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PRODUCTION OF HIGH VALUE FLUORINE GASES FOR THE SEMICONDUCTOR INDUSTRY

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5 INTRODUCTION

The US DOE is responsible for managing over 700,000 metric tons of depleted uranium hexafluoride (DUF₆). This material represents the so-called "tails" from the several gaseous diffusion enrichment plants located in Paducah, KY, Portsmouth, OH and Oak Ridge, TN. This material, stored as a solid in carbon steel cylinders, has accumulated over a period of 50 years. Originally, it was thought that the tails would be used as a feed material for the fast breeder reactor fuel cycle. However, with the national policy abandoning that use, this material has grown to be the largest amount of nuclear material in DOE inventory without significant application. Legislation enacted by Congress has led to the development of a *Depleted Uranium Hexafluoride Materials Use Roadmap*¹ which details potential pathways in which the DUF₆ resource may be converted to useful products in the future.

DOE has evaluated numerous management options for the DUF₆ inventory in their Programmatic Environmental Impact Statement (PEIS)². The strategy, based on the published *Record of Decision for Long-Term Management and Use of Depleted Uranium Hexafluoride*³, is to extract as much value as possible through beneficial re-use in order to reduce the costs of managing the DUF₆ surplus and ultimately convert the uranium into uranium oxide, uranium metal or a combination of both. This strategy also includes converting the 225,000 metric tons of fluorine contained in the DUF₆ stockpile into valuable fluorine products and using the uranium oxide by-product in applications such as radiation shielding⁴.

Several companies⁵ have demonstrated various hydrolysis methods for converting DUF₆ into uranium oxide (U₃O₈) and recovery of hydrogen fluoride (HF) as an anhydrous gas or aqueous mixture. This technology, while well known, produces a commodity chemical which has a market value of \$0.40-\$0.50/lb² for 70% aqueous HF and \$0.70-\$0.90/lb² for anhydrous hydrogen fluoride. Consequently, while such "salvage value" will reduce the cost of conversion to the DOE, it has a minor impact.

This body of work presented here describes a new technology that can convert the fluorine in DUF₆ into high-value, semiconductor specialty gases such as SiF₄, BF₃, GeF₄, SF₆ and WF₆. These specialty gases are used extensively in the electronics industry. Detailed sales volumes of such gases are held proprietary by existing vendors. However, some indication of the market potential for these gases can be deduced from the data in **Figure 1**.

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Phase II Final Report

PRODUCTION OF HIGH VALUE FLUORINE GASES FOR THE SEMICONDUCTOR INDUSTRY

1 EXECUTIVE SUMMARY

The chemistry to manufacture high purity GeF_4 and WF_6 for use in the semiconductor industry using *Starmet's* new fluorine extraction technology has been developed. Production of GeF_4 was established using a tube-style reactor system constructed of nickel 200 alloy in which conversion yields as high as 98.1% were attained. Collection of the fluoride gas improved to 97.7% when the reactor sweep gas contained a small fraction of dry air (10-12 vol%) along with helium. The quality of fluoride gas produced throughout the program was analyzed by FT-IR spectroscopy. The $(\text{UF}_4 + \text{GeO}_2)$ reaction was shown to begin above 400°C . The lab-synthesized product was shown to contain the least amount of infrared-active and elemental impurities when analyzed at contracted and independent analytical laboratories and compared with a reference material certified at 99.99% purity. Analysis of the "as-produced" gas using ICP-MS showed that uranium could not be detected at a detection limit of 0.019ppm-wt. *Argonne National Laboratory* was subcontracted to develop two new methods to detect trace uranium in GeF_4 . Samples of lab-synthesized gas were analyzed by ultraviolet optical absorption spectroscopy for determining the level of U as UF_6 in GeF_4 . In two separate trials, no absorbance due to UF_6 could be detected in either the unfiltered or the filtered batch of fluoride at their respective detection limits of 0.75 and 0.64ppm-vol. The second analytical technique for trace uranium determination involved laser-induced photoluminescence spectroscopy. Trials to detect luminescence of uranyl species in glassy GeO_2 were unsuccessful due to the formation of impurity species whose luminescence decay overlapped that of the uranyl ions in the glassy matrix. Alternative techniques involving the conversion of hydrolyzed GeO_2 to GeCl_4 were unsuccessful in producing a residue containing UO_2Cl_2 species for quantitative analysis by laser induced phosphorescence. Finally, conceptual drawings of a production-scale reaction system were made for generating up to 2kg of GeF_4 per day using six tube-style reaction stations. Construction of the production apparatus was postponed to a later date as a result of a global slump in the electronics and semiconductor sectors over the previous 18 months.

