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THE REDUCTION OF URANIUM HEXAFLUORIDE BY CARBON TETRACHLORIDE

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1. INTRODUCTION

The provision of uranium enriched in the fissile U235 isotope may form an important part of an atomic energy project based on uranium fuel. This enrichment is carried out on a large scale in the gas phase using uranium hexafluoride ("Hex") but, up to the present, there is no reactor system which uses uranium in this form and virtually the whole output of the isotope separation plants must be converted to other compounds of uranium or to metal. The conversion of Hex to uranium tetrafluoride is a most important stage in this sequence since the latter compound can either be reduced further in a single stage to metal or can be readily converted to other uranium compounds by conventional methods.

There exists, therefore, a need for an efficient process to convert UF_6 to UF_4 to meet the output of large scale isotope separation plants. In addition to the steadily increasing outputs from such sources, the fluoride process for recovering uranium as UF_6 from irradiated fuel elements, if it is adopted on a significant scale, may also require a Hex reconversion process.

2. REVIEW OF POSSIBLE RECONVERSION PROCESSES

The apparently attractive direct reduction of UF_6 to UF_4 by hydrogen was examined at a very early stage by groups at Ames who reported that the reaction was only moderately fast and was incomplete even at temperatures above 500°C(1). Corrosion of structural materials at such high temperatures made the above reaction appear less attractive and a wide range of catalysts was tried without

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effect. Similar observations were made (in 1943) by British workers who also found that the reaction required a considerable energy of activation (2,3). A successful reconversion process based on this reaction has only recently been reported (4) in which the high activation energy required is supplied by a hydrogen/fluorine reaction in the presence of Hex, enabling the reaction to proceed without the corrosion attending the use of high wall temperatures.

Reduction by hydrogen halides was reported at lower temperatures and with hydrogen bromide the reaction proceeded smoothly at 80°C(5). Both in Britain and in the U.S.A. some success had been achieved with HCl reduction but serious difficulties were experienced with corrosion and correspondingly high impurity levels in the UF_4 product(5,6).

The following thermodynamic estimates were reported (5) for the reduction of UF_6 by hydrogen and the two hydrogen halides (at 25°C)

$$UF_6\ (\text{solid}) + H_2\ (\text{gas}) \rightarrow UF_4\ (\text{solid}) + 2\ HF_{(\text{gas})}$$

$$\Delta F = -68.9 \text{ kilocalories}$$

$$UF_6\ (\text{solid}) + 2\ H\ Br_{(\text{gas})} \rightarrow UF_4\ (\text{solid}) + 2\ HF\ (\text{gas}) + Br_2$$

$$\Delta F = -43.5 \text{ kilocalories}$$

$$UF_6\ (\text{solid}) + 2\ H\ Cl_{(\text{gas})} \rightarrow UF_4\ (\text{solid}) + 2\ HF\ (\text{gas}) + Cl_2\ (\text{gas})$$

$$\Delta F = -23.4 \text{ kilocalories}$$

Other reducing agents which were examined included sulphur dioxide, ethylene, trichlorethylene, propane, ammonia, silicon tetrachloride, thionyl chloride, phosphorus trichloride etc., but with indifferent success from the point of view of an industrial scale chemical process.

The measure of this lack of success is demonstrated by the fact that, the following indirect and multistage aqueous route was used both in Britain and in the U.S.A. for some years:-

$$UF_6 \xrightarrow[2\ H_2O]{\text{hydrolysis}} UO_2\ F_2 + 4\ HF \xrightarrow[\text{ammonia}]{\text{precipitate}} \begin{matrix} (NH_4)_2\ U_2\ O_7 \\ (NH_4)_3\ UO_2\ F_5 \end{matrix}$$

$$\xrightarrow[H_2]{\text{dry, calcine \& reduce}} UO_2 \xrightarrow[HF]{\text{hydrofluorinate}} UF_4$$

e above possessed all the disadvantages of a multistage process ner with the need, in the case of highly enriched material, for close criticality control over its numerous stages.

