WM'01 Conference, February 25-March 1, 2001, Tucson, AZ

PRODUCTION OF HIGH-VALUE FLUORIDE GAS FROM URANIUM TETRAFLUORIDE USING A ROTARY CALCINER

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ABSTRACT

Starmet Corporation has developed a process to extract the fluorine value from uranium tetrafluoride (DUF_4) produced from depleted uranium hexafluoride (DUF_6) reduction and produce a stable uranium oxide (1). The process involves mixing low cost silica (SiO_2) with near-stoichiometric amounts of UF_4 and roasting the mixture in a rotary calciner at temperatures above 500°C. The two react to form silicon tetrafluoride (SiF_4) and either uranium dioxide (UO_2) or triuranium octaoxide (U_3O_8), depending on atmosphere used. The SiF_4 product gas is filtered to remove uranium particulates. The product gas is substantially pure and free of uranium contamination as produced, without extensive purification. The gas may be then captured via compression and condensation prior to packaging. The gas so produced is significantly higher valued than the equivalent amount of HF, if produced from UF_4, while the production costs are roughly equal.

INTRODUCTION

Over the past 50 years the US Department of Energy (DOE) and its predecessors have stockpiled more than 560,000 metric tons of depleted uranium hexafluoride (DUF_6) at facilities in Oak Ridge, TN, Paducah, KY, and Portsmouth, OH. Depleted UF_6 is the residue from the enrichment process used to make nuclear grade enriched uranium for reactors and weapons. There is currently no use for this material, and DOE is now planning to convert the UF_6 into a more stable form such as UF_4 or an oxide of uranium. If this action occurs, DOE would be forced to pay for disposal of their entire DUF_6 inventory (2). Disposal costs have been estimated at $1.4 billion, however, more realistic cost projections based on current technology and capabilities are in the range of $3-4 billion. To reduce the cost of managing the DUF_6 inventory, Starmet Corporation has been working to develop alternative approaches for producing uranium and recovering fluorine from uranium hexafluoride.

Silicon tetrafluoride (SiF_4) is used by members of the microelectronics industry for several applications, including ion implantation, plasma etching, and deposition of fluorinated silica and silicon nitride films. New markets are also growing, using SiF_4 as a dopant gas for fiber-optic cables and as a feed for the enrichment of Silicon-28 (^{28}Si) for chip manufacture. The price of SiF_4 is very sensitive to the amounts of specific impurities such as arsenic, phosphorus, and sulfur, in addition to the overall level of purity.

Starmet Corporation has developed a process to extract the fluorine value from uranium tetrafluoride (UF_4) produced from depleted uranium hexafluoride (DUF_6) reduction and produce SiF_4 and a stable uranium oxide. The process involves mixing low cost silica (SiO_2) with near-stoichiometric amounts of UF_4 and roasting the mixture in a rotary calciner at temperatures above 500°C, according to the following chemical equations:

$UF_4 + SiO_2 + O_2(g) \rightarrow U_3O_8 + SiF_4(g)$ (Eq. 1)
$UF_4 + SiO_2 \rightarrow UO_2 + SiF_4\ (g)$ (Eq. 2)

As shown, the uranium oxide produced can be ether UO_2 or U_3O_8 depending on the atmosphere used. The SiF_4 product gas is filtered to remove uranium particulates. The product gas is substantially pure and free of uranium contamination as produced. In addition, since the starting materials are free of arsenic, phosphorus, and sulfur, these contaminants are not introduced into the product (3).

EXPERIMENTAL SETUP AND PROCEDURE

Equipment

The experimental setup consisted of a drum rotator, a flexible screw conveyor, a volumetric feeder, the calciner, the bottling station, a small 'product' scrubber, plus a ventilation system that included a large scrubber and HEPA filtration system. The system setup is illustrated in **Fig. 1**.

The primary piece of equipment is the Bartlett-Snow Laboratory Rotary Calciner (4). This calciner is an indirect-fired, electrically heated unit. The calciner is 6 ½" internal diameter, with an overall calciner tube length of 7'6 $^5/_8$". The heated zone is 28" long, with a water spray cooling section attached. The seals consist of graphite stationary seal rings installed onto the bellows, purged with air or nitrogen during operation. The calciner was also equipped with knocking hammers riding on cams on the outside of the tube, which were used to knock any material that accumulated on the interior of the tube walls during operation off the wall. Two hammers ride on cams on the outside of the calciner, striking the calciner every half rotation on each side. The hammers were opposed so that every quarter rotation a hammer would fall, either on the front or the rear consecutively.

