PROCESSING OF URANIUM HEXAFLUORIDE IN A ROTARY PLASMA REACTOR

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Abstract

UF_6 plasma decomposition resulted in conversion to UF_4 and elemental fluorine only. Introduction of silicon vapors or methane into reaction zone as fluorine scavengers partially off set the reverse reactions giving rise to the formation of elemental uranium in the condensed reaction products.

1. Introduction

Uranium hexafluoride (UF_6) is the main intermediate in the production of nuclear fuels (e.g. enriched uranium metal or oxide) [1]. However, the conventional process of UF_6 reduction has not been distinctly improved since the 2nd World War. Thus, the uranium industry has incentives for a new technology - a direct decomposition of UF_6. This endothermic reaction has been the subject of numerous studies in plasma systems with conflicting results. Burk [2] reported the detection of uranium metal on cathode tip during UF_6 decomposition in argon arc plasma. However, Tumanov et al. [3, 4] carried out both experimental and theoretical studies on UF_6 plasma decomposition and found out that due to a limited quenching rate only a partial conversion of the starting material to UF_4 was possible. According to their calculations only quenching rates exceeding 10^7 K/s could prevent the reverse fluorination of uranium metal vapors formed. One should mention here that such quenching rates are rather difficult to attain in plasma systems.

The presented work was carried out to study the plasma decomposition of UF_6. A test was also performed in the presence of elemental silicon vapor which could act as

fluorine scavenger. It was found earlier [5] that silicon tetrafluoride was relatively stable under similar plasma conditions. It could, therefore, inhibit the reverse reaction between uranium metal vapors and free fluorine formed.

Uranium hexafluoride also finds an application in production of environmental friendly Freons of HFC 120 to 150 group in a reaction with unsaturated hydrocarbons under conventional conditions [6] when a partial conversion of UF_6 into UF_4 occurs. Thus, it seemed reasonable to expect that under plasma conditions the proposed process

$$UF_6 + CH_4 \rightarrow U + C_2H_xF_y + HF \qquad (1)$$

with $x + y = 6$

is also feasible once total decomposition of reactants is achieved. Thus not only uranium metal but also other products of high interest (Freons $C_2H_xF_y$) could be obtained in a one-step plasma reaction.

2. Experimental

The experiments were carried out in the setup presented in Figures 1 and 2 which was described in details earlier [5, 7]. To ensure a sufficient contact time between reactants in the case of heterogeneous reaction, a rotary (450 rpm) reactor was used. The runs were performed in a flow system with the composition of effluent gases continuously monitored on-line by a VG Quadruple mass spectrometer. Solid products were either condensed on the surface of the collecting chamber or separated from the gas stream using a porous metal filter.

The collected powder was characterized by XRD, BET and wet chemical analysis. A summary of the operational parameters for all tests performed are presented in Table 1.

Table 1. Experimental conditions used.

Test set #	Reactants	Torch power (kW)	Plasma gas (slpm)	Test duration (min)	Feeding rate (g/min.)	Initial charge (g)	Mass of solid products (g)	Condensation rate (g/min.)
I	UF_6	13.2	Ar (25)	9	15.1	-	8.8	0.1
		18.2	N_2 (25)	7	10.8	-	48.5	7.0
		22.2	N_2 (25)	7	10.7	-	66.5	9.5
II	UF_6 + Si	36.0	N_2 (25)	9	UF_6 (2.9)	623.0 (Si)	10.0	1.1
III	UF_6 + CH_4	31.5	Ar (12.5) N_2 (12.5)	10	UF_6 (2.9) - CH_4 (2.9)	-	18.0	1.8

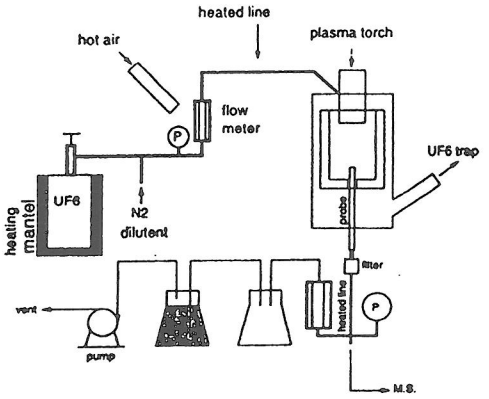

Figure 1. Experimental setup.