Development of a process to make WF_6 from WOF_4 was also pursued during the later half of the SBIR program. Results from milligram-scale reactions showed that the oxyfluoride compound could be made using either WO_2 or WO_3 in reaction with UF_4 in the 700°C - 800°C temperature range. When conducted in a bench-sized nickel tube reaction system, capture efficiency for the white crystalline residue ranged from 48.5% to 67.1% of the theoretical yield. After determining suitable reactants and conditions, focus shifted to probing the reactivity of WOF_4 . The oxyfluoride intermediate did not appear to react with either UF_4 or SiO_2 up to a temperature of 196°C , contrary to prediction by thermodynamic calculations of the spontaneous *Gibbs* free energy change. When WOF_4 was reacted with TiF_4 , there were some indications of a gaseous product being released. Investigation was broadened to study the reaction between WO_2 and TiF_4 . When staged in a bench-top apparatus, gaseous reaction products released around 185°C showed a component whose infrared absorbance bands emerging at frequencies consistent with those for WF_6 . Further experimentation is required to determine if the $(\text{WO}_2 + \text{TiF}_4)$ pathway is feasible for producing WF_6 of high purity.

Semiconductor Specialty Gas Market (1997)

Figure 1. Market Data on Semiconductor Specialty Gases (EMCON 98).

These gases are used for ion-implantation, chemical vapor deposition (CVD), cleaning, and as starting materials for some other processes including the production of high purity silicon. Retail prices for some of the gases from *BOC Edwards* are shown in Table 1. Purchase price for such gases from producers was stated to be about 25% to 30% of retail values.

Table 1.
Retail Pricing of Specialty Gases from *BOC Edwards* (2003).

Gas	Grade	Purity %	Container Size (lbs.)	Cost \$	Price (\$/lb.)
BF ₃	Electronic	99.5	1.6	186	116.25
	VLSI	99.99	1	518	518.00
WF ₆	Electronic	99.9	204	29,328	143.76
	ULSI	99.999	90	18,078	200.87
SiF ₄	Electronic	99.99	50	7,293	145.86
	VLSI	99.999	40	8,946	223.65
SF ₆	Electronic	99.8	95	1,611	16.96
	VLSI	99.996	100	2,030	20.30

In addition to considering higher value products than HF, it is also important to develop technology that can produce a number of different high value fluorine gases. For example, if all of the DUF₆ were converted to SiF₄, this would produce about 32 million pounds per year based on a 20-year conversion campaign. This quantity far exceeds known demand. Consequently, any successful conversion effort for fluorine products other than HF, must use the DUF₆ to produce a variety of end products in quantities consistent with market demands.

Traditionally, the problem with extracting fluorine using hydrolysis reactions from DUF_6 (a gas at temperatures above about 56°C) is that uranium will readily carry over to the product, lowering value and limiting commercial usage. Consequently, to minimize the uranium carryover, an alternate approach using DUF_4 – a nonvolatile solid – has been developed and higher valued fluorine products have been identified. Depleted uranium hexafluoride is readily converted to DUF_4 in a hydrogen reduction process operated by *Starmet Corporation* at its South Carolina site. The advanced technology presented in this report reacts crystalline DUF_4 ($T_m = 960^\circ\text{C}$) with a solid metal oxide (such as GeO_2 or WO_2) in a high temperature fusion process above 700°C to form a gaseous product (such as GeF_4 or WF_6) that readily separates as a high purity gas and leaves a uranium oxide residue. *Starmet* has used this same technology to produce SiF_4 from SiO_2 ⁶ in a pilot-scale demonstration plant as well as high-purity BF_3 from B_2O_3 in laboratory production trials.

Current cost estimates from the DOE UF_6 PEIS² project the cost of conversion of UF_6 using hydrolysis technology at \$3.00 per kg- UF_6 . The total cost to the DOE for the inventory conversion is near \$2 billion with credits for aqueous or anhydrous HF sale. *Starmet* has estimated that by converting the UF_6 to higher value fluorine products, a reduction in conversion cost to DOE of \$1.5 to \$2.00 per kg- UF_6 is possible. Thus, a cost savings for DOE of over \$1 billion for conversion of the UF_6 inventory is possible⁷.

