THERMAL PLASMA REDUCTION OF UF6 TO UF4 WITH HYDROGEN - LABORATORY TO PILOT PLANT

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The reaction between UF_6 and H_2 is exothermic at ambient temperature with $\Delta_f H^\circ(298.15\ K) = -510$ kJ/mol. However, the high activation energy prevents the reaction from proceeding. In the conventional process for the reduction of 235-enriched UF_6 to UF_4, the activation energy is supplied by the combustion of hydrogen and fluorine. A thermal plasma process using a hot cathode plasma burner was developed to reduce UF_6 to UF_4 with approximately stoichiometric amounts of hydrogen. The UF_4 product was subsequently used for further reduction to uranium metal by calcium metal and proved to be of the necessary grain size and purity. The process was scaled to 10 kg UF_6/hour, and it was shown that an increase in UF_6 feed rate did not require a proportional increase in the plasma power input.

INTRODUCTION

After beneficiation of the natural uranium ore it is converted by the mining company to either an oxide or ammonium diuranate slurry. If a centrifugal type of enrichment plant is to be used the material is converted to uranium hexafluoride. The uranium hexafluoride has a vapour pressure of 14,93 kPa at 25°C /1/. For the isotope enrichment process the uranium hexafluoride, in the RSA case, is mixed with hydrogen.

Depending on the deposit, natural uranium has a content of ca 0.7% of the U^{235}-isotope. If enrichment is done above 90% U^{235} it means that for every 100 tonne of uranium hexafluoride fed into the enrichment plant, more than 90 tonne of depleted UF_6 (mainly U^{238}-isotope) will be available as waste. The U^{235} depleted UF_6 can either be stored in safe containers for further enrichment at a later stage when better technology becomes available or must be converted to more useful or lower safety risk material.

URANIUM METAL

In order to obtain uranium metal the depleted UF_6 must first be converted to uranium tetrafluoride. Further reduction of UF_4 to uranium metal is accomplished by metallothermic reduction with calcium or magnesium metal in a bomb reduction unit. Other methods for the reduction of UF_6 to the metal do exist /2,3,4/. However for economic reasons calcium metal as reducing agent is preferred.

The UF_4 to be reduced must exhibit some of the following properties:

- It should preferably be a noin-calcined powder form
- The powder must have a density above 1.5 g/cm^3 to ensure that enough heat per unit volume is generated during the reduction to melt and separate the uranium metal and the calcium fluoride slag
- It is also preferred to have some UO_2F_2 (ca. >6%) present for ignition of the reduction process.

USES OF METAL

Uranium metal depleted of the radio-active U^{235} isotope can be used for some of the following applications. The two properties mainly utilized are the high density (18.95 g/cm^3) and the pyrogenic reaction when U-metal is exposed to air (oxygen) at elevated temperatures.

- Counter weights in mechanical devices eg gyroscopes, inertial guidance devices
- Due to the high density it can be used for the manufacture of bullets covered by a hard protected outer layer
- Due its exothermic and pyrophoric reaction at elevated temperatures it is sometimes used for armour piercing devices.

Two conventional processes for the reduction of UF_6 exist.

THE HOT WALL PROCESS

The layout of the process is similar to that of the Cold wall Process which is depicted in Figure 1.

In the Hot wall process a gas stream consisting of UF_6 and a 30% stoichiometric excess amount of hydrogen is passed through a kiln preheated to 650°C. The UF_4 agglomerates as a slag against the reactor walls. The slag is removed by means of heavy duty pneumatic vibrators and is subsequently pulverized by means of a hammer mill. The powder is then thermometallically reduced to the metal.

Due to the agglomeration this process can not be used for any UF_6 mixture containing more than 5% U^{235} because of nuclear safety requirements.

COLD WALL-PROCESS

The Coldwall-Process for the reduction of UF_6 to UF_4 can be utilized for both U^{235}-enriched and U^{235}-depleted UF_6. A schematic layout is depicted in Figure 1.