In the Research and Development Branch of the U.K.A.E.A. at Windscale, attention was therefore directed towards the provision of a fundamentally simple method, which in addition to possessing the normal advantages of a single stage process would also include the virtues of exceptionally high efficiency, simple criticality control with expensive enriched material, and freedom from severe corrosion conditions.

In view of the alternative processes being investigated elsewhere (e.g. Martin (7) and Keen at A.E.R.E. were having some success in overcoming the initial problems associated with trichlorethylene reduction), and because of the difficulties inevitably attending the hydrolysis of UF_6, investigations were limited at Windscale to reaction in non-aqueous solvents. In the course of this work it was shown that at temperatures of 100°C-200°C uranium hexafluoride was rapidly reduced by carbon tetrachloride in a quantitative manner to give the desired product, UF_4. This reaction was studied essentially from the point of view of its application as a reconversion process and was successfully developed as such(8).

3. THE CARBON TETRACHLORIDE PROCESS - DESCRIPTION OF THE REACTION

Uranium hexafluoride dissolves readily in carbon tetrachloride to give a solution which is stable at room temperatures for some weeks(9). The solubility at temperatures up to 35°C is shown in Fig. 1(8). When these solutions are heated in an autoclave to about 150°C, however, an extremely rapid reaction takes place which is accompanied by a rise in temperature and pressure. The reaction products are UF_4, chlorine and a mixture of chlorofluoromethanes, suggesting reactions of the type:-

$$UF_6 + 2\ CCl_4 \rightarrow UF_4 + Cl_2 + 2\ CCl_3F$$

i.e. UF_6 fluorinates the CCl_4 by a direct substitution reaction liberating gaseous chlorine. The reaction products, other than UF_4, are volatile and possible contamination of the UF_4 with polymeric carbonaceous material is much less likely than from reactions with unsaturated organic reducing agents. The presence of intermediate fluorides (UF_5, U_2F_9, U_4F_{17}) was indicated by the detection of hexavalent uranium in an aqueous extract of the product and by direct X-ray analysis. The amount of intermediate fluoride was reduced to less than one percent by bleeding off the pressure due to chlorine and the chlorofluoromethanes and reheating for a short time to the initial reaction temperature. The need for a pressure vessel was solely to retain the reagents until the reaction had taken place and high pressures appeared to maintain an equilibrium position which could only be disturbed by removal of the gaseous reaction products.

Experiments with varying ratios of reactants showed that the reconversion did not go to completion at $CCl_4 : UF_6$ ratios of 1:1 or less, but that a ratio of 4:1 gave essentially complete reduction to UF_4. The relative proportions of the various chlorofluoromethanes varied with the amount of excess CCl_4, more of the trifluoro compound ($CClF_3$) being obtained at the low ratios and larger quantities of CCl_3F occurring with a large excess of CCl_4.

A value for $\Delta F_{(25^{o}C)}$ of -31.5 kilocalories/mole UF_6 was calculated for the reaction with a $CCl_4:UF_6$ ratio of 4:1. Experimental results agree reasonably well with this calculated value.

The rate of heating used to initiate the reaction has a significant effect on the density of the UF_4 formed. At rapid rates a lower density powder is produced. For the conditions shown in Fig. 2, the tap density is >2.0.

Reaction Mechanism

There is experimental evidence that the reaction proceeds by way of the intermediate fluorides before going finally to UF_4. Various reaction paths may be postulated, each involving a combination of two or more of the following reaction types:-

$$UF_6 + CCl_4 \rightarrow UF_4 + \text{chlorofluoromethanes} + Cl_2$$

$$UF_6 + CCl_4 \rightarrow \text{Intermediate fluorides} + CCl_n\,F_{(4-n)} + Cl_2$$

$$\text{Intermediate Fluorides} + CCl_4 \rightarrow UF_4 + CCl_n\,F_{(4-n)} + Cl_2$$

$$\text{Intermediate Fluorides} \rightleftharpoons \begin{cases} UF_4 + UF_6 \\ \text{Lower Intermediate Fluorides} + UF_6 \end{cases}$$

There is also evidence that the reaction is somewhat slower to initiate in a new vessel and for this reason it is believed that traces of UF_4 assist in promoting an autocatalytic reaction.