The reactant mixture typically consisted of approximately 80 kg of UF_4 combined in a drum with a 2% stoichiometric excess of diatomaceous earth pool filter aid(5). The drum was then sealed and placed on a drum rotator to mix overnight. A Convert-a-Cone® (6) flange was attached to the drum and then entire drum tipped onto the conveyor hopper. The mixture was then allowed to flow into the conveyor hopper. From the hopper the feeder was filled with about 150 kg (relative, including some feeder weight) to about 200 kg relative, as needed. Feed rate was not varied during the course of the experiments.

The solid products were removed from the system via an airlock and collected in a drum. The drum lid and connection to the airlock was gas tight, to allow the solids to be safely collected during an experiment. The solid products were analyzed by x-ray diffraction (XRD) and scanning electron microscopy (SEM) for composition and microstructure.

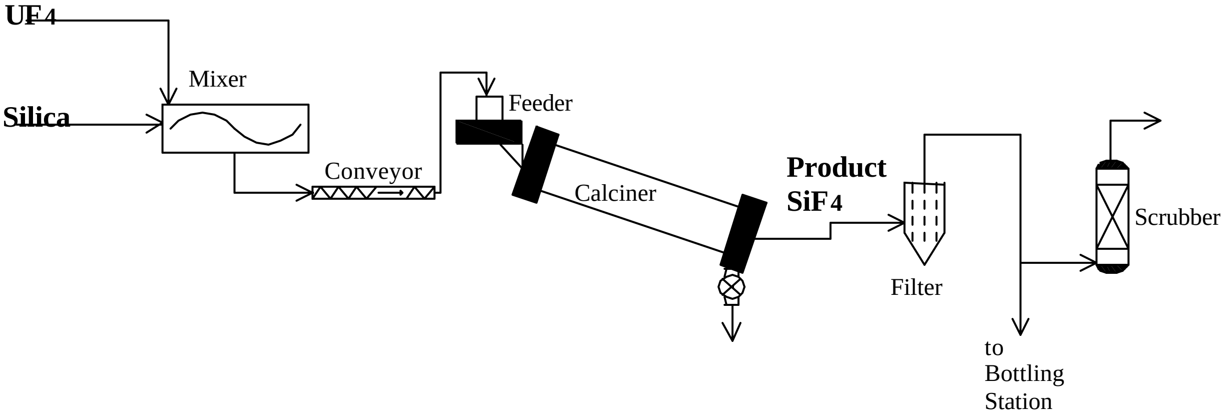

Fig. 1: Calciner system schematic

The product gas exited the calciner and was filtered using polypropylene spun-wound depth cartridges in a stainless steel housing. The gas was then passed directly to the product scrubber to make derivative silicon fluoride salts. A small slipstream of the gas was taken into a Fourier Transform-Infrared (FT-IR) spectrometer by vacuum eductor in order to monitor the quality and quantity of gas produced during the reaction. Samples of the gas could be taken by cryogenically cooling the incoming gas using liquid nitrogen, followed by allowing the product gas to flash into a second cylinder. This method was expedient, however, any standard bottling technique could be used.

Experiment matrix

Table below gives the experimental setup used for each experiment. The major variables examined were:

- Atmosphere (dry air vs. nitrogen)
- Temperature (550 °C, 600 °C, 700 °C, 800 °C)
- Rotational speed (0.96-2.3 rpm)
- Purge gas flow direction (Co-current vs. counter current)
- Use of hammers (with and without)
- Feed time (5 min – 4 hrs)