The necessary energy for initiating and sustaining the reduction reaction is obtained by the addition of fluorine to the UF_6-feed and by utilizing the heat generated by the reaction between fluorine and hydrogen.

$$1/2\ F_2(g) + 1/2\ H_2(g) \rightarrow HF(g) \quad \Delta H_{298} = 269\ \text{kJ/mole}$$

The reactor wall temperature is maintained between 100 and 200°C. The process requires an excess of 100 - 500% hydrogen and 0.05 to 0.08 kg F_2/kg UF_6

For continuous operation a fluorine gas production unit must simultaneously be operated. A large excess of HF is formed. Although a suitable product is produced the process is dangerous and expensive.

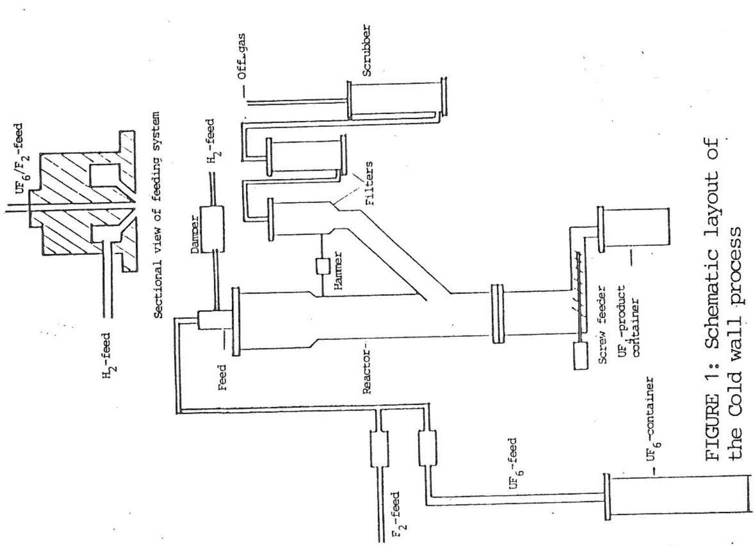


FIGURE 1: Schematic layout of the Cold wall process

THE PLASMA PROCESS

Plasma processes normally produce very fine, sometimes submicron powders with a typical density of $<0.1 g/cm^3$. Calcination can be prevented under certain conditions.

For the plasma process to be competitive the following requirements must be met as far as possible:

- Oxygen and water vapour must be absent during the reduction process
- The UF_4 product must not be calcined
- The density of the UF_4 product must be higher than $1.5 g/cm^3$
- In flight reduction is preferred and agglomeration of the powder is to be prevented
- The use of fluorine and excess hydrogen is to be excluded
- The plasma process must be more economical.

Advantages of using a plasma process:

- Apart from the reaction between hydrogen and fluorine all other flame processes utilise oxygen for combustion and produce CO, CO_2 and water. UF_6 is highly reactive towards water vapour through hydrolysis to produce oxyfluorides
- Because a plasma can be obtained from a single gas like nitrogen, further gas separation actions are simplified
- Due to the high enthalpy of the plasma flame utilization stoichiometric amounts of hydrogen should be feasible
- If required all or a portion of the hydrogen can be used as plasma gas
- The walls of the reaction chamber can be kept at a low temperature and subsequent contamination and corrosion be kept at a minimum.

EXPERIMENTAL

LABORATORY EXPERIMENTS

The laboratory unit consisted of a hot cathode plasma burner followed by a UF_6/H_2 feed section (see Fig.2), a 100mm diameter reactor of 500 mm length and metal filter and sodium carbonate gas scrubber.

