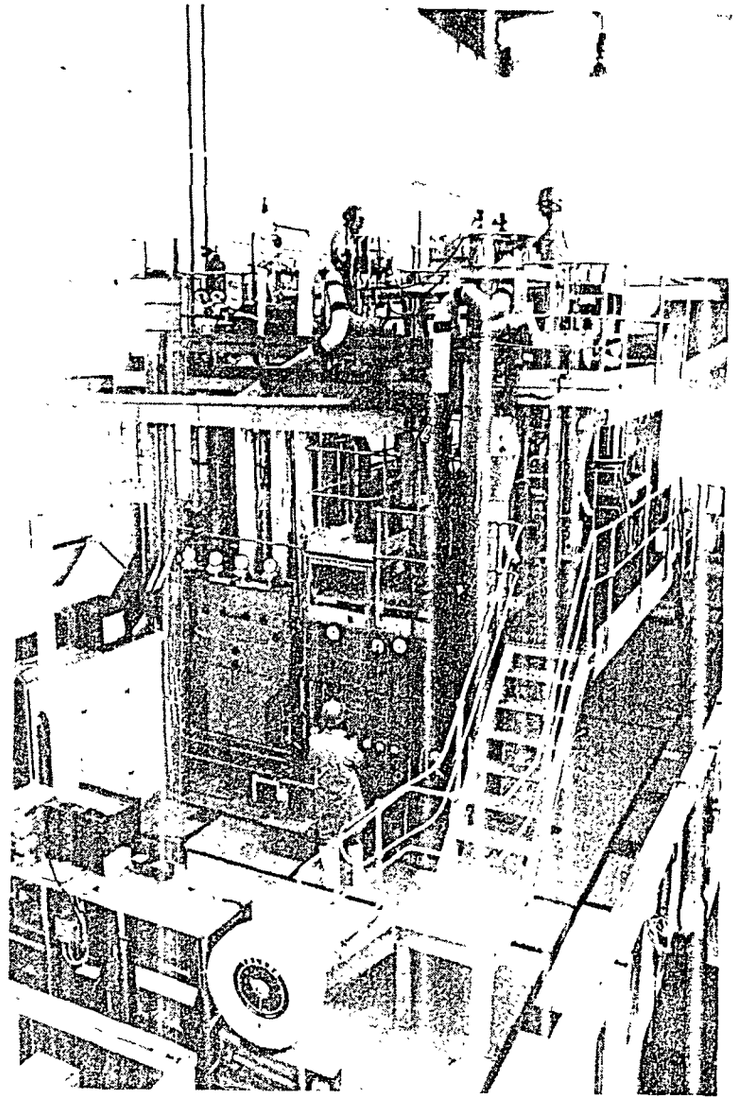


FIGURE 2. GENERAL VIEW OF PILOT PLANT

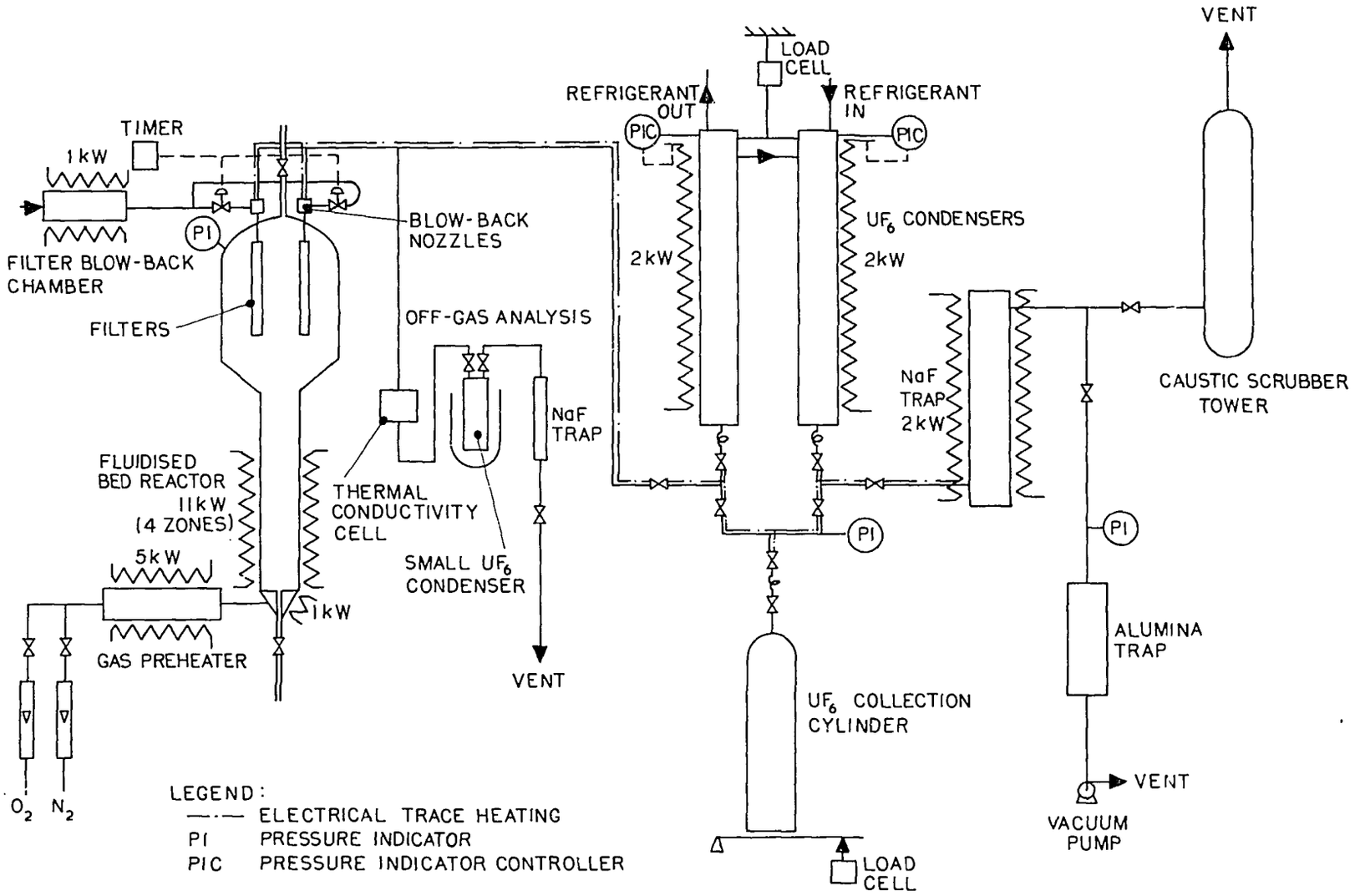


FIGURE 3. FLOWSHEET OF PART OF PILOT PLANT FOR UF_6 PRODUCTION

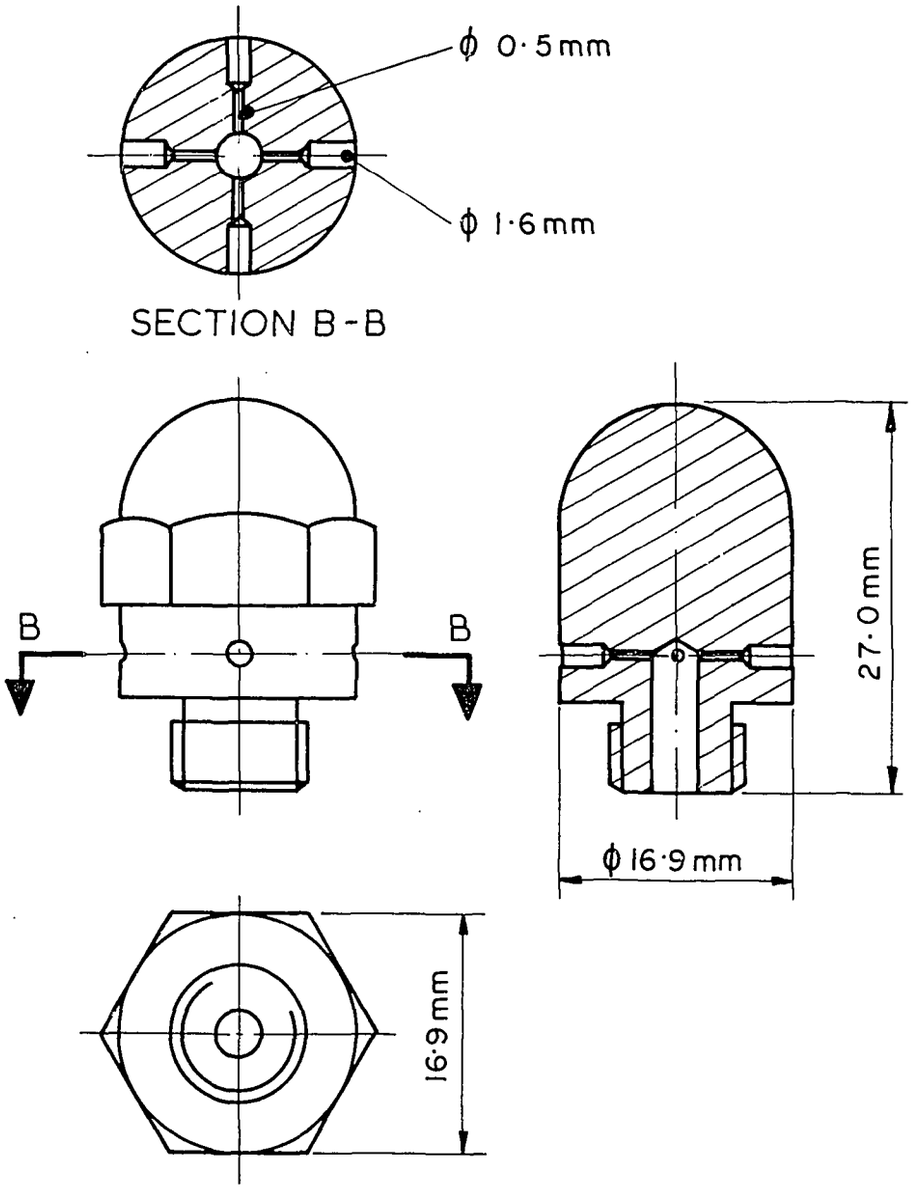