The gas used to provide the atmosphere was used both in the calciner tube and to purge the vented seals. Gas flow was at a minimum of 5 cfh/seal. Temperature refers to the setpoint on the calciner itself, which translates to the temperature of the calciner furnace. The interior of the calciner tube was at least 50 °C lower. Rotational speed values were chosen to be roughly 'slow', 'medium', and 'fast'. Gas flow direction refers to whether the purge gas and the product gas were exiting at the same end as the oxide (co-current) or at the opposite end of the calciner (counter-current). Counter current flow had the effect of passing the gas stream back over the heated oxide and unreacted UF_4/SiO_2 mixture. The length of time that the feeder was turned on and feeding material was also varied until the time to reach steady state was determined. Calciner pitch, stoichiometric mix, and feed rate were not varied. The configuration and chemistry of the product scrubber was adjusted in response to plugging and other difficulties, but were not systematically varied. The gas quality was monitored using in line FT-IR starting during the experiment on 1/26/00 and used in all subsequent experiments.

The matrix of experiments can be divided into experiments performed in air and experiments performed in nitrogen. The initial series of experiments at 600 °C were performed to determine the baseline operating conditions of the system. The goal of adjusting the feed time was to determine the minimum amount of time to achieve steady state at each temperature/rotational speed combination. The aim was to be able to sample gas quantity at steady state while reducing the source term. Once the minimum time for steady state was established at a rotational speed of 1.82 rpm in counter-current mode, the rotational speed was varied at the same temperature. The temperature was then changed and a series of experiments at different rotational speeds were performed at various temperatures. During the first experiment at 800 °C, it was observed that the material was sticking to the walls of the calciner tube. Consequently the hammers were inserted and were used for all subsequent experiments. Finally, 700 °C was chosen at a temperature that produced a reasonable yield in a reasonable time, and the flow direction was changed to co-current. Fewer experiments were required in a nitrogen atmosphere, as the need for hammers and the optimum feed time had been established. The first three experiments were performed in co-current mode with varying rotational speeds. The next three experiments were performed using similar rotational speeds in counter-current mode. The last three experiments were used for gas bottling.

The gas bottling experiments were performed using parameters determined during the previous series of experiments to provide a reasonably clean gas and a reliable steady state. When bottling was initiated after steady-state conditions through the calciner were achieved, the amount of input material was limited to ensure the sample bottle couldn't be over-filled with condensed gas. This led to shorter total feed times for these experiments.

Data from the experiments took several forms. The temperature, pressure, HF sensor readings, and pH data for the system were gathered using LabView^{TM} software and a Data Acquisition System. The oxide samples were examined using x-ray diffraction (XRD) and scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS). In addition, samples of the oxide were dissolved in 15% nitric acid solution, filtered, and analyzed using inductively coupled plasma spectroscopy (ICP). The filtrate was also dissolved in a nitric acid/boric acid solution and analyzed via ICP. The purpose of the ICP analysis was to determine quantitatively the amount of UF_4 remaining in the oxide as a measure of completeness of reaction. As mentioned, gas quality was monitored continuously during the experiments using a Midac M-series FT-IR with a zinc selenide (ZnSe) beam splitter and a 2-cm heated gas cell with zinc selenide (ZnSe) windows. The bottled gas was sampled and sent to Voltaix, Inc. for impurity analysis for H_2O, HF, O_2, N_2, and other gaseous impurities. The analysis at Voltaix was performed by gas chromatography (GC), gas chromatography coupled with mass spectrometry (GC-MS), and FT-IR. In addition, a sample of gas was hydrolyzed in a known scrubber solution and also analyzed for uranium via kinetic laser phosphorescence analysis (KPA).