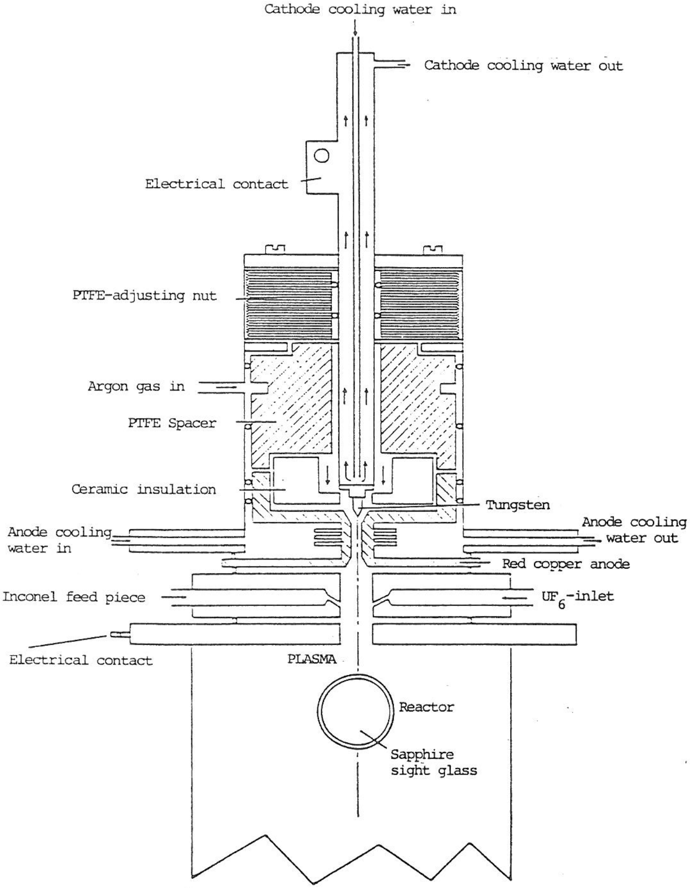
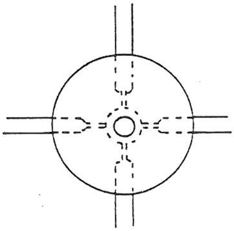


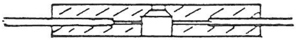
FIGURE 2: Laboratory apparatus

After the unit was tested for leaks, the plasma was initiated with argon gas at 60 kPa (absolute) reactor pressure. The argon was replaced with mixtures of argon /hydrogen or nitrogen/hydrogen. After a 15 minute stabilization period the UF_6/hydrogen gas mixture was introduced through the feed plate (Figure 3). Due to safety reasons the maximum feed in the laboratory was 0.5 kg UF_6/h with a plasma energy of 5-10 kW.

The formed UF_4 product was removed and analyzed. A few hundred experiments were performed and only the general results will be discussed. At low feedrate and below atmospheric reactor pressure, low density amorphous UF_4 was formed. An X-ray diffraction spectrum of crystalline material removed from feedplate is illustrated in Figure 4.



UF_6/H_2-feed. Top view



UF_6/H_2-feed. Cross section view

FIGURE 3: UF_6/H_2-FEED SECTION

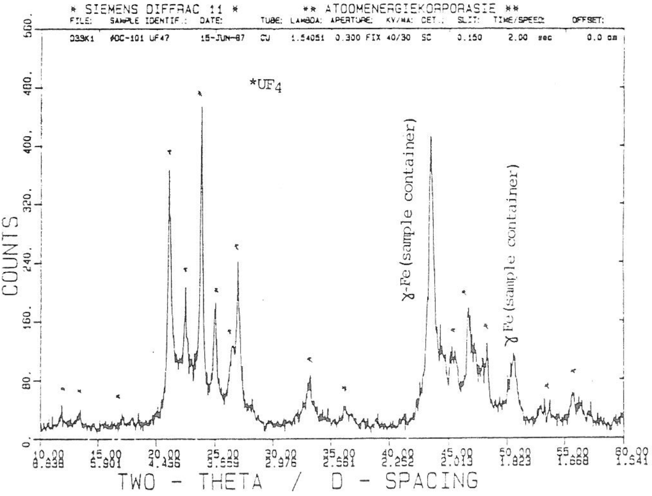


FIGURE 4: X-ray diffraction spectrum

The results of thermodynamic calculations based upon minimizing of the Gibbs free energy for various UF_6/H_2-ratios /5/. With a three times stoichiometric excess hydrogen, a 100 % condensed UF_4- yield at 1000 K can be obtained.