FIGURE 4. DESIGN OF TUYERES IN GAS DISTRIBUTOR OF FLUIDISED BED REACTOR

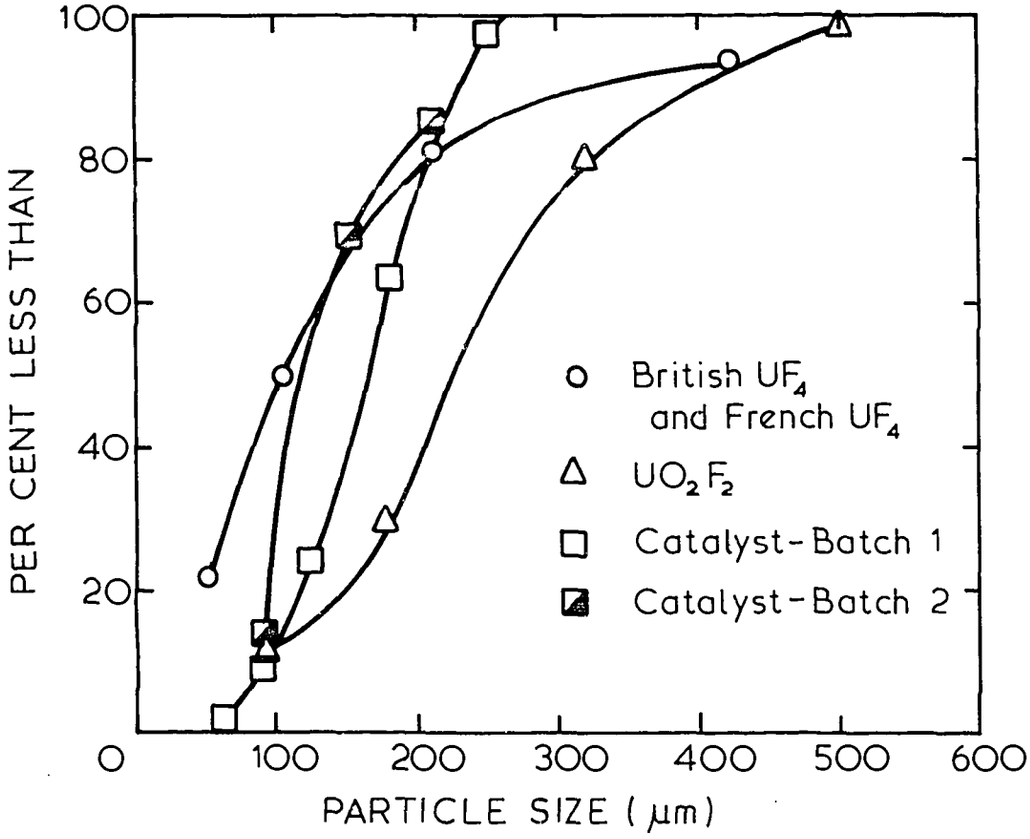
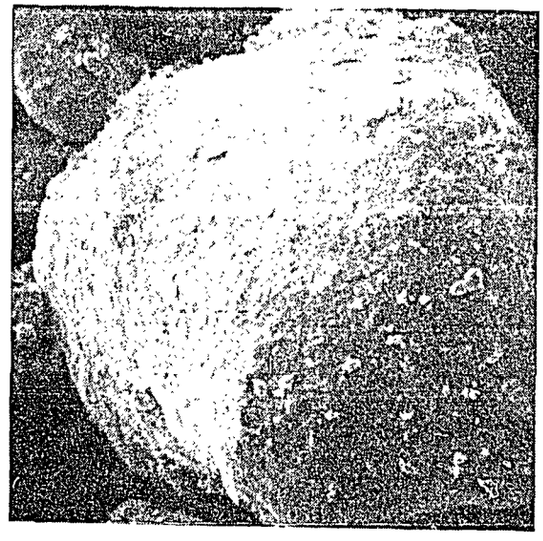
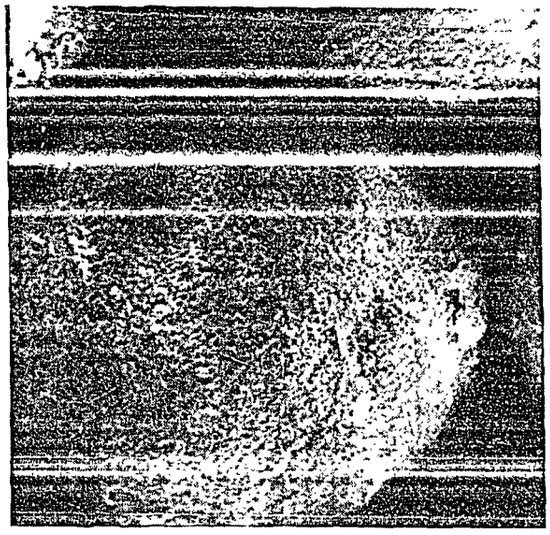