A traditional process for manufacturing either GeF_4 or WF_6 involves the direct fluorination of the respective base metal with fluorine gas. This method is expensive due to the cost of fluorine gas and requires special safety and handling considerations due to the extreme reactivity of this reagent. In the case of GeF_4 , it has also been manufactured by several alternative processes^{8,9,10,11} including the reaction of a finely powdered suspension of GeO_2 in sulfuric acid with UF_6 ¹².

As mentioned above, the traditional process for producing WF_6 reacts the metal with fluorine. Here the metal is first obtained by reduction of WO_2 , which also adds to the downstream production costs of the fluoride. Typical impurities in the tungsten oxide can include uranium and thorium oxides that are easily fluorinated and carry over as gaseous contaminants requiring additional purification steps to insure their concentrations remain below the 50ppb and 10ppb limits (respectively) often specified by the semiconductor industry. In comparison, the new *Starmet* process has the advantage that WF_6 is formed by a fusion reaction where all uranium and thorium (if present) remain as stable oxides. If needed, the WF_6 gas may be subjected to another purifying step that involves another phase change, further ensuring excellent gas purity. For the electronics industry, process gas purity of 99.9% to 99.995% is generally required.

The new technology being developed by *Starmet* will

- demonstrate a relatively simple and robust process for producing high purity fluoride gases,
- utilize a highly refined source of fluorine, UF_4 , which can be recovered from the immense inventory of UF_6 surplus
- virtually eliminate the potential for uranium carryover into the gas phase by reacting two solids to produce the desired high-value gaseous fluoride products and

- provide more downstream economic value and beneficial reuse of the fluorine bound to uranium compared to commodity grade HF and uranium oxide.

6 OBJECTIVES OF THE PHASE II PROGRAM

The primary objectives of the Phase II SBIR program for producing high purity fluorine gases for use by the semiconductor industry are shown below.

The objectives for GeF_4 are:

- to develop a production process including reactor design and processes for generation, capture and purification to the point that the end product is market-ready for existing semiconductor applications at the completion of Phase II;
- to develop higher purity GeF_4 than is currently available on the market, tailored for photovoltaic applications.

The objectives for WF_6 are:

- to develop and scale-up the process for manufacturing WF_6 from the reaction between DUF_4 and WO_2 ;
- to design and develop a reactor system for producing WF_6 via a two-stage reaction wherein the suitable mixing, contact and control of the second stage reaction between the tungsten oxyfluoride intermediate (WOF_4) and DUF_4 can be achieved.

7 PHASE II WORK PLAN

The work plan to accomplish the Phase II objectives was structured in two subdivisions consisting of separate plans for GeF_4 and WF_6 due to the inherent differences in the chemistry and process requirements for making each gas. The scope of work associated with GeF_4 was divided into nine tasks whereas the effort on WF_6 was parceled among four tasks. The list of tasks for each product is shown in Table 2. The plan was carried out by focusing first on the development of a marketable GeF_4 product during the first year of the program followed by the pursuit of a pathway to WF_6 during the second year.

Table 2.

Task structure for the Phase II Program.

Task structure for producing GeF_4 .

- Task 1: Reactor design for producing GeF_4
- Task 2: Materials of construction for production of GeF_4
- Task 3: Optimization of product yield
- Task 4: Development of analytical technology for identifying trace U in GeF_4
- Task 5: Particulate filtration
- Task 6: Process scale-up
- Task 7: Gas ultrapurification
- Task 8: Product qualification
- Task 9: Design and construction of low production rate equipment

Task structure for producing WF_6 .

- Task 1: Bench-scale process development for WF_6 from WOF_4
- Task 2: Selection of suitable materials of construction for producing WF_6
- Task 3: Reactor design
- Task 4: WF_6 product characterization

A summary of each task as it was performed for each of the fluoride gases is presented below.

7.1 Tasks for Producing GeF_4 .

Task 1: Reactor design for producing GeF_4 .

Production of GeF_4 was studied using two different reactor designs in a batch operation. Experiments conducted in the crucible reactor showed high reaction conversions (~95%) between DUF_4 and GeO_2 but raised issues concerning product purity. Trials conducted using a tube reactor yielded even better performance (>98% conversion) especially when suitable materials were found from which to fabricate the reaction hardware and favorable reactions conditions established.