Table I: Matrix of calciner experiments

Date	**Temp °C**	**Speed (rpm)**	**Gas Direction**	**Hammers**	**Atmosphere**	**Feed time hr:min:sec**
12/3/99	600	1.82	Counter current	No	Dry Air	0:05:00
12/8/99	600	1.82	Counter current	No	Dry Air	0:05:00
12/13/99	600	1.82	Counter current	No	Dry Air	0:30:00
12/14/99	600	1.82	Counter current	No	Dry Air	1:00:00
12/20/99	600	1.82	Counter current	No	Dry Air	0:36:00
12/22/99	600	1.82	Counter current	No	Dry Air	1:00:00
1/4/00	600	1.82	Counter current	No	Dry Air	0:31:00
1/5/00	600	1.82	Counter current	No	Dry Air	0:16:00
1/11/00	600	1.82	Counter current	No	Dry Air	1:00:00
1/14/00	600	1.82	Counter current	No	Dry Air	1:18:52
1/15/00	600	1.82	Counter current	No	Dry Air	0:45:00
1/18/00	600	1.82	Counter current	No	Dry Air	2:23:00
1/19/00	600	1.82	Counter current	No	Dry Air	4:46:00
1/20/00	600	2.63	Counter current	No	Dry Air	2:33:00
1/21/00	600	1.28	Counter current	No	Dry Air	4:11:00
1/26/00	700	1.78	Counter current	No	Dry Air	4:00:00
1/27/00	700	2.48	Counter current	No	Dry Air	2:20:00
1/31/00	700	1.31	Counter current	No	Dry Air	3:55:00
2/3/00	550	1.31	Counter current	No	Dry Air	4:00:00
2/4/00	550	0.96	Counter current	No	Dry Air	4:05:00
2/7/00	600	0.96	Counter current	No	Dry Air	4:00:00
2/8/00	700	0.96	Counter current	No	Dry Air	4:00:00
2/9/00	800	0.96	Counter current	Inserted during experiment	Dry Air	4:00:00
2/11/00	800	0.96	Counter current	yes	Dry Air	4:00:00
2/16/00	700	0.96	Co-current	yes	Dry Air	4:00:00
2/17/00	700	1.82	Co-current	yes	Dry Air	3:00:00
2/18/00	700	2.48	Co-current	yes	Dry Air	3:00:00
2/22/00	700	2.48	Co-current	yes	Nitrogen	2:10:00
2/23/00	700	1.77	Co-current	yes	Nitrogen	3:00:00
2/28/00	700	0.96	Co-current	yes	Nitrogen	3:01:00
3/9/00	700	0.98	Counter current	yes	Nitrogen	3:33:00
3/21/00	700	1.88	Counter current	yes	Nitrogen	3:00:00
3/22/00	700	2.38	Counter current	yes	Nitrogen	2:30:00

4/24/00	700	1.83	Counter current	yes	Nitrogen	0:50:00
4/27/00	700	1.83	Counter current	yes	Nitrogen	1:38:00
4/28/00	700	1.83	Counter current	yes	Nitrogen	1:42:00

RESULTS

The yields from several of the experiments are given in **Table 2**. It was found that temperature significantly affected yield of product and conversion of UF_4 to oxide. It was found that temperatures below 600°C caused the reaction to proceed very slowly, resulting in long residence times to achieve at least 50% conversion. At 700 and 800°C, residence times of less than 40 minutes were sufficient to produce yields of better than 97%. It was found that choice of atmosphere had little impact on the yield of gas, although it did affect the oxide form produced. Use of dry air as the ambient atmosphere produced U_3O_8 while an inert (nitrogen) atmosphere produced a mixture of UO_2 and U_3O_8. The direction of gas flow (counter-current or co-current) may make a slight difference in gas purity, but no conclusions can be drawn presently.

Table II: Yield from selected experiments

Temp (°C)	Rotation (rpm)	Gas Direction	Gas	Yield (%)
600	1.82	Counter-current	Dry air	92
600	2.63	Counter-current	Dry air	55
600	1.28	Counter-current	Dry air	73
700	1.78	Counter-current	Dry air	96
700	2.48	Counter-current	Dry air	88
700	1.31	Counter-current	Dry air	97
550	1.31	Counter-current	Dry air	45
550	0.96	Counter-current	Dry air	37
600	0.96	Counter-current	Dry air	57
700	0.96	Counter-current	Dry air	73
800	0.96	Counter-current	Dry air	96
800	0.96	Counter-current	Dry air	>99
700	0.96	Co-current	Dry air	98
700	1.82	Co-current	Dry air	97
700	2.48	Co-current	Dry air	94
700	2.48	Co-current	Nitrogen	95
700	1.77	Co-current	Nitrogen	97
700	0.96	Co-current	Nitrogen	98
700	0.98	Counter-current	Nitrogen	98
700	1.88	Counter-current	Nitrogen	98
700	2.38	Counter-current	Nitrogen	97

