THERMAL PLASMA REDUCTION OF UF_6

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ABSTRACT

This paper describes the experimental demonstration of a process for the direct plasma reduction of depleted uranium hexafluoride to uranium metal. The process exploits the large departures from equilibrium that can be achieved in the rapid supersonic expansion of a totally dissociated and partially ionized mixture of UF_6, Ar, He, and H_2. The process is based on the rapid condensation of subcooled uranium vapor and the relatively slow rate of back reaction between metallic uranium and HF or F_2 to reform stable fluorides. The high translational velocities and rapid cooling result in an overpopulation of atomic hydrogen which persists throughout the expansion process. Atomic hydrogen shifts the equilibrium composition by inhibiting the reformation of uranium-fluorine compounds. This process has the potential to reduce the cost of reducing UF_6 to uranium metal with the added benefit of being a virtually waste free process. The dry HF produced is a commodity which has industrial value.

INTRODUCTION

In the centrifugal enrichment of natural uranium the mined material is converted to UF_6. After enrichment the U^{235}-enriched UF_6 is converted to uranium metal or oxide reactor fuel and the depleted UF_6 stored. Assuming 90% enrichment, for every 100 tons of UF_6 fed into the enrichment process, more than 90 tons of depleted UF_6 are generated. Historically, vast quantities of depleted UF_6 have been generated as a byproduct of the enrichment process and much of it has been held in storage since the 1950s. UF_6 has a vapor pressure of 14.93 kPa at 298 K and is perceived to be an environmental liability. One method of dealing with the large amounts of stored UF_6 is to convert it to metal which is a lower safety risk material and has value as a high density shield material for the storage and shipping of high level nuclear waste and may also have use a feed stock for advanced isotope separation processes.

The process commonly used for the production of uranium metal from UF_6 is the thermite-type reduction using magnesium and/or calcium metal. The process is carried out batch-wise in a bomb-reduction unit and produces a large volume of uranium contaminated waste. In the process the UF_6 is sequentially reduced by hydrogen to the tetrafluoride, then the tetrafluoride is reduced with an alkali metal to metallic uranium and a halide salt. The wastes generated in step two of the process contain 1 to 2 % dispersed uranium and represent approximately one pound of waste for every pound of metal produced. Because of the difference in densities between UF_6 and MgF_2 there is an approximate 6-fold increase in solid waste volume. The two step equilibrium process is shown in equations 1 and 2 below.

$$UF_6(g) + H_2(g) \rightarrow UF_4(s) + 2HF(g) \quad (1)$$

$$UF_4(s) + 2Mg(s) \rightarrow U(s) + MgF_2(s) \quad (2)$$

The hydrogen reduction of UF_6 to UF_4 (equation 1) in thermal plasmas has been previously studied [1,2,3]. The process is thought to be scalable to industrial throughputs and to represent a cost effective alternative to the conventional process [3]. A simplified equilibrium diagram for the U-F-H system is shown in Figure 1. For temperatures above 6000 K the U-F-H system is almost totally dissociated. From this diagram it is clear that an equilibrium process for the single step hydrogen reduction of UF_6 to uranium metal is not possible. For "slow" cooling rates which allow the system to approach equilibrium the thermodynamically favored product is UF_4. This result was obtained in [3] and in [4] where a very small amount of metallic uranium was also recovered from the cathode of the plasma torch used. It has been suggested that cooling rates in excess of 10^{10} K/s are required [4,5] to remove uranium as metal from a totally dissociated plasma stream. A different approach has been suggested at Los Alamos National Laboratory [6]. In this approach UF_6 is directly reduced to metal by the reaction of equation 3.

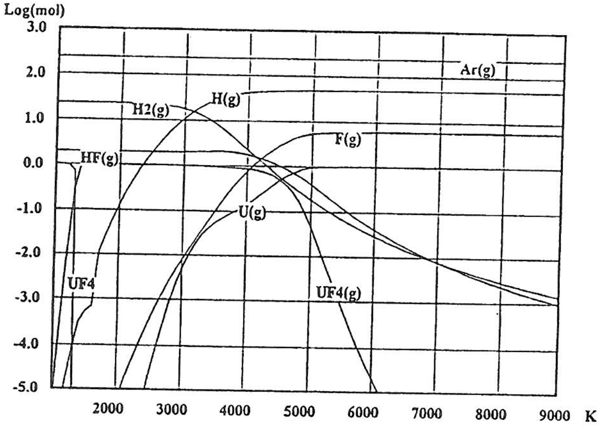

Figure 1: Simplified equilibrium diagram for $UF_6 + 24H_2 + 240Ar$.

$$UF_6(g) + 6H(g) \rightarrow U(s) + 6HF(g) \quad (3)$$

This reaction takes advantage of the increased reducing potential of atomic hydrogen relative to diatomic hydrogen and avoids the high temperatures required for thermal dissociation. A simplified equilibrium diagram for the U-F-H system, disallowing H_2 is shown in Figure 2. Clearly, the presence of atomic hydrogen alters the equilibrium state and, for temperatures less than about 2500 K, makes the formation of metallic uranium