Task 2: Materials of construction for production of GeF_4 .

A search for suitable materials from which to fabricate a production scale reactor was undertaken. A range of materials including a *Haynes* HR160[®] alloy and nickel were subjected to gaseous reaction products and reaction mixtures under simulated and actual reaction conditions and examined in detail using scanning electron microscopy (SEM) and x-ray diffraction (XRD) to follow the formation of corrosion products. Several materials were found that offer greater resistance to attack by GeF_4 when pretreated first and could be used to build a reaction system to manufacture the gas.

Task 3: Optimization of product yield.

Experimentation focused on producing larger quantities of fluoride gas in each batch reaction. Reaction hardware was fabricated to hold larger amounts of $\text{DUF}_4/\text{GeO}_2$ mixtures and gas collection hardware was modified to achieve greater capture efficiency. Issues concerning liberation of moisture in the product stream led to exploration of an alternative pathway for producing GeF_4 using powdered germanium metal. Further testing at the milligram scale using the thermogravimetric analyzer was performed to better define the onset of reaction in order that moisture adsorbed on the reagents not compromise the purity of the final GeF_4 product.

Task 4: Development of analytical technology for identifying trace U in GeF_4 .

Routine analysis of GeF_4 produced by the reaction between DUF_4 and GeO_2 using standard indirect analytical techniques such as inductively coupled plasma (ICP) and kinetic phosphorescence analysis (KPA) has shown no evidence of uranium carryover into the final

product beyond background levels. However, direct analysis for U in the fluoride gas is necessary in order to demonstrate what can be achieved using the new process technology and to qualify the material for use in semiconductor applications. A program to explore the applicability of two analytical methods involving laser-induced photoluminescence and optical absorption spectroscopy was established in collaboration with Dr. James V. Beitz at *Argonne National Laboratory* (Argonne, IL). Samples of GeF_4 produced in lab-scale trials were analyzed using these techniques. Quantitative determination of uranyl species in glassy GeO_2 using photoluminescence was found to be unsuitable for ultratrace analysis due to interferences introduced during the formation of the glassy GeO_2 matrix. An alternative technique to convert hydrolyzed GeF_4 to volatile GeCl_4 that is removed before measuring the luminescence of uranyl species was also found to be ineffective due to the formation of unreactive hexagonal GeO_2 during the hydrolysis step that was resistant to chlorination. Luminescence measurements performed on hydrolyzed GeO_2 particulate dissolved in HF solution were also compromised due to the presence of impurities leached from the walls of the fluoropolymer container used to contain the dissolved material. Analysis of lab synthesized GeF_4 by ultraviolet absorption spectroscopy for the presence of DUF_6 was also performed at *ANL*. No absorbance attributable to DUF_6 gas was detected.

Task 5: Particulate filtration.

Although no evidence of uranium carryover in the gas phase was observed, contamination by solid phase uranium particulate created during formation and release of GeF_4 from the reaction zone, was of potential concern. For laboratory trials, a 0.45μ stacked PTFE[®] membrane filter enclosed in a polypropylene shell (*Osmonics*, Westborough, MA) was incorporated into the line at the entrance to each gas cylinder to remove any entrained particulate. Information about gas filtration technology was also supplied by *Starmet's* development partner, *Voltaix, Inc.*, regarding the filtering devices they use for removing particulate from other semiconductor grade materials they sell.

Task 6: Process scale-up.

Based on what was learned during the bench-scale trials to produce GeF_4 , a multi-station reaction manifold and gas collection station were designed with capacity to process multi-kilogram quantities of reagents per batch. A prototype of the closed-end, vertical tube reactor was fabricated and tested. The gas collection station consisted of a pass-through condensation cylinder for cryogenically trapping GeF_4 prior to final packaging. Both the reactor and gas collection segments of the production apparatus were redesigned using results gathered from the prototype reactor trial and technical recommendations made by *Voltaix* for improving gas production and handling.

Task 7: Gas ultrapurification.