FIGURE 5 AS-RECEIVED SIZE DISTRIBUTION OF POWDERS



(× 400)

FIGURE 6a. BRITISH UF_4 PARTICLES WITH NON-POROUS SURFACE APPEARANCE



(× 400)

FIGURE 6b. FRENCH UF_4 PARTICLES WITH CORAL-LIKE SURFACE APPEARANCE

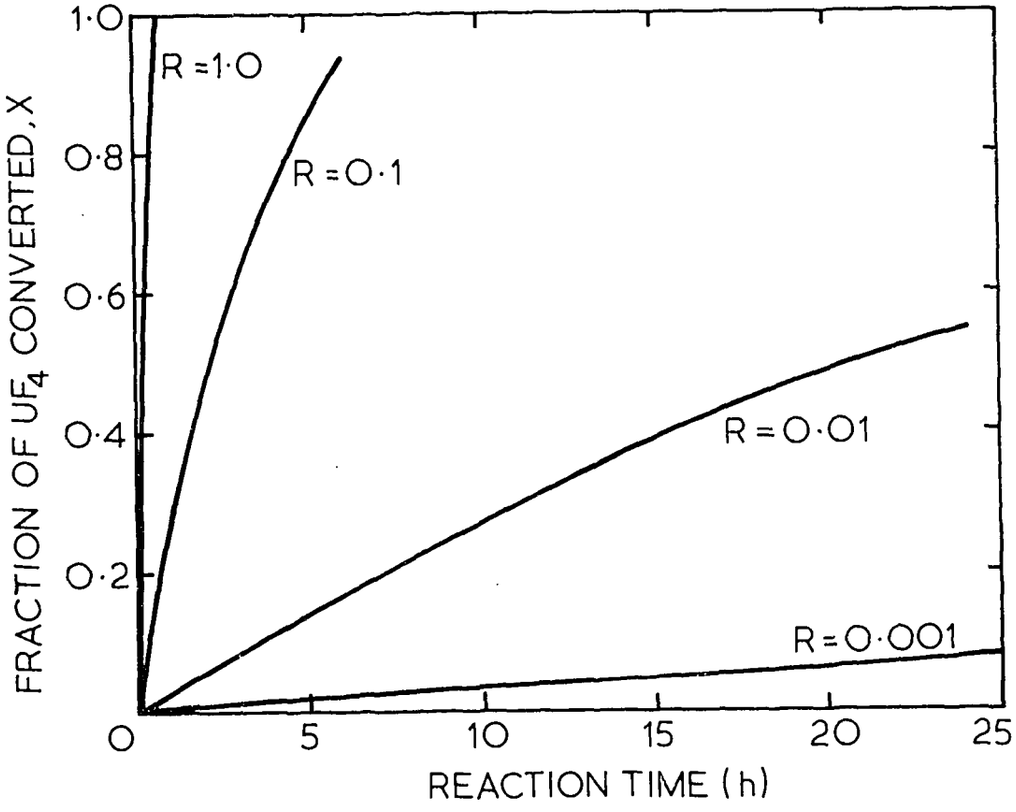