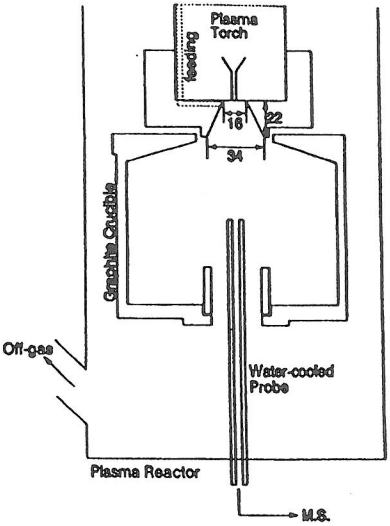

Figure 2. Rotary plasma reactor.

3. Results and discussion

The results of elemental, XRD and BET analysis of collected solids for all tests performed are presented in Table 2.

Table 2. Analysis of solid products

Test set #	Product from	Elemental analysis, wt %					X-ray diffraction	Specific surface (m^2/g)
		U	F	C	Si	N		
I	chamber	65.1	20.5	-	-	-	UF_4	2.6
	filter	68.5	21.7	-	-	-	as above	3.3
II	chamber	45.0	13.7	0.5	18.3	1.0	mostly UF_4, Si	-
	filter	50.4	13.6	0.4	11.9	0.8	as above	-
III	chamber	67.7	23.0	1.2	-	-	mostly UF_4	5.3
	filter	73.6	18.9	1.1	-	-	as above	-

Experiments on UF_6 plasma processing were carried out with MS sampling probe located in the reaction zone. Thus, the progress of the reaction could be followed by monitoring the off-gas composition along the reactor axis (Fig. 2). The gaseous reactants were sampled as a function of distance, L, from plasma torch nozzle (L varied between 1 and 11 cm) and the intensity of a peak at m/e = 333 (UF_5^+ ion) in the spectrum of the sampled gas was measured as an indicator of UF_6 decomposition.

Elemental analysis of U and F content in solid products for all three runs performed showed that almost stochiometric UF_4 (99% purity) was obtained with no traces of uranium metal. The conversion degree of UF_6 ranged between 36 ... 98% depending on a torch power (see Fig. 3). Even at relatively low power almost total decomposition of UF_6 occurs. However, from the results of analysis carried out at different probe location (Fig. 4, run at the torch power equal to 13.2 kW) it is evident that the decomposition does not occur instantly. The specific surface of UF_4 formed

was 3-4 times lower than the condensed products obtained earlier in other processes [5, 7]. Some irregularities observed at L between 4 and 5 cm (Fig. 4) could be related to the mixing phenomena.

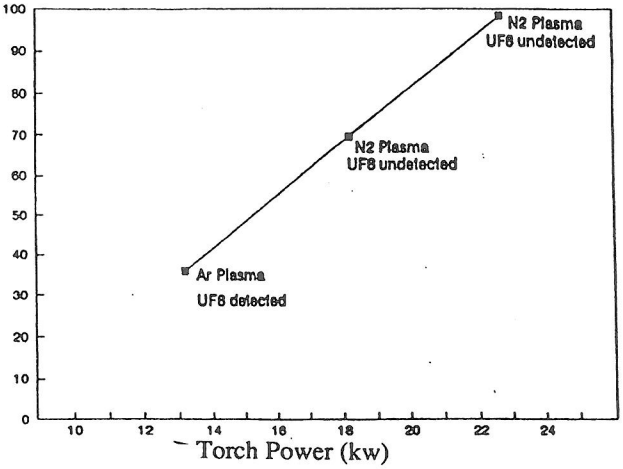

Figure 3. UF_6 conversion as function of the plasma power level (test set #I).