As part of the collaborative effort to develop and market germanium tetrafluoride, *Voltaix* was subcontracted to characterize the purity of the 'as-produced' gas. Material produced in laboratory trials was subjected to analyses by Fourier transform infrared spectroscopy (FT-IR) to determine IR-active impurities such as HF, CO_2 , H_2O , SiF_4 and gaseous organic species and by

ICP-MS to measure the concentration of 37 elemental impurities including uranium. Similar tests were performed on a purchased material with certified purity of 99.99%, providing a standard to which the *Starmet* product could be compared. The gas produced by the new fusion chemistry was found to contain less elemental impurities than the reference and no uranium could be detected at the detection limit of 19ppb-wt. From all the analytical testing performed on laboratory synthesized GeF_4 , the quality of the 'as-produced' gas was of sufficient purity to qualify for use in the semiconductor industry.

Task 8: Product qualification.

Laboratory trials have shown that GeF_4 can be produced at a purity sufficient to meet current market specifications. As development moves forward to production, the quality of gas produced in the production-scale equipment must also be verified that it also meets or exceeds current specifications for entry into the marketplace.

Task 9: Design and construction of low production rate equipment.

A process flow diagram for the GeF_4 production process was drawn and costs based on making 100kg/yr were calculated. Designs of a multi-station gas manifold and gas collection station were completed as part of **Task 6** above. However, due to the weak economic performance and stalled growth seen in both the electronic and semiconductor markets over the last 18 months, the demand for fabrication materials has fallen off, forcing a delay in construction of the production-scale reaction system.

7.2 Tasks for Producing WF_6 .

Task 1: Bench-scale process development for WF_6 from WOF_4 .

Investigation into the chemistry to produce WF_6 from WOF_4 started with milligram-scale experiments to determine effective reaction parameters such as temperature, reagent stoichiometry and form of tungsten oxide reactant. The same solid by-product, UO_2F_2 , was produced using either WO_2 or WO_3 in the fusion reactions at temperatures in the range between 700°C - 800°C . Bench trials were conducted using a nickel tube reactor where larger samples of WOF_4 were collected. Several two-stage reactions were performed to explore the reactivity of WOF_4 with probe molecules such as UF_4 , SiO_2 and TiF_4 . A new pathway to WF_6 was explored encompassing the reaction of TiF_4 with WO_2 , first using milligram quantities followed by reactions involving gram quantities in a 100ml-benchtop reaction vessel. Analysis of the product from this reaction by FT-IR spectroscopy showed the first indication of WF_6 formation.

Task 2: Selection of suitable materials of construction for producing WF_6 .

Much of the bench-scale experimentation performed to develop a pathway to WF_6 was accomplished using a 1" diameter tube made of nickel as well as a nickel boat to hold the reactants. After observing large pieces of debris on the surfaces of reaction by-products and the progressive deterioration of the boat itself after many trials, an investigation into the corrosion

occurring with nickel was conducted. It was determined that the surface of nickel was first oxidized to nickel oxide in the high temperature fusion environment followed by reaction of the fluoride intermediate, WOF_4 , and NiO to produce NiF_2 and NiWO_4 . Passivation of the Ni surface with fluorine to form a tightly bound layer of unreactive NiF_2 for guarding against oxidation was recommended. With this pretreatment, nickel could be an effective material from which to build the production system for WF_6 .

Task 3: Reactor design.

Design of a reaction system to accommodate the two-step conversion involving the evolution of WOF_4 and subsequent transformation to WF_6 was not completed since the investigation into determining a suitable fluorinating agent was not completed.

Task 4: WF_6 Product characterization.

All issues dealing with the purity of WF_6 could not be addressed since collection of useable quantities of material was not synthesized amongst the bench-scale trials performed during this investigation.

8 GeF₄ PRODUCTION

8.1 Experimental Procedures - GeF₄.

8.1.1 Reactor design for producing GeF₄.

Production of GeF₄ was studied using two different reactor designs in a batch-type process for manufacturing material of exceptional purity. Due to the low volume (in the range of 100-200kg/yr) and high value (\$3-\$5 per gram) of the product, a batch process was pursued since it is best suited for controlling reaction yield and product quality. The two system configurations examined in detail involved a crucible reactor and a tube reactor. Each design offered certain distinct advantages, which were examined as **Task 1** was accomplished.

A schematic of the crucible reactor system used to produce GeF₄ is shown in **Figure 2**. This design provided for easy material transfer and accommodated sufficient reagent volume to produce up to 1kg of gas per batch. Characteristics of this design such as the large freeboard (internal void volume) above the heated zone and large internal surface area within the reaction chamber were issues of concern.