FIGURE 7. CALCULATED REACTION CURVES FOR APPARENT REACTION RATE CONSTANTS, R = 0.001, 0.01, 0.1 AND 1.0 h^{-1}

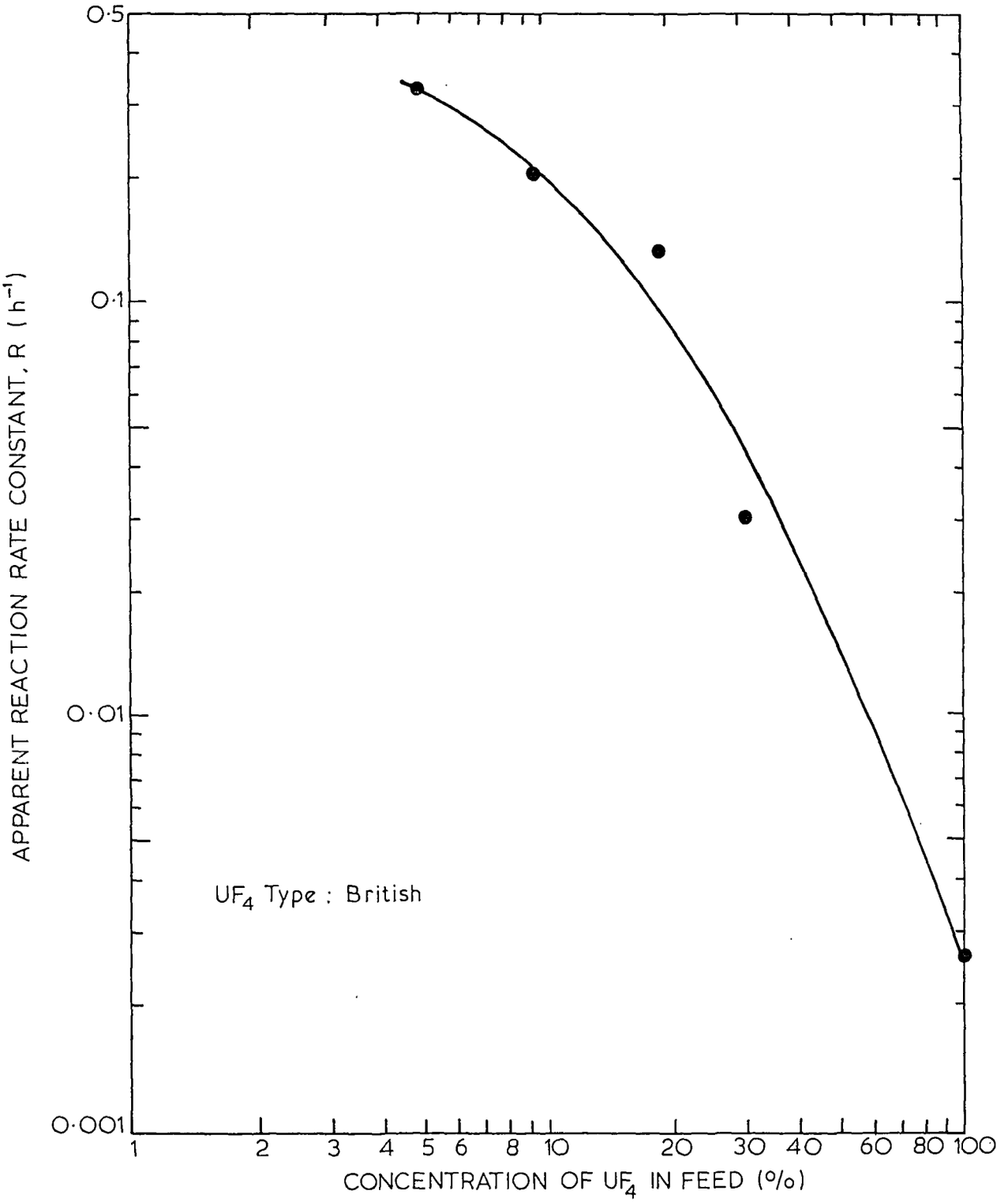


FIGURE 8. EFFECT OF UF_4 CONCENTRATION IN ALUMINA ON UNCATALYSED REACTION RATE

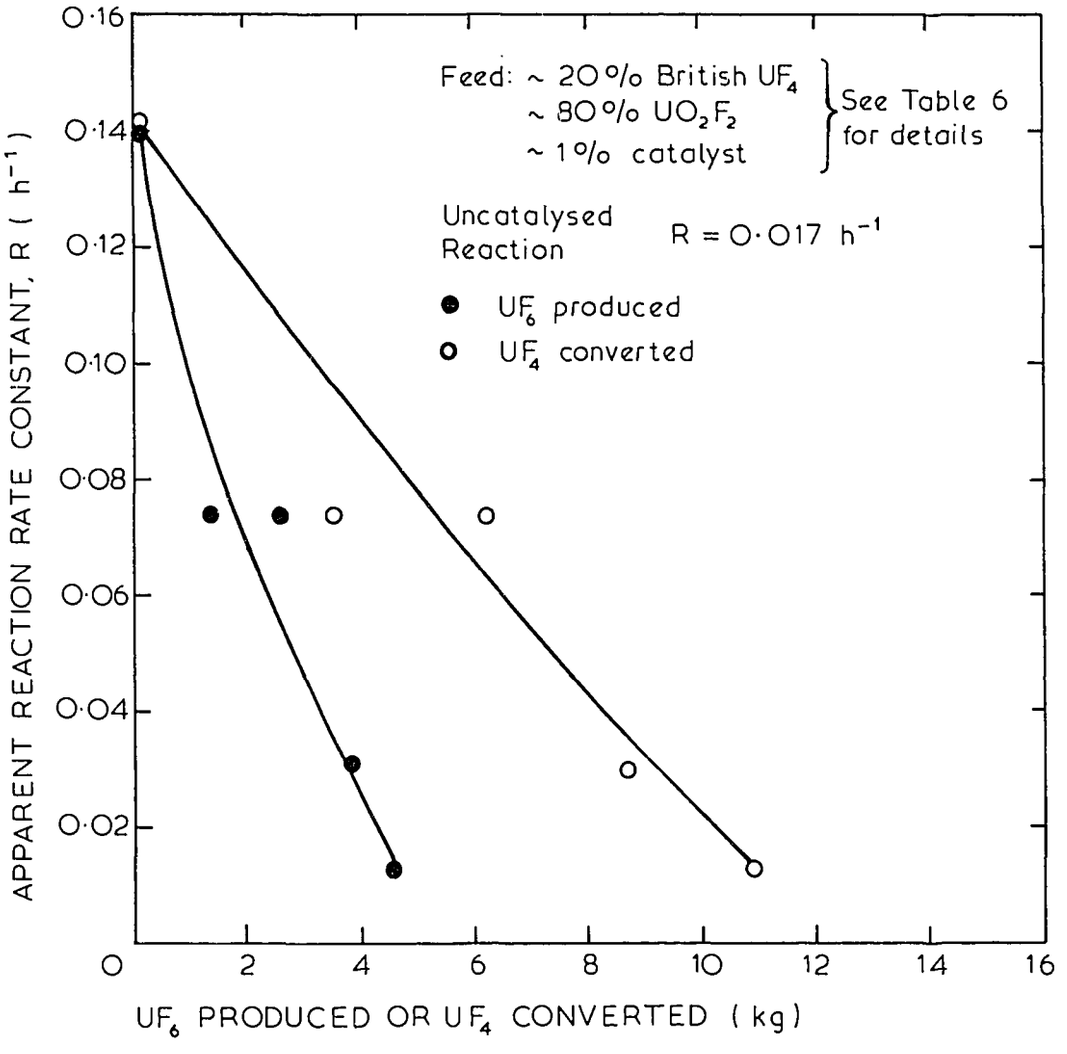


FIGURE 9. APPARENT REACTION RATE CONSTANT v. CATALYST AGE.