4. APPLICATION TO BATCH RECONVERSION ON A ROUTINE PRODUCTION SCALE

Description of Equipment

One design of vessel which was developed for routine reconversion of highly enriched UF_6 by a batch process is shown in Fig. 3.

The reactor took the form of a cylindrical nickel-lined steel pressure vessel recessed at the bottom third to accommodate a loose fitting nickel container. The steel base plate was designed to be easily removable and was provided with cooling facilities to assist in introducing the UF_6 from its original container. The whole of the reactor, apart from the head, was provided with resistance heating and the head, with its associated valves, pipelines and instruments was fitted into a heated box. The connections to this head included a nickel bursting disc, a pressure gauge, thermocouple pocket, and lines for Hex and CCl_4 inlet as well as for gaseous effluent. The effluent gas line led through a water-cooled condenser, for the removal of the excess CCl_4 to a simple glass scrubber charged with caustic soda solution to remove chlorine. The residual gases (CCl_3F, CCl_2F_2 and $CClF_3$) passed through a filter into a vent duct which led to an effluent stack.

Provision was made for evacuating the reactor prior to charging it with Hex and CCl_4.

Operational Procedure

The vessel was cooled, evacuated and the required quantity of UF_6 (about 1 kg for a 10 litre reactor) transferred into it. Carbon tetrachloride was added (~ 1 litre per kg UF_6) without releasing the vacuum and the sealed vessel was heated to 150°C over the period of an hour. A rapid increase of pressure showed that the reaction had taken place. The reactor heaters were switched off at this point and the temperature was allowed to climb to a steady value of about 200°C, the pressure developed in a 10 litre vessel being 350-400 p.s.i. (The course of typical pressure and temperature changes is shown in Fig. 2). After two hours the vessel was cooled to 50°C and the gas pressure released through alkali scrubbers to trap the chlorine. A further heating stage was carried out to complete the conversion (no external indication of further reaction is noted) the gas pressure was bled off and the excess CCl_4 distilled before the vessel was opened.

The UF_4 was located in the base of the removable nickel liner in the form of a loose friable cake. A very small proportion was deposited on the walls of the remainder of the reactor interior. No uranium was detectable in the gaseous effluent and the uranium mass balance showed process efficiencies regularly exceeding 99.7%. Examination of gaseous effluents confirmed the presence of chlorine, and the chlorofluoromethanes. Phosgene was also present if the evacuation stages were inefficient or if inleakage of air occurred.

The UF_4 required heating in a current of air at 120°C to remove chlorine and other absorbed gases before being reduced by calcium or magnesium to uranium metal.

The nickel lining showed extremely high resistance to corrosion, about 15 ppm appearing in the UF_4. The following is a typical analysis:-

Impurity	Fe	Cr	Ni	C	Si
ppm	<100	25	10	250	25

The level of carbon contamination was further decreased during the reduction stage to metal.

5. DEVELOPMENT OF THE REACTION FOR CONTINUOUS OPERATION AT ATMOSPHERIC PRESSURE

While the above batch process in a pressure vessel was suited to kilogram amounts of highly enriched UF_6 it had obvious limitations in its application to the tonne scale reconversion of low enrichment material. The kinetic data accumulated during development and operation of the batch process, however, also indicated that the reaction was sufficiently rapid to permit operation at near atmospheric pressure thus giving rise to the possibility of a continuous process.

In order to investigate the conditions under which such a process might operate, a small scale system was designed to permit continuous removal of the product UF_4 as well as providing adequate contact time for the reduction of the intermediate fluorides (the rate determining step). The design was based on the principle of an inclined rotary kiln, a version of which is shown in Fig. 4.

For a given temperature and reactant ratio the kiln dimensions were determined by the residence times required for both solid and gas. Earlier data showed that at 200°C all the UF_6 would have reacted within two minutes to produce solids. Solid residence time was calculated from the equation developed by Sullivan (10) for a reactor of this type:-

$$T = \frac{L \sin B}{2\pi Rn \sin A}$$

where T = residence time

L = kiln length

B = angle of repose

R = kiln radius

n = speed of rotation

A = angle of inclination of kiln.