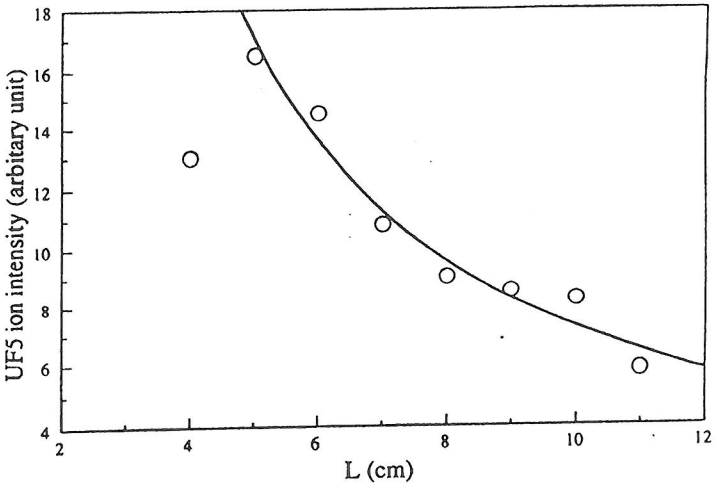

Figure 4. UF_5^+ intensity profile along the reactor axis.

In test set #2 the rotating graphite container was loaded with silicon. Thus, UF_6 fed into plasma zone could react with silicon vapors. Mass spectrometry analysis of gaseous reactants confirmed the total decomposition of UF_6 (no UF_6 peaks in gaseous products). Also, a distinct peak related to SiF_4 appeared. Solid reaction products contained mostly elemental silicon and uranium tetrafluoride. The main reaction route can be described by

$$2\ UF_6 + Si \rightarrow SiF_4 + 2\ UF_4 \qquad (2)$$

However, the uranium content in products (45 - 50 wt %) was higher compared to the stoichiometric content (42.4 wt %) which could be estimated from the fluorine concentration obtained (within 13.6 wt %). The "excess" uranium could result from the reaction

$$2\ UF_6 + 3\ Si \rightarrow 3\ SiF_4 + 2\ U \qquad (3)$$

which can also occur in the system. In a side reaction up to 2.5 wt % of silicon nitride was formed as well (Table 2).

Regarding UF_6 reduction with methane (test set #III) the total decomposition of reactants was confirmed by mass spectrometry analysis. A large excess of methane (CH_4 / UF_6 molar ratio above 20) is used in this case in the reaction mixture. Methane decomposition gave rise to the formation of acetylene and hydrogen which further reacted with fluorine. It is of interest to note that very low soot formation was noted in the process. This indicates that the temperature in a reaction zone was generaly below 3300-3500 K. Such a relatively low temperature (see torch power) could result from the highly endothermic nature of both CH_4 and UF_6 decomposition reactions, the main reaction route could be written as;

$$3\ UF_6 + 2\ CH_4 \rightarrow C_2H_2 + 3\ UF_4 + 6\ HF \qquad (4)$$

As before (test set #II) the U content in a resulting condensate (Table II) was higher compared to the value expected for the fluorine content which confirms again the

possibility of total decomposition of UF_6 into elemental uranium and the possible presence of elemental uranium in the solid products. No compounds of $C_2H_xF_y$ type (Freons) were delected in gaseous products despite the relatively high concentration of acetylene and fluorine presence in the reaction zone. Hydrogen fluoride formation is evidently more favorable under process conditions than partial fluorination of acetylene (formed from methane decomposition).

4. Conclusion

In conclusion, the results of experiments showed that under plasma conditions UF_6 undergoes a decomposition into UF_4 and possibly elemental uranium. However, the quenching rates available are not high enough to prevent reverse reactions which finally yield uranium tetrafluoride. The introduction of Si and CH_4 into the high temperature zone can effectively act as fluorine scavenger thus giving a way to the formation of elemental uranium in the system.

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