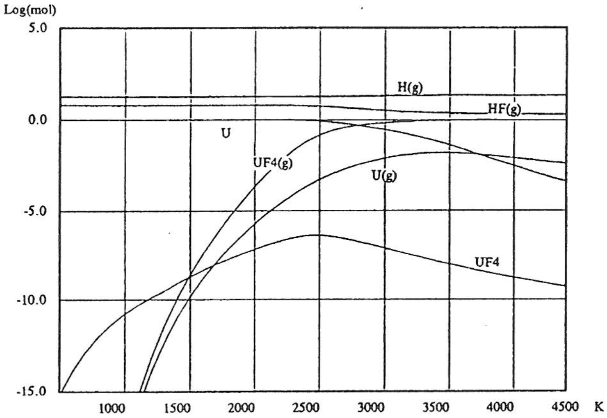

Figure 2: Simplified equilibrium diagram disallowing the existence of H_2.

thermodynamically favorable. A nonequilibrium population of atomic hydrogen may be generated and maintained at relatively low temperatures by an RF or microwave discharge.

This paper describes the extraction of uranium metal from UF_6 in a rapidly quenched thermal plasma process [7]. In this process rapid quenching is accomplished by the expansion of a partially ionized and totally dissociated mixture of $Ar/He/UF_6/H_2$ through a converging/diverging supersonic nozzle. The nozzle is essentially an adiabatic device and when the upstream to downstream pressure ratio is sufficiently high the velocity of the gas reaches sonic velocity at the throat, and becomes supersonic in the diverging section. The increase in velocity is accompanied by the conversion of internal energy to kinetic energy of the bulk flow, decreasing the temperature. The average cooling rate attainable is on the order of 10^7 K/s, and in the throat region can be two orders of magnitude higher [8,9]. Rapid expansion designs can yield even higher average cooling rates [10]. The rapid cooling results in large departures from equilibrium and the possibility of "freezing" out chemical species that would normally be consumed in chemical reactions if the temperature change were on a slower scale. In order to avoid reheating the products by standing shock waves generated as the flow adjusts to the receiver pressure some precautions must be taken in product recovery. The approach used here is to mix with a co-flowing stream of cold gas that lowers the enthalpy of the product stream. In order to inhibit back reactions, the solid products and reactive gases should be rapidly separated. Separation is achieved in dual cascaded cyclones, buffered with hydrogen to dilute the concentrations of HF and F_2.

The complete dissociation of UF_6 requires approximately 750 kcal/mole and occurs at approximately 6000 K. To avoid the problems associated with reactive gases in the discharge region the UF_6 is introduced at the torch exit. The enthalpy of an argon plasma (10,000 K) is on the order of 50 kcal/mole. This ratio of enthalpies limits the rate at which UF_6 can be introduced into the plasma and results in a relatively low concentration of reactants in the current reactor.

The vapor pressure of uranium at 1000 K is lower than the vapor pressure of UF_4 by more than 10 orders of magnitude, at 600 K the difference is > 100 orders of magnitude. This means that if the mixture is quenched at a rate faster than the UF_n molecules recombine, then uranium will be the first material to condense. If the cooling rate is too slow UF_4 will form, and unless the ultimate temperature is near room temperature, or hydrogen is present, the uranium metal will back react to UF_6. Estimates (and our experiments) suggest that for cooling rates on the order of 10^6 K/s UF_4 is the product formed. For cooling rates on the order of 10^8 - 10^9 K/s we have observed the extraction of metallic uranium from a U-F-H mixture carried in an Ar-He plasma.

EXPERIMENTAL

A schematic of the apparatus used appears in Figure 3. The plasma torch is of conventional design. Typical operating conditions were 600 A at 31 volts on a mixture of $Ar/He/H_2$ (54.8 : 43.8 : 1.4) for a total flow rate of 43 slm. The torch exit, and nozzle inlet pressure, was 3 atm. Operating at 3 atm the torch was only 20% thermally efficient.

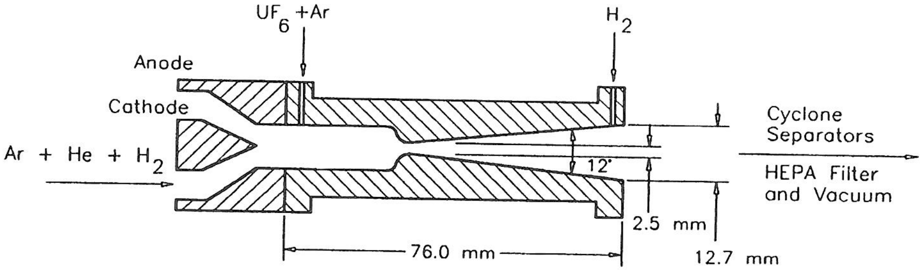

Figure 3: Schematic of experimental apparatus.