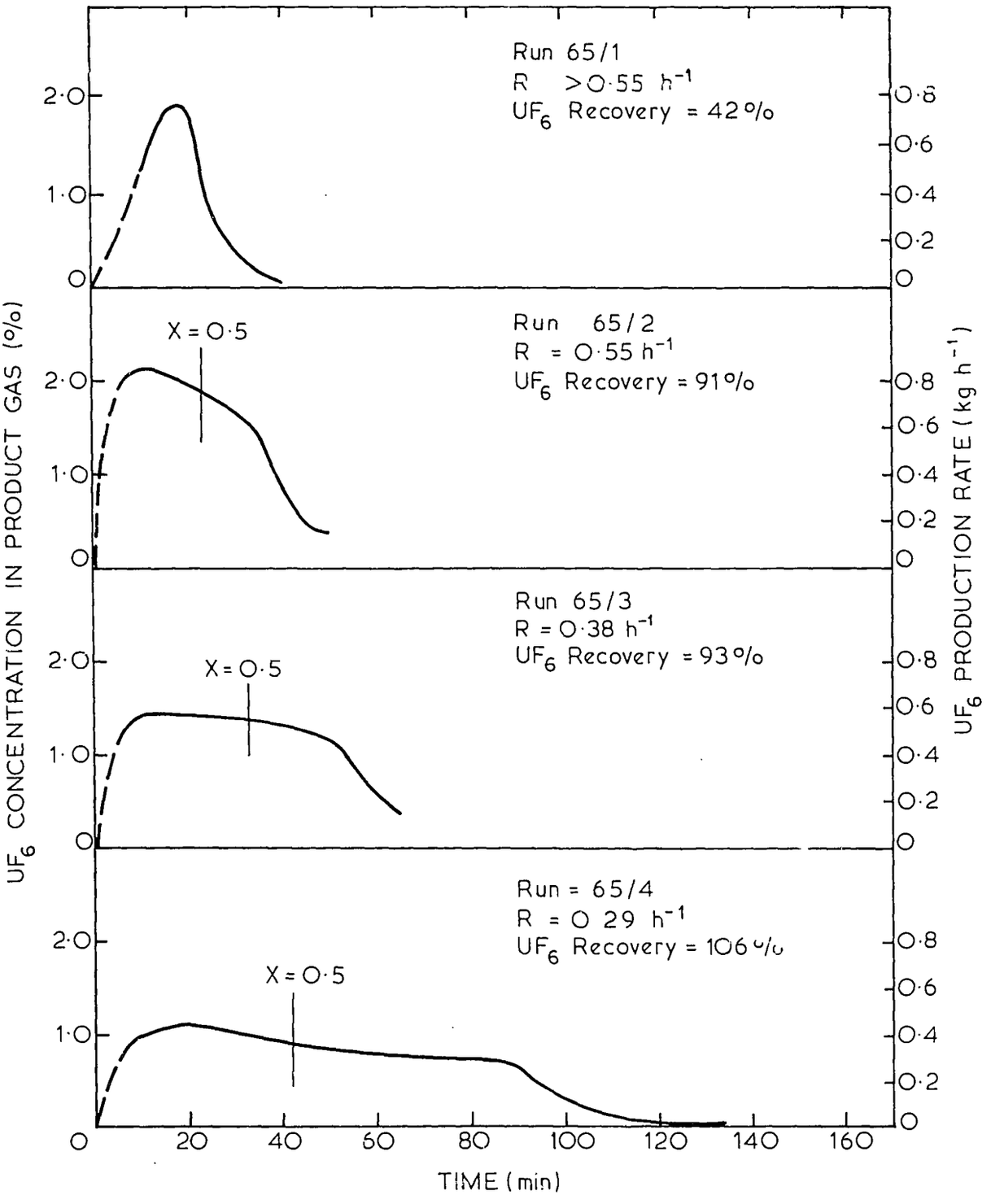


FIGURE 10. UF_6 PRODUCTION IN BATCH-CONTINUOUS EXPERIMENT

(× 80)

FIGURE 11a. AS-RECEIVED PLATINUM/ALUMINA CATALYST

(× 80)