The experiments performed focused on residence time, atmosphere used, temperature, and direction of gas flow. It was found that temperature significantly affected yield of product and conversion of UF_4 to oxide. It was found that temperatures below 600°C caused the reaction to proceed very slowly, resulting in long residence times to achieve at least 50% conversion. At

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DISCUSSION

The overall reaction was extremely robust, as had been noted in the bench scale experiments. In some of the initial experiments, the air flow was lower than planned. Nevertheless, the gas flowed out of the calciner, the reaction was to a large extent complete, and the product gas was reasonably pure. Another interesting observation was that the UF_4 required no special treatment. The UF_4 was used as received from CMI, with no drying, sizing or screening. Although some slag was found in the product oxide, the reaction kinetics and completion did not seem to be affected. The reaction took about 30 minutes from the time the reactants entered the hot zone to the time the oxide entered the cooling zone. Residence time is given as

$$T_r = \frac{L}{2\Theta Dp} \qquad \text{(Eq. 3)}$$

where L is heated length, Θ is rotational speed, D is diameter and p is pitch. The pitch is 0.0212 in/inch, Θ varies from 0.96 to 2.36 rpm, D is 6.5" and the effective L is 23", based on Equation 3. The residence time then was varied from 35 to 87 minutes. Generally, the yield data shows that at 700° and 800°C, the reaction goes to completion as expected. The graph shown in **Fig. 2** as that the average amount of UF_4 unreacted at 700°C decays exponentially with rotational speed (or the inverse of the residence time). The faster the rotational speed, the lower the yield, as expected. The averages follow a reasonable peusdo-first order kinetics model: an expected result.

This is in very good agreement with the bench scale results, despite the larger volume of the material and the moving vs. static sample conditions (7). No substantial difference in reaction was noted between experiments in air and in nitrogen. Decreasing the temperature decreased the amount of gas produced, below 700°C furnace temperature. In general, the amount of time spent in the hot zone, once above 600 °C, had the most effect on the outcome, but otherwise the reaction was largely unaffected by changes in variables. It should be noted that the difference between 700 and 800°C was small, but the intermediate temperatures should be investigated further.