The length of kiln was chosen to give a solid residence time of 10 minutes at 10 rpm with a 2° slope. These criteria gave a minimum ratio of length to diameter of 14:1.

The kiln, which was constructed of stainless steel lined with nickel, had an internal diameter of $4\frac{1}{4}$ in. and an overall length of 5 ft 6 in. heated by a resistance furnace. The UF_6 and CCl_4 were carried into the kiln through a concentric nozzle or through separate tubes which impinged the jets. The exit end of the kiln entered a settling chamber by way of a PTFE collar. Provision was made for intermittent or continuous removal of the UF_4 from this chamber. The effluent gases left the top of the reactor through a copper pipe to a scrubbing system. A form of flow diagram is shown in Fig. 5.

The interior of the kiln was designed to provide a range of experimental conditions, but normally fins were fitted towards the exit end and the remainder of the upper part of the kiln was kept free from solid build up by a tumbler or by a stationary scraper arm.

In operation the kiln was purged with nitrogen and CCl_4 before the Hex was introduced. The kiln was run to equilibrium for a series of operating conditions and the effects of the various parameters were observed by analysis of the product and by temperature measurements.

For each condition of Hex flowrate and reactant ratio there was a minimum temperature needed to obtain a satisfactory product and a decrease of even a few degrees below this critical condition resulted in an increase in the amount of intermediate fluoride in the product (Fig. 6). A reduction in the excess of CCl_4 under these critical conditions also had an adverse effect on the product quality but this could be restored by raising the temperature. An over excess of CCl_4 could also result in lowered quality because of the accompanying reduction in the gas residence time caused by the associated increased flowrate.

The mean solid residence time was about 15 minutes with a kiln slope of $7\frac{1}{2}^{\circ}$; the distribution of residence time over the mean is shown in Fig. 7.

Normally the kiln was run at 1-2 mm above atmospheric pressure. Occasional reduction of pressure to below atmospheric when operating at near critical conditions resulted in increased amounts of uranyl fluoride - possibly arising from inleakage of air.

The information gained from this investigation enabled satisfactory operating conditions to be defined for the continuous large scale reduction of UF_6 to UF_4.

Reaction at Higher Temperatures

During normal operation at 200-300°C, the bulk of the UF_4 produced was continuously discharged from the end of the kiln. A significant amount of deposit built up on the walls of the kiln however and necessitated the use of a scraper or tumbler. Because of the possibility that these deposits arose from the transitory formation of intermediate fluorides (in small scale experiments with a fluidised bed the formation of these compounds stopped the fluidisation at low reaction temperatures), some experiments were done at 400-500°C at which temperatures these compounds are quite unstable with respect to their disproportionation to UF_6 and UF_4.

The higher temperatures were achieved by preheating the Hex and CCl_4 feeds to 300°C as well as by heating the kiln, initially, to a little below the required operating temperature. In these experiments the reaction was so rapid that it became self-sustaining and the kiln heaters could be turned off, the operating temperature being controlled by adjustments of the reagent feed rates. The output of the kiln at 450°C was more than twice that at 300°C and the temperature distribution through the kiln indicated that the reaction was taking place almost completely in the gaseous phase in the form of a high temperature "flame". A significant reduction was obtained in the amount of UF_4 adhering to the kiln walls.

6. SUMMARY

The reaction between UF_6 and CCl_4 provides an efficient method for the reconversion of enriched UF_6 to UF_4. It possesses all the advantages of a single stage process and in the case of highly enriched material it considerably eases the problem of criticality control. A very high output is possible from quite a small plant and the hold-up of expensive product is correspondingly low. The reaction temperatures are low although some advantage can be gained by operating at 400-500°C. Additional economies are achieved since two thirds of the original fluoride content of the Hex are retained compared with none in the aqueous route. The by-product chlorofluoromethanes are of significant industrial value, and on the large scale are worth recovering.