UF_6 was transversely injected in an argon carrier at a velocity of approximately 100 m/s through a 0.75 mm diameter nickel orifice. Prior experience [11] indicated that these conditions should yield reasonably good mixing. The UF_6 injection system was temperature controlled to maintain a constant UF_6 vapor pressure. The flow rate of UF_6 was 1 gm/min. These conditions resulted in a H:F ratio of 3:1 at the nozzle inlet. In a typical experiment 10 gm of UF_6 was processed. The receiver pressure was maintained at 85 torr by a vacuum pump. This pressure ratio yields an estimated maximum Mach number of 2.85 and a corresponding terminal temperature of 1880 K. The temperature at the nozzle throat is estimated to be 5000 K. The calculated average rate of cooling is 8.5×10^8 K/s. Room temperature H_2 was injected at the nozzle exit at a rate of 33 slm. The measured gas temperature in the receiver after hydrogen injection was approximately 600 K. The condensed material is collected in dual cascaded cyclones and handled in a low oxygen, but not oxygen free environment. The fine particulate material collected is transferred to a die and pressed into 1 cm diameter pellets for XRD analysis.

RESULTS AND DISCUSSION

A typical XRD analysis appears in Figure 4. The primary constituents are U and UO_x with some evidence of fluorides and oxy-fluorides. The level of oxygen contamination in the feed gases is not high enough to account for the oxides formed, hence it is thought that the oxides are the result of post processing exposure. The fine particulate material generated has a very high surface to volume ratio and spontaneously ignites on exposure to air. Even though the material is handled in an argon environment through the process of pressing the sample pellets, there is ample opportunity for exposure to 1-2 % oxygen. After pressing, the pellets are exposed to air which results in the formation of a surface oxide layer. The fluorides and oxy-fluorides are assumed to be the result of incomplete mixing/dissociation and the fact that some of the material becomes entrained in the cold wall boundary layer where back reactions may also take place. Because of the large surface-to-volume ratio of the small experimental reactor it is impossible to avoid the presence of some material in the cold boundary layer. This reactor concept benefits from scaling to larger sizes so long as the high cooling rates are retained. Many of the other peaks in the XRD data are consistent with nickel, stainless steel, and copper corrosion products, the materials from which the reactor is constructed.

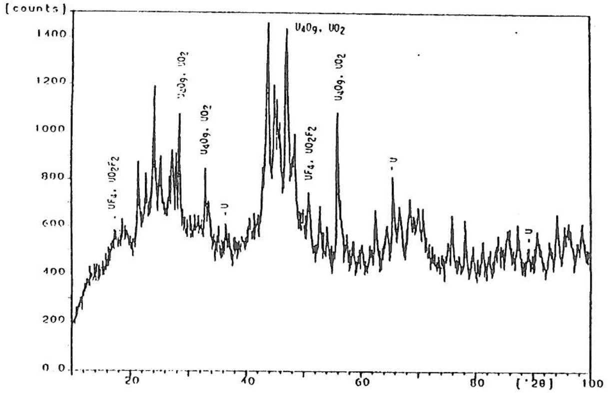

Figure 4: Typical XRD analysis.

The recombination of the hydrogen and fluorine and the formation of HF was numerically modeled. The reactions considered are shown below, where M is a collision partner which may include Ar or He. The first three equations are three-body reactions which proceed at a relatively slow rate as compared to the nozzle transit time. The relative slowness of these reactions results in elevated non-equilibrium populations of

$$H + H + M \rightarrow H_2(g) + M \quad (4)$$
$$H + F + M \rightarrow HF(g) + M \quad (5)$$
$$F + F + M \rightarrow F_2(g) + M \quad (6)$$
$$H_2 + F \rightarrow HF(g) + H \quad (7)$$
$$H + F_2 \rightarrow HF(g) + F \quad (8)$$

atomic hydrogen (and also atomic fluorine) in the expansion process. The presence of atomic hydrogen may play an important role in the process by limiting the back reaction to UF_n. Reactions 7 and 8 are two body reactions which proceed at a rate significantly greater than reactions 4-6. For a completely dissociated mixture the formation of HF is limited by the rate at which reactions 4-6 proceed. The reaction of room temperature uranium metal with F_2 and HF is known to be a relatively slow process [12,13]. The rate of reaction with atomic fluorine is not known but has the potential to be a significant mechanism for reformation of uranium fluorides because of its high reactivity. It is therefore probably advantageous to remove the atomic fluorine by the introduction of molecular hydrogen at the nozzle exit. When molecular hydrogen is introduced the two-body reactions 7 and 8 rapidly proceed to form HF. The addition of cold gas has the added benefit of further cooling the mixture.

The uranium metal extraction efficiency is estimated to be on the order of 30%. This number is derived from the total weight of the material recovered and the total amount processed and is thought to be conservative. An unknown amount of material escaped collection in the cyclones and was deposited in a downstream HEPA filter, the piping, and vacuum pump. No attempt has been made to optimize the process.

The scaling and economics of the process described have been examined in detail [14]. The results indicate that the process has potential to produce metallic uranium at approximately one-half the cost of the alkali metal reduction process. Since the products are uranium metal and dry HF, a product with commercial value (all other gases are recycled), the process has the added benefit of producing essentially no waste.

ACKNOWLEDGMENTS

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