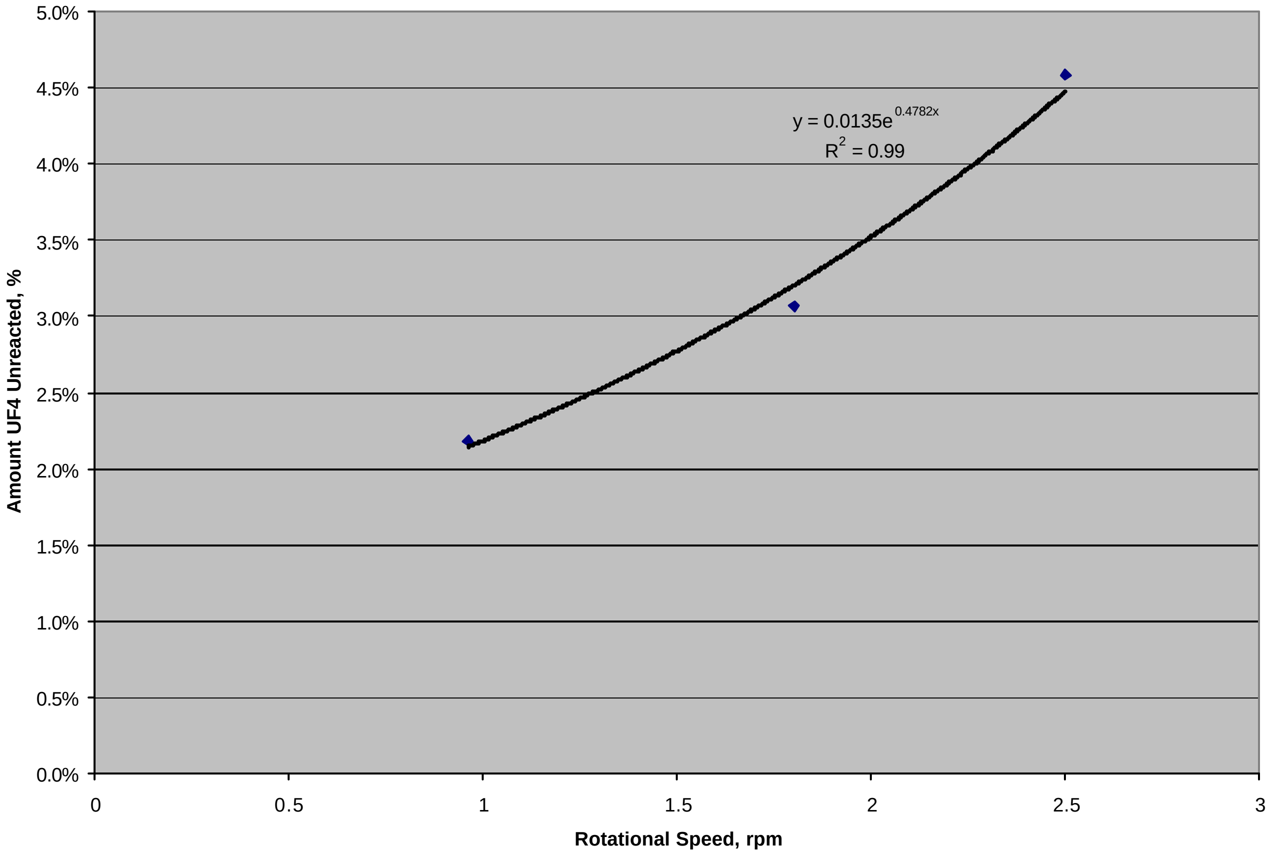

Fig. 2. Yield of Reaction with Rotational Speed

Gas produced is of good quality. A typical FT-IR result is shown in **Fig. 3**. This spectra is an expanded spectra that shows area of interest for gas analysis. The spectra shown are as-produced from the calciner at 700°C using inert gas (nitrogen), a representative HF spectra (a typical impurity), a spectrum taken from a batch experiment from the bench, and finally the bottom spectrum is that of 10% of 99.99% SiF_4 mixed in high purity nitrogen purchased from Matheson Gas. The major peaks of SiF_4 all compare well while little or no HF is seen in the gas produced by calciner. Carbon dioxide (at approximately 2300 cm^{-1} is absent (as seen by the negative peak), an artifact of the atmosphere used to purge the instrument.