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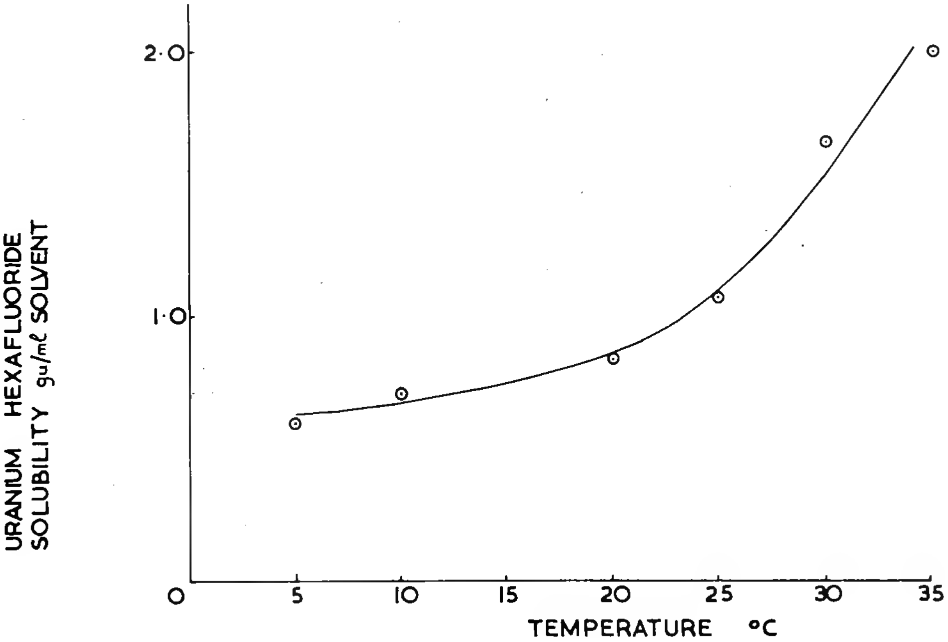

FIG. I SOLUBILITY OF URANIUM HEXAFLUORIDE IN CARBON TETRACHLORIDE

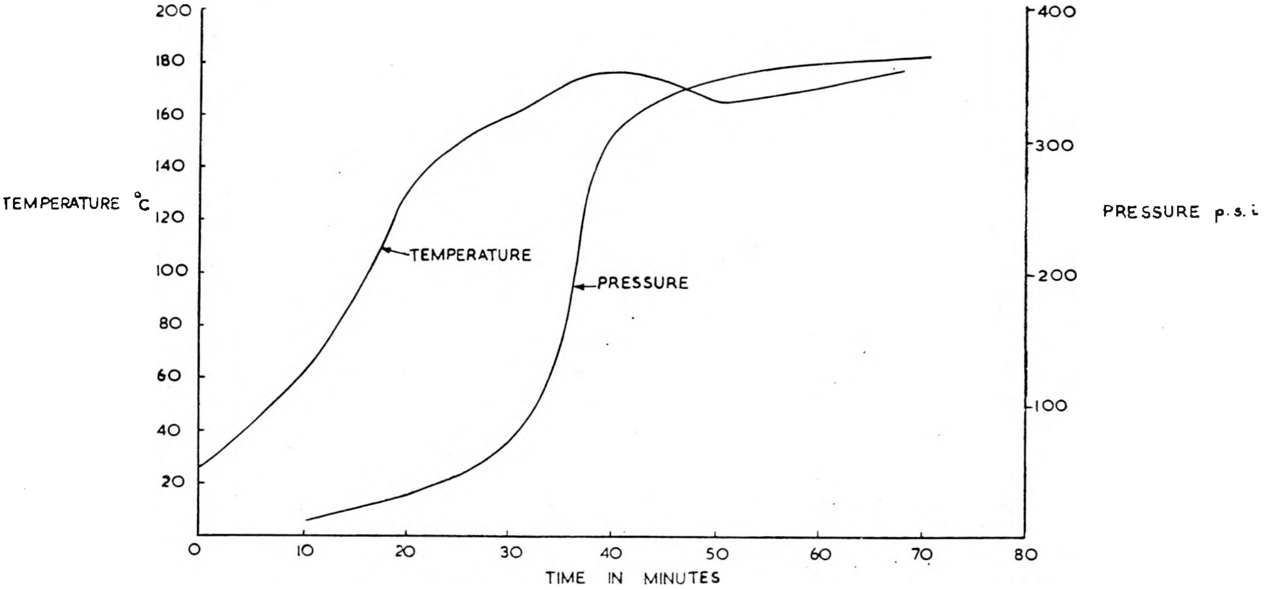

FIG. 2. TYPICAL PRESSURE & TEMPERATURE CHANGES DURING REACTION BETWEEN UF_6 & CCl_4.