FIGURE 11b. CATALYST CONDITIONED WITH UF_6

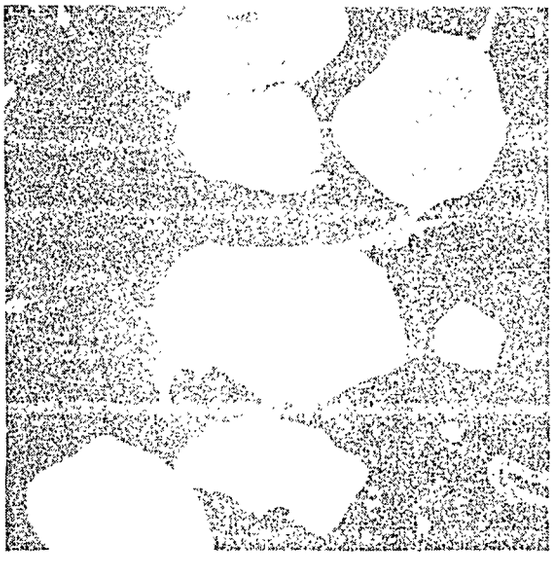


FIGURE 11c. POISONED CATALYST FROM BATCH-CONTINUOUS EXPERIMENT

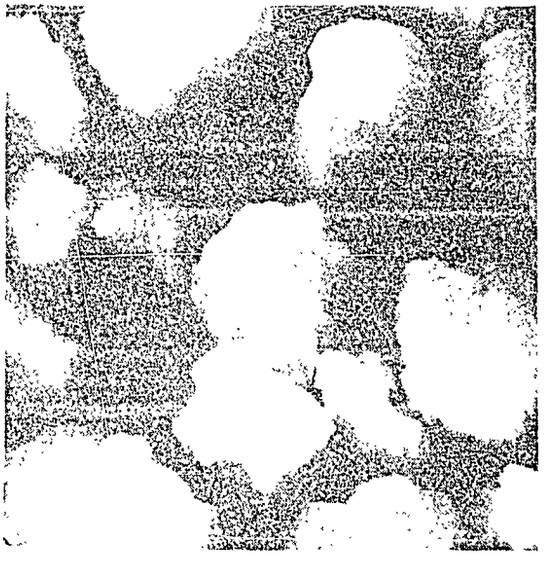


FIGURE 11d. REGENERATED CATALYST

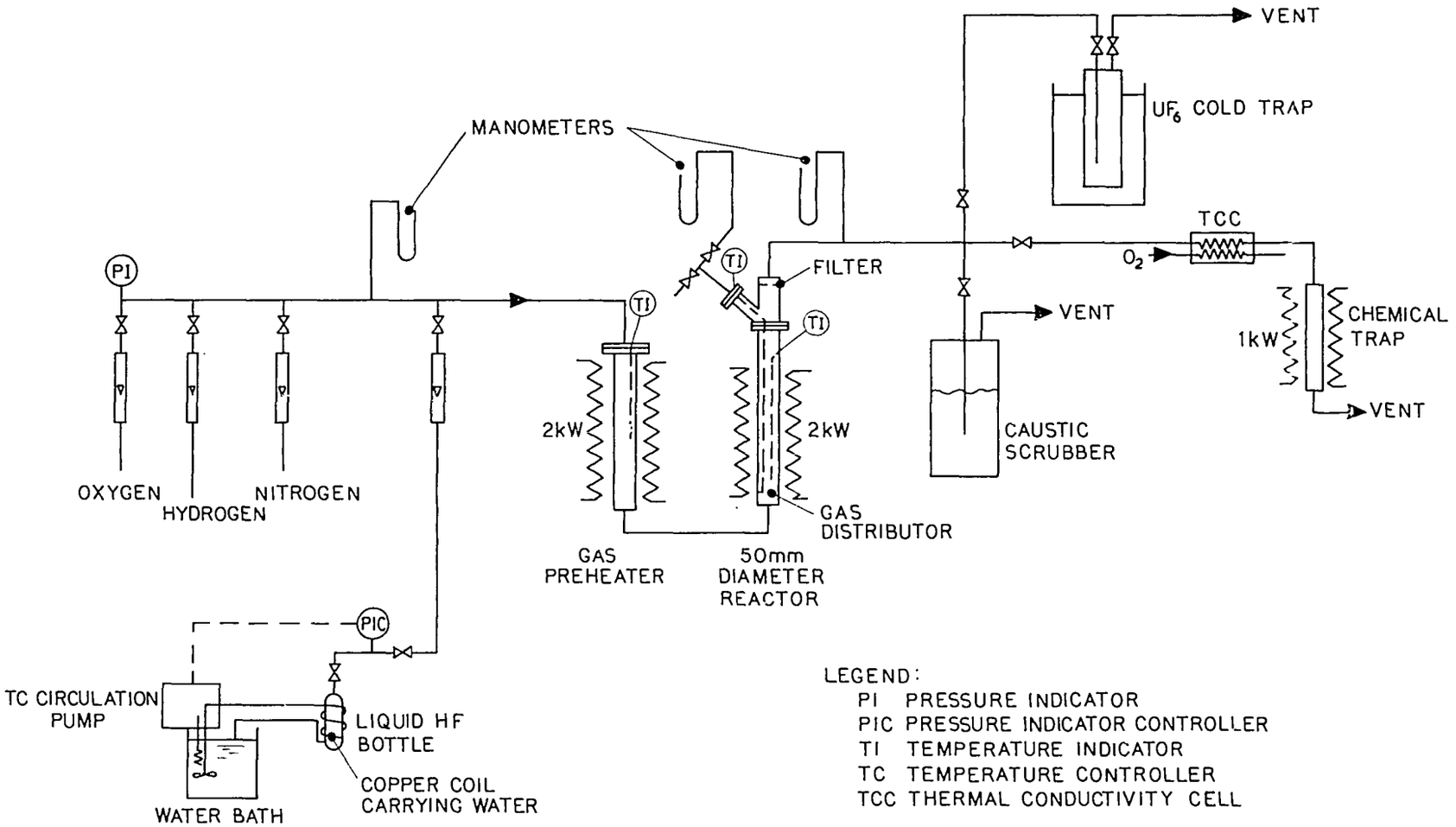


FIGURE 12. BENCH-SCALE 50 mm DIAMETER VERTICAL REACTOR SYSTEM

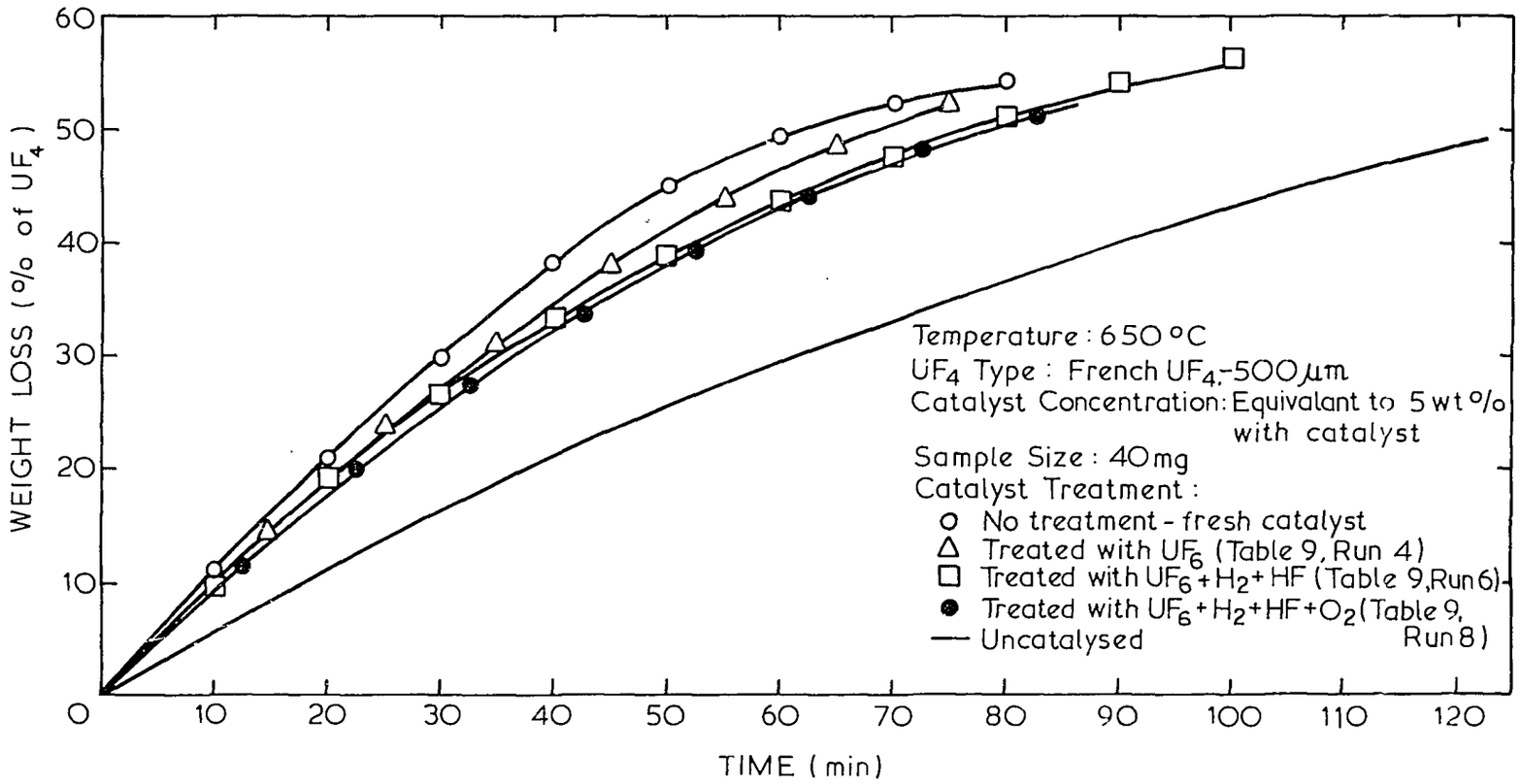


FIGURE 13. THERMOBALANCE MEASUREMENTS SHOWING EFFECT OF CATALYST TREATMENT ON THE RATE OF FLUOROX REACTION (CATALYST 124-178 μm)