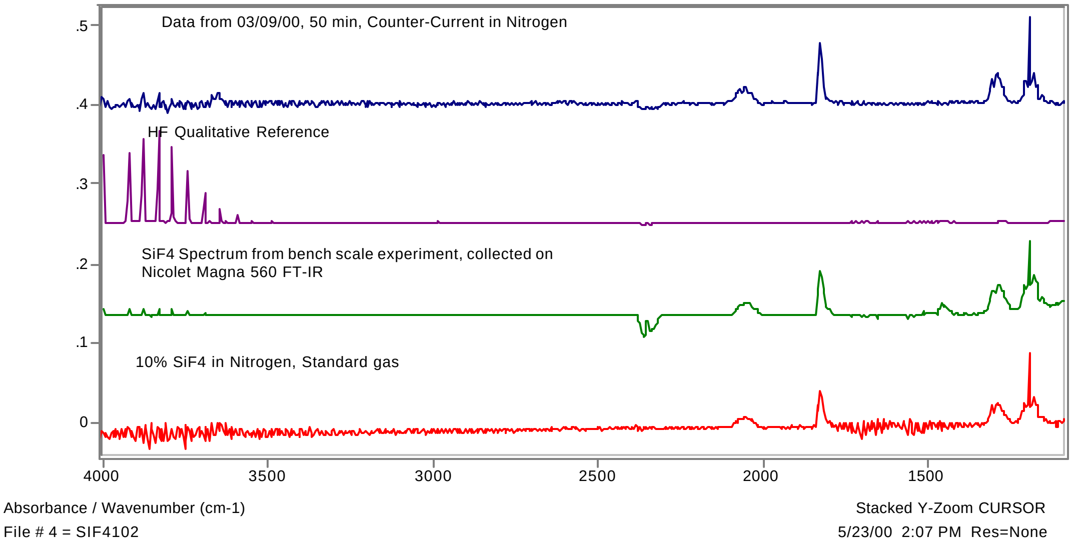

Fig. 3. Expanded Spectra of Gas produced Compared to Other Spectra

Analysis of the gas for the hexafluorodisiloxane ($(SiF_3)_2O$), by comparing the major $(SiF_3)_2O$ peak height to SiF_4 peak height was performed. The results are in arbitrary units, as there is no standard for the impurity. However, based on the work of Reents, et al (8), the total $(SiF_3)_2O$ content of the worst material is less than 2%. The best material is well below 1000 ppm (0.1%). Typical $(SiF_3)_2O$ contents are between 0.1 and 1%. Interestingly, it was found that the atmosphere makes a large difference. **Fig. 4** shows that inert gas produces little or no $(SiF_3)_2O$ while dry air produces a significant amount at high concentrations of SiF_4. This phenomenon is interesting because production of the disiloxane is thought to be a hydrolysis reaction; reaction of water with SiF_4 to make HF and $(SiF_3)_2O$. The figure shows at least a tendency to curve upwards with increased concentration of SiF_4, which may indicate an equilibrium with something in the dry air (either water or the oxygen in the air) or simply that the dry air has some amount of water present that the nitrogen doesn't have. This phenomenon does show that gas substantially free of the oxide impurity can be made easily by eliminating the source of oxygen.