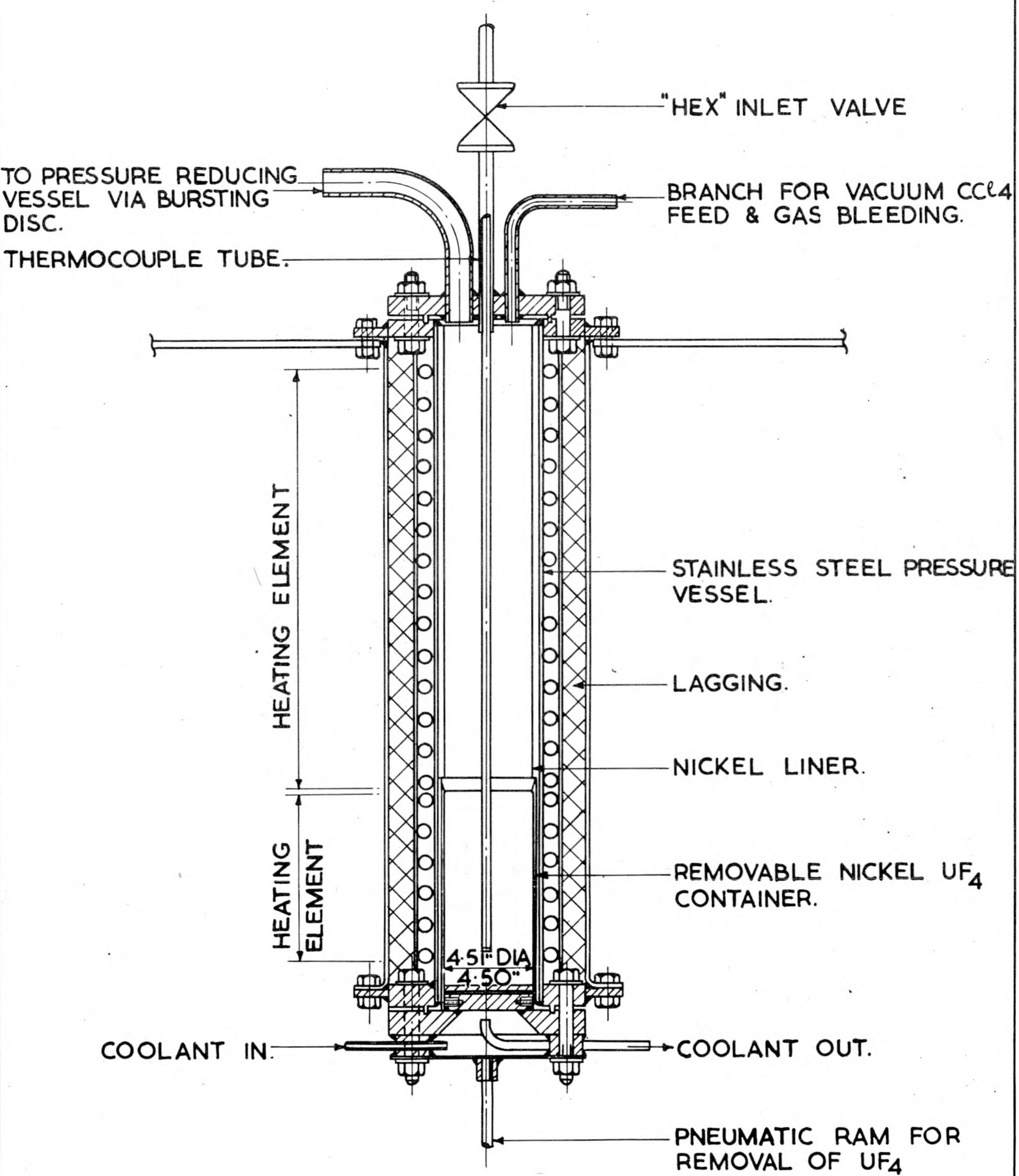

FIG. 3. HEX RECONVERSION REACTOR.