PILOT PLANT EXPERIMENTS

For safety reasons the maximum UF_6-feed in the laboratory was limited to 500g UF_6/hr for 20 minutes. On the pilot plant a feedrate as high as 10 kg/hr at 15 kW energy input, for periods of less then 20 minutes was attained. To obtain high feedrates the UF_6 cylinder was heated to 200°C to give a vapour pressure of approximately 500 kPa.

The UF_6 was premixed with a 5x stoichiometric excess of hydrogen, although during laboratory investigation stoichiometric quantities also proved successful. The existing Cold wall pilot plant was used and only the $F_2/H_2/UF_6$ unit was replaced with a plasma system similar to the one used in the laboratory experiments.

Comparison of the conventional Coldwall process with the plasma process gave the following results:

- Due to the required continuous operation of the fluorine cell for the production of fluorine, a 24h/day and 7 days/week was compared to a 16h/day 5 days/week plasma process. This resulted in 66 days required for the Cold wall process and 99 days for the plasma process to produce 100 kg U-metal from the produced UF_4 from 1485 kg UF_6.

The plasma process, even on this small scale showed a 33% saving in labour, a 56% saving in electrical and a 66% saving in material costs.

THE FOLLOWING GENERAL TRENDS WERE OBSERVED

- At a given UF_6-feedrate a decrease in reactor pressure to 40 kPa absolute will result in a decrease in density of the UF_4-product
- At a constant same plasma energy input an increase in UF_6 feedrate will increase the density of the UF_4-product until incomplete reduction starts taking place. The latter is possibly also due to insufficient residential time in the plasma zone
- At a reactor pressure of 10 kPa below atmospheric pressure (for safety reasons) and a 7.0 kg/hr UF_6-feedrate, a UF_4-product with a density as high as 2.17 g/cm^3 was obtained. Due to the increase in the viscosity of the plasma gas with increased temperature, penetration of the UF_6/H_2 gas mixture caused some problems
- Blockages in the feeding system occurred more frequently at lower feedrates
- The UF_4-product produced was amorphous apart from the material which was collected close to the feeding section, where it was crystalline.

Nevertheless both the crystalline material and the amorphous material gave excellent results during the subsequent reduction to uranium metal with calcium metal. A typical analysis of the UF_4-product is given in Table 1.

TABLE 1 ANALYSIS OF PILOT PLANT PLASMA PRODUCED UF_4

	Lot 1	Lot 2
% UF_4	80.86	85.51
% UF_4 (calc)	9.76	4.77
% UO_2F_2	9.18	8.85
% HF	0.20	0.87

CONCLUSIONS

- On a conservative basis the plasma process is more economical than the Cold wall process
- Less HF is produced with the plasma process and because it is a dry process it needs only to be separated from the excess hydrogen and the nitrogen plasma gas
- It is believed that with a better reactor design where the UF_6/H_2 -mixture penetrates the centre of the plasma flame the use of stoichiometric $UF_6:H_2$-ratios will be possible
- By varying the plasma and reactor parameters UF_4 of different densities and crystallinity can be produced
- A chemical process in which all the reagents and products apart from the wanted product are vapours or gases and the wanted product is thermodynamically stable, will be most suitable for plasma activation. Other examples are the plasma production of SiO_2 from $SiCl_4$ or SiF_4, TiO_2 from $TiCl_4$ and ZrO_2 from $ZrCl_4$. Ceramic carbides can also be produced from volatile halides. If the solid product is less stable, a quenching step will be required
- A plasma is the only convenient flame heat source (apart from the F_2/H_2-reaction) which does need oxygen with the formation of CO, CO_2 and H_2O
- The plasma process is more economical, safer and allows intermittent operation.

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