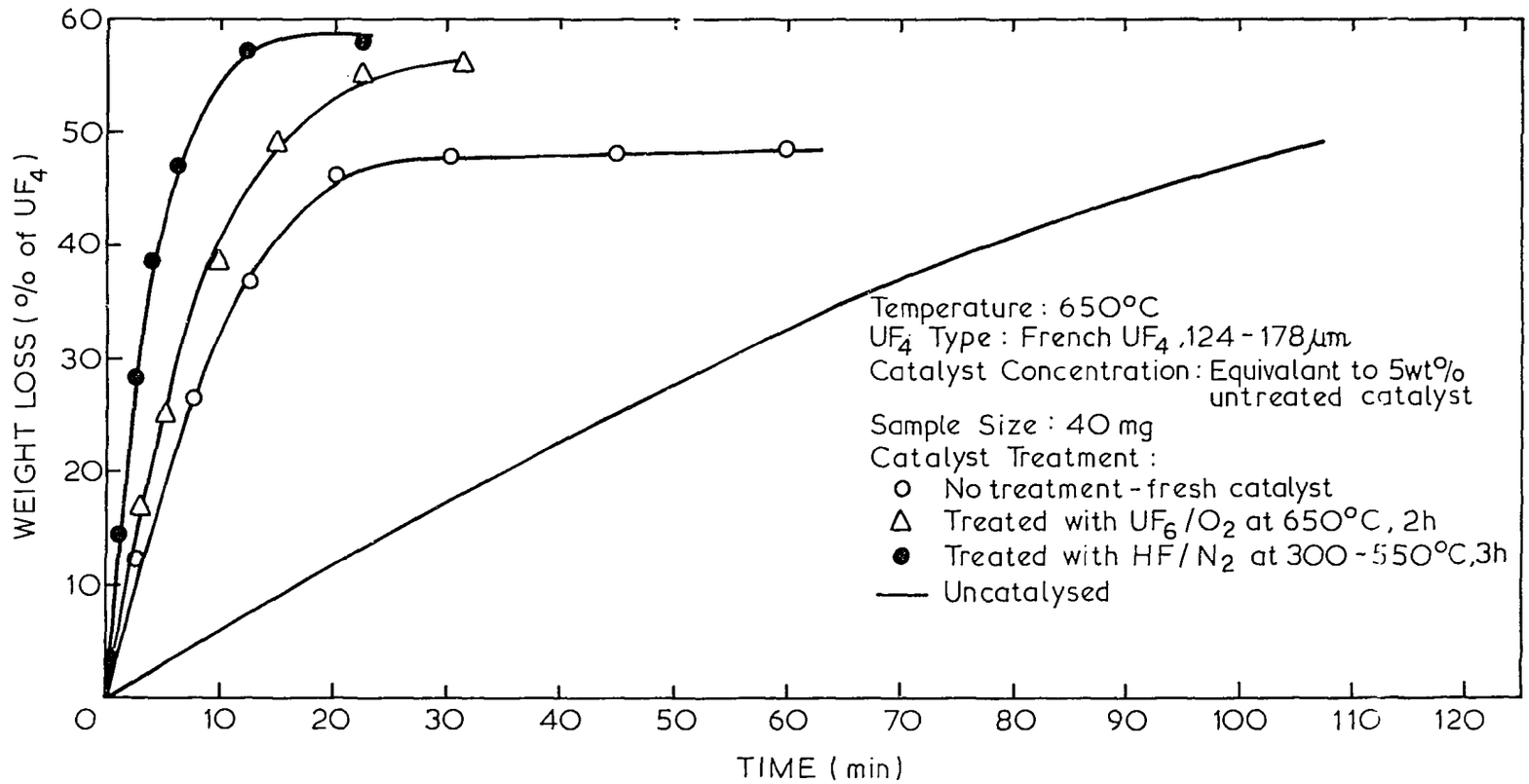


FIGURE 14. THERMOBALANCE MEASUREMENTS SHOWING EFFECT OF CATALYST TREATMENT ON THE RATE OF FLUOROX REACTION (CATALYST -45 μm)

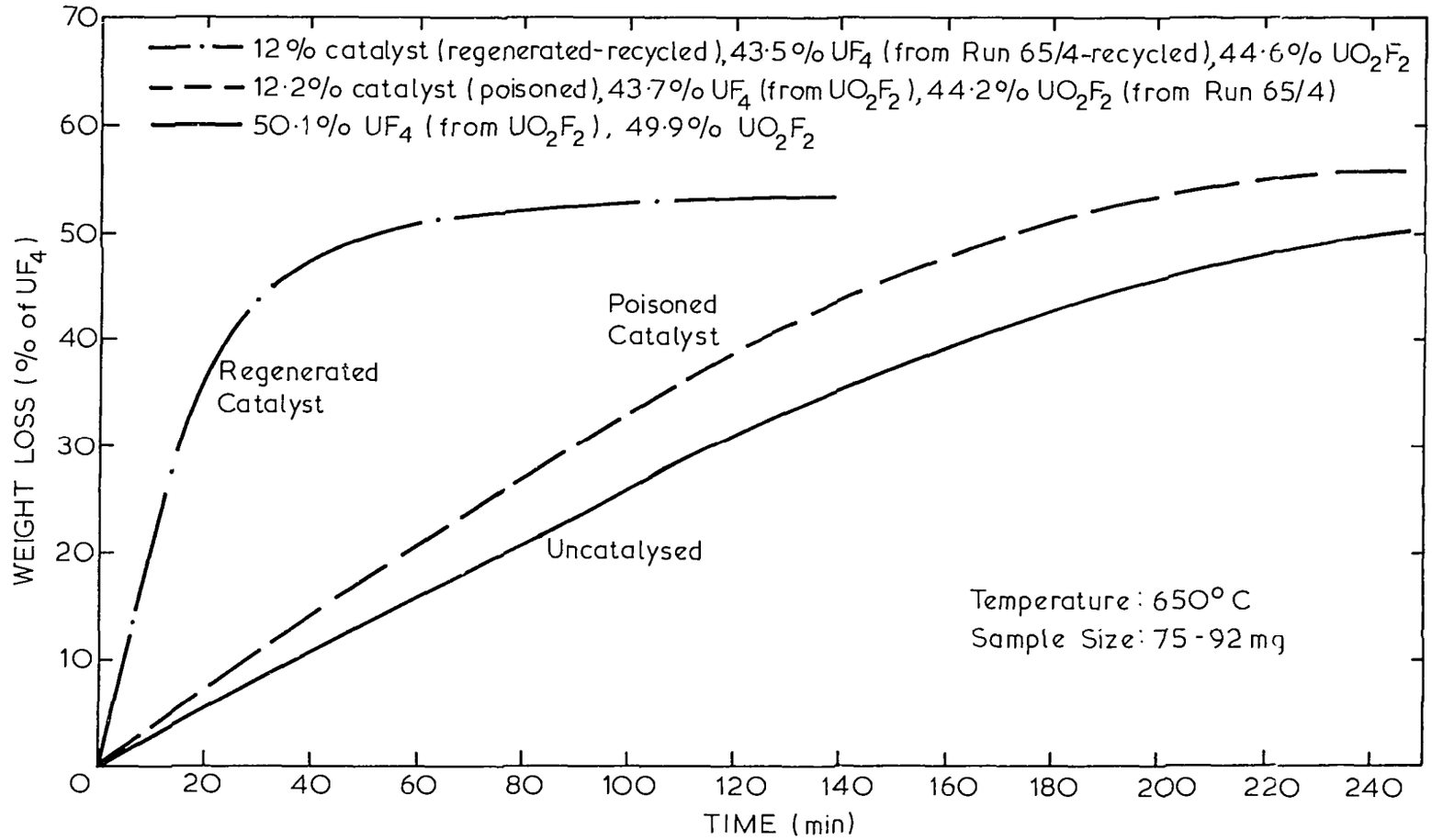


FIGURE 15. THERMOBALANCE MEASUREMENTS OF THE RATE OF FLUOROX REACTION SHOWING REGENERATION OF CATALYST BY RECYCLE REACTIONS