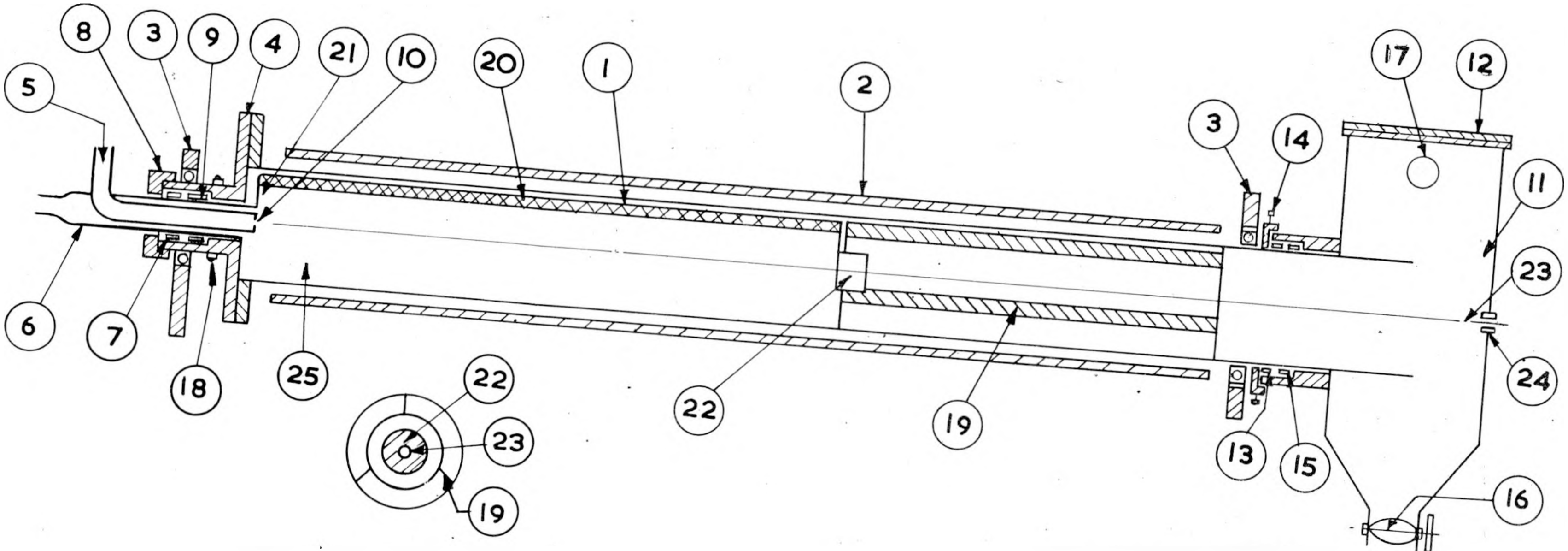

FIG.4 SECTIONAL VIEW OF ROTARY KILN.

1. Kiln reaction chamber
2. Resistance furnace
3. Roller Bearings
4. Flange joint
5. Hex inlet
6. Carbon tetrachloride inlet
7. P.T.F.E. collar (inlet)
8. Gas seal bearing cap (inlet)
9. Gas seal compression collar (inlet)
10. Hex inlet orifice
11. Settling chamber
12. Settling chamber lid
13. P.T.F.E. collar (outlet)
14. Gas seal bearing-cap (outlet)
15. Gas seal compression collar (outlet)
16. Butterfly valve
17. Effluent gas outlet
18. Chain-drive
19. Radial fins
20. Scraper arm
21. Scraper arm bracket
22. Scraper arm bearing
23. Thermocouple pocket
24. P.T.F.E. plug
25. Deflector plate