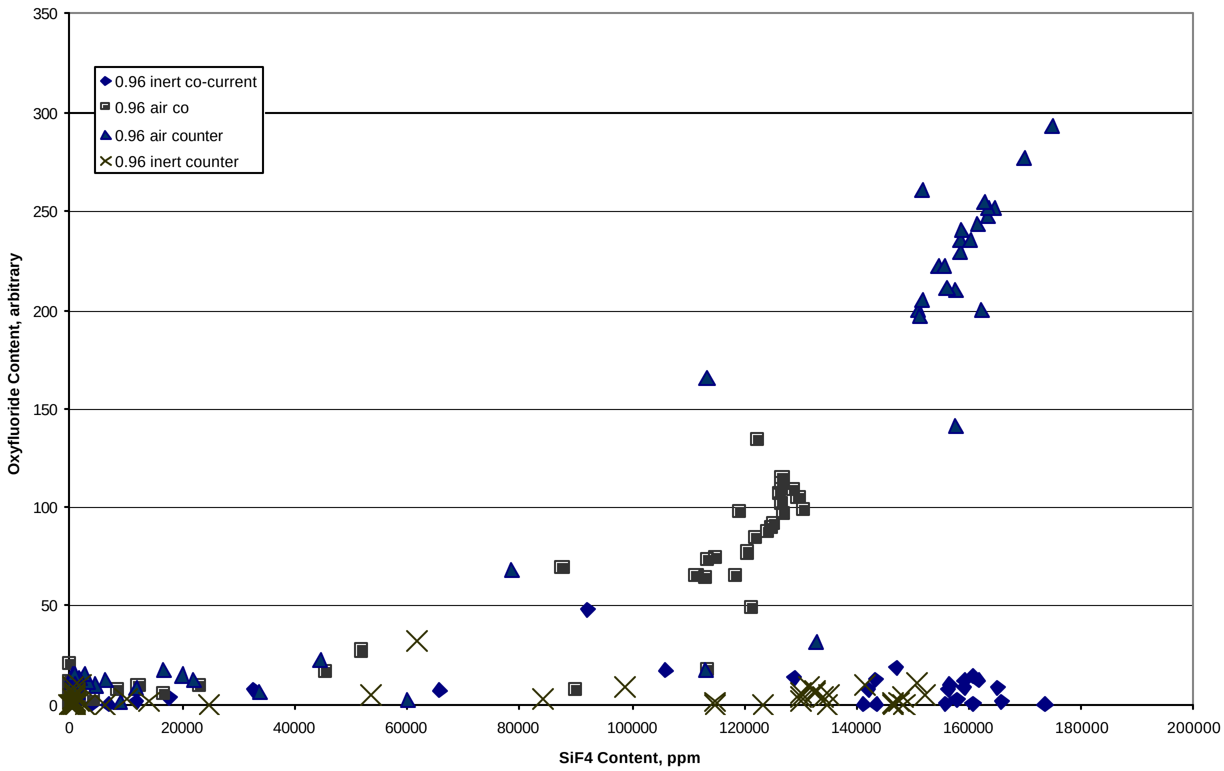

Fig. 4. Hexafluorodisiloxane Content versus Atmosphere

CONCLUSIONS

The process successfully produced SiF_4 gas of good purity, and uranium oxide. The process was robust, and was not affected greatly by changing variables such as temperature (over some threshold above 600 °C outside temperature), rotational speed, gas flow direction, and atmosphere. The reaction is not limited by heat transfer in this type of equipment, and no preparation of the reagents is needed to achieve a good reaction. It was additionally demonstrated that increased yields are a function of residence time at temperatures so that more complete conversion to oxide requires longer time at temperature.

Analysis of the oxide residue showed few impurities, other than unreacted diatomaceous earth. The solid products did contain slag, due to the fact that the UF_4 raw material was not screened or sized. This issue will have to be addressed in future scale-up. In addition, analysis of the solids produced in the scrubber showed pure K_2SiF_6 or Na_2SiF_6. This shows that contamination from upstream processes are not an issue. In addition, this shows that one could easily make these solid fluoride products for sale if desired.

The gas produced was very pure. The impurities detected by FT-IR were small amounts of HF and water. One of the difficulties with the FT-IR data was the fact that it is impossible to tell the difference between water in the gas stream and water present in the atmosphere that was drawn into the chamber. Because of this, supplemental analysis of the gas was performed at Voltaix, Inc using gas chromatography coupled with a quadruple mass spectrometer. Results showed small amounts of impurities, including CO_2, most likely a result of C contamination in the diatomaceous earth and $(SiF_3)_2O$, which is a common impurity in SiF_4. Investigation of $(SiF_3)_2O$ production showed that use of inert gas decreases final concentration of that impurity to insignificant levels. Further analysis of the gas product was accomplished by analyzing the Product Scrubber solution via KPA to determine uranium uptake. The results show that very little, if any, uranium is present in the gas stream and the uranium concentration in the gas is probably well below one part per billion.

The process to produce SiF_4 from UF_4 is robust. It was found that the small calciner system was very easy to operate and automate. It is expected that scale up will be straightforward. Economic analysis shows the process is viable. Outstanding issues that require further investigation are scale-up of gas collection equipment, investigation of intermediate temperatures between 700 and 800 °C and feed rate optimization.

REFERENCES

1. Bulko, John B., William T. Nachtrab and David S. Schlier, "Recovery of High Value Fluorine Products from Uranium Hexafluoride Conversion", Spectrum '98, September 13-18, 1998, Denver, Co, In press.
2. US DOE Office of Nuclear Energy, Science, and Technology, Draft Programmatic Environmental Impact Statement for Alternative Strategies for the Long-Term Management and Use of Depleted Uranium Hexafluoride: Summary, DOE/EIS-0269 (December, 1997).
3. W. Nachtrab and J. Bulko, "Method for producing uranium oxide and silicon tetrafluoride from uranium tetrafluoride, silicon, and a gaseous oxide," US 5,901,338 (1999).
   W. Nachtrab and J. Bulko, "Method for producing silicon tetrafluoride from uranium tetrafluoride," US 5,888,468 (1999).
   W. Nachtrab and J. Bulko, "Method for producing uranium oxide from uranium tetrafluoride and a solid oxide compound," US patent allowed, issuance in process (1999).
4. The Air Preheater Company, Raymond® and Barlett-Snow™ Products, A Division of Combustion Engineering Inc., 650 Warrenville Road, Lisle, IL, 60532: personal communications with David Dahlstrom and Al Sindt, documentation and start-up assistance
5. Dacalite® Pool Filter Aid, Great Lakes Carbon Corporation
6. Sterling/Fleishman, Inc., Malvern Industrial Park, Malvern, PA 19355
7. Starmet Corporation, UF_6 Deconversion Technology Development Program, May, 1999, presented to USEC

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8. Reents, Wood, Mujsce, "Impurities in Silicon Tetrafluoride Determined by Infrared Spectrometry and Fourier Transform Mass Spectrometry", Anal. Chem, Vol 57, pg 104-109, 1985.