APPENDIX A
METHODS OF ANALYSIS OF SOLID PRODUCT

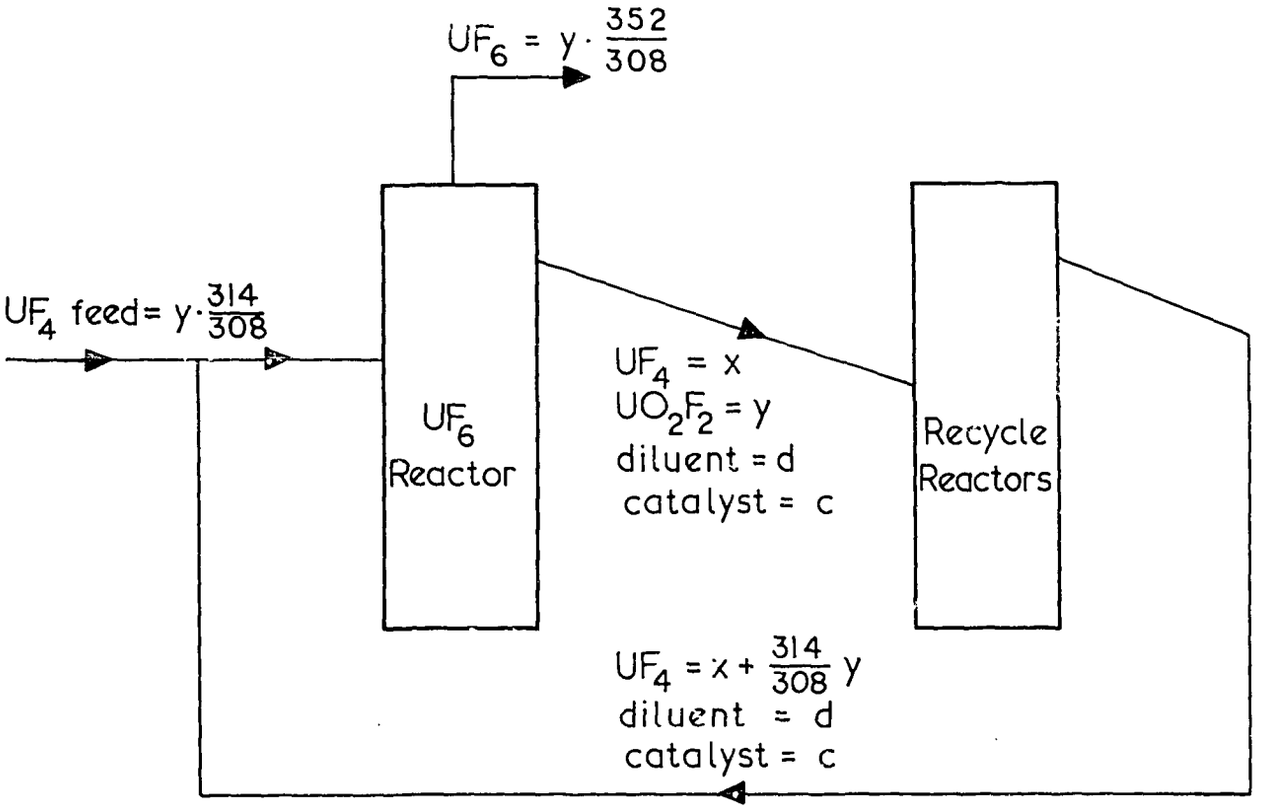
The composition of solids in the reactor at the end of an experiment was determined by solubility tests. Samples of approximately 25 g each were digested in water and aluminium nitrate or ammonium oxalate solution for two hours at 60°C, filtered, dried and weighed. The soluble fraction was given by the loss in weight of the sample. The quantities of reagents were 2 g of $Al_2(NO_3)_2$ per gram of sample and 12 g of ammonium oxalate per gram of sample.

Only UO_2F_2 is soluble in water, but both UO_2F_2 and UF_4 are soluble in aluminium nitrate or ammonium oxalate solutions. Thus the fraction soluble in water corresponded to the UO_2F_2 in the solid product while the difference between the fraction soluble in water and aluminium nitrate (or ammonium oxalate) corresponded to the UF_4 in the product. The fraction insoluble in aluminium nitrate or ammonium oxalate was taken to be catalyst and this was verified by platinum analyses.

The solubility method was also verified by U(IV) and total uranium analyses using titrimetric methods, and fluoride ion analysis using a specific ion electrode.

When oxides of uranium were suspected to be in the solid product, dissolution in ammonium oxalate was used because oxides of uranium are soluble in aluminium nitrate but not in ammonium oxalate.

APPENDIX B
SCHEMES FOR CATALYSED FLUOROX PROCESS WITH REGENERATION OF POISONED CATALYST



x = concentration of UF_4 in UF_6 reactor
y = concentration of UO_2F_2 in UF_6 reactor
d = concentration of inert powder in UF_6 reactor
c = concentration of catalyst in UF_6 reactor

Assume that the powder in the reactors is well mixed and the exit concentrations are the same as in the reactors.

Basis of calculation: 100 kg h^{-1} of powder leaving UF_6 reactor

Amount of UO_2F_2 leaving UF_6 reactor, y, is

$$y = 100 - x - d - c \quad \text{kg } h^{-1}$$

The UF_6 production rate is

$$(100 - x - d - c)\ \frac{352}{308}\ kg\ h^{-1}$$

At equilibrium, weight of UF_6 produced per kg catalyst, say z, is

$$z = \left(\frac{100 - x - c - d}{c}\right)\ \frac{352}{308}$$

With British UF_4, the catalyst was completely poisoned after production of 19.6 kg UF_6 per kg catalyst. With French UF_4, only 1 kg UF_6 was produced per kg catalyst. Therefore, to maintain a reasonably well catalysed rate, z should be at least 39.2 for British UF_4 and 2.0 for French UF_4.

Scheme 1

Increased catalyst concentration
No inert powder d = o
Assume x = 5

(a) British UF_4

$$z = \left(\frac{100 - 5 - c}{c}\right)\ \frac{352}{308} = 39.2$$

$$c = 2.9\%$$

(b) French UF_4

$$z = \left(\frac{100 - 5 - c}{c}\right)\ \frac{352}{308} = 2$$

$$c = 93\%$$

Scheme 2

Increased rate of recycling
Low catalyst concentration

(a) British UF_4
Assume x = 5
c = 1

$$z = \left(\frac{100 - 5 - 1 - d}{1}\right) \frac{352}{308} = 39.2$$

$$d = 60\%$$

(b) French UF_4

Assume $x = 5$

$c = 5$

$$z = \left(\frac{100 - 5 - 5 - d}{5}\right) \frac{352}{308} = 2$$

$$d = 81\%$$