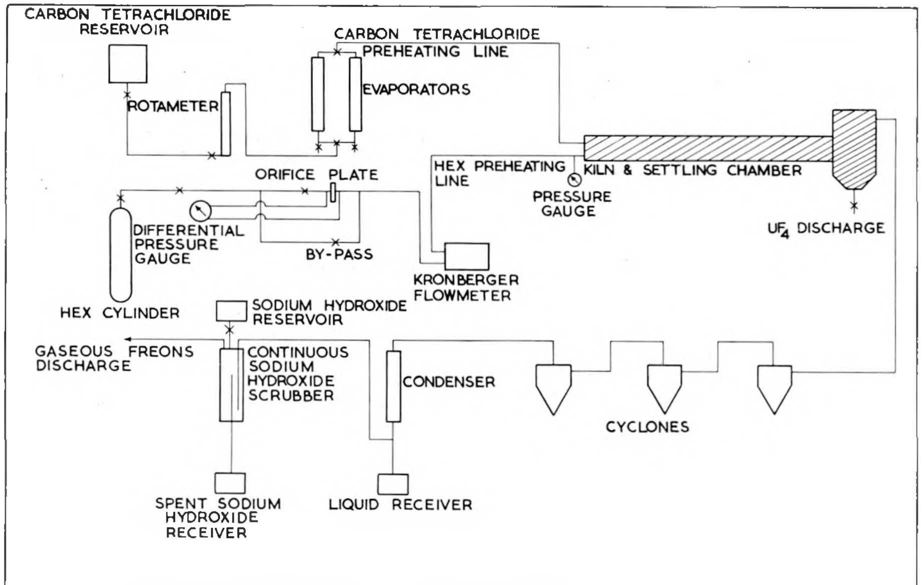

FIG. 5. DIAGRAMMATIC REPRESENTATION OF CONTINUOUS HEX RECONVERSION PROCESS.

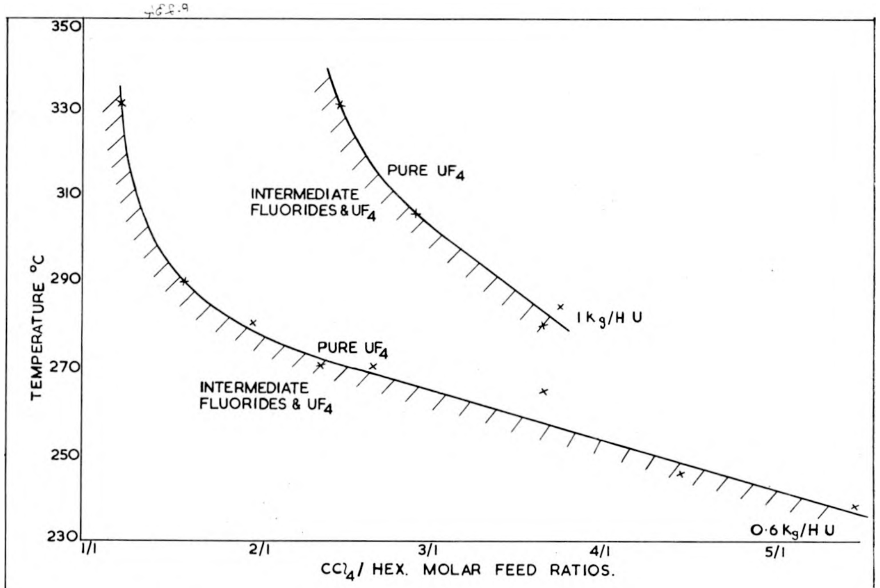

FIG. 6. CRITICAL CONDITIONS.

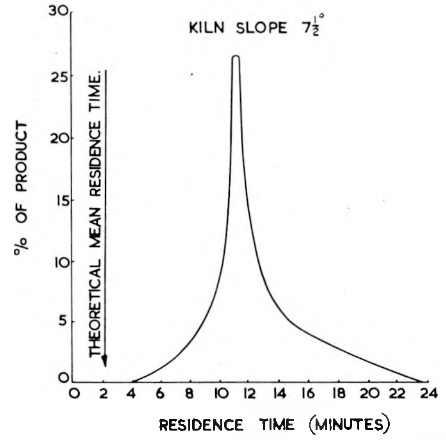

FIG. 7 DISTRIBUTION OF RESIDENCE TIME.