Figure 2. Schematic of crucible reactor setup with gas cylinder attached to collect GeF₄.

Five experiments were performed using the crucible reactor setup in order to assess the performance of this design with respect to conversion yield and gas capture efficiency. The list of trials is shown in **Table 3**, showing reaction time, temperature and reagent make-up.

Table 3.

Experiments Performed in the Crucible Reactor Setup.

Experiment ID	Reagent Vessel	Reaction Temperature (°C)	Reaction Time (hr)	Reagent Weight (gm)	GeO ₂ Weight Fraction (%)
GeFusn-19	Ni beaker	875	2	30.284	25.451
GeFusn-20	Ni beaker	875	2	30.842	23.977
GeFusn-21	Ni beaker	925	2	28.691	23.946
GeFusn-22	Cu cup	925	2	31.065	23.979
GeFusn-23	Ni beaker	925	3	32.444	23.999

For each experiment, the reagent mixture of UF₄ and GeO₂ was contained in a 250 ml beaker made of nickel. For the GeFusn-22 trial, the reagent container was switched to a copper cup along with a copper tube insert in an attempt to direct the gas product out of the reactor faster. This was done to reduce the effects that the large internal volume (freeboard) and surface area may have (i.e. possible side reactions) on the GeF₄ produced in the hot zone of the reaction chamber. A schematic of the copper cup/'chimney' insert is shown in **Figure 3**.

Except for the first experiment, GeFusn-19, the composition of the reactant mixture was such that there was a slight molar excess (~5wt%) of UF₄ over GeO₂ in order to promote complete reaction of all germania to gaseous product. The reaction parameters for each experiment are listed in **Table 3**. The approach was to find a set of conditions which maximized both conversion yield and capture efficiency. Chromatographic grade helium (specified as grade 5.5 from *AirGas East*, Salem, NH) was used as the motive gas to convey the GeF₄ out of the reaction vessel and through a small gas sample cylinder (150cc internal volume) used as the collection vessel. Each cylinder was made of type 316 stainless steel and was equipped with 2 valve closures and an outage tube to deliver the gas stream to about the midpoint of the cylinder interior. A partially filled dewar of liquid nitrogen was used to cool the cylinders for trapping the GeF₄ within the cylinder volume. Prior to each experiment, the collection vessel was heated and out-gassed under vacuum to remove adsorbed moisture to prepare the sample cylinder to receive GeF₄. It was weighed prior to and after collection to record the amount of volatile product captured. In addition to the weight change of the vessel, the weight of the container holding the reagents was recorded prior to and after reaction.

A step by step description of the procedure followed is included here as a representative example of the experimental process. The procedure started with the preparation of a fresh mixture of constituents for each experiment. Once prepared, the mixture was placed in the nickel beaker which was lowered to the bottom of the HR160[®] alloy reactor (internal volume ~4 liters). The reaction chamber was sealed at the top flange opening using a teflon[®] gasket and a

source of high purity helium connected via gas-tight compression fittings. To effectively purge the atmosphere of air inside the vessel, a vacuum was carefully established using a mechanical pump followed by back-filling with helium to ambient pressure. After completing three vacuum/backfill cycles, the flow of helium carrier was established at the desired rate. The gas stream exiting the reactor was sent through a tee where one branch led to the collection vessel and the other to a vent line. The crucible furnace (*Blue M/Lindberg*) was connected to a 16-segment programmable controller. The heating profile followed is shown in **Table 4**. After maintaining the reaction for the desired period, the flow of gas from the reactor was allowed to continue through the collection vessel for 30 minutes following the start of the cooling segment to allow for collection of product entrained inside the reactor's freeboard. Once gas collection was terminated and the sample cylinder closed to flow, the gas stream was redirected through the vent line while the reactor cooled to ambient under a flow of helium. After cooling to ambient, the reaction vessel was opened to retrieve the nickel beaker containing reaction residue. In each case, the beaker was weighed and solid residue recovered.

Figure 3. Schematic of crucible reactor with copper cup and 'chimney' insert used in GeFusn-22.

Table 4.

Heating Profile for the Crucible Reactor Experiments.

Segment	Heating Rate °C/minute
Ambient → 400°C	15
Dwell @ 400°C	60 min
Ramp 400°C → 800°C	15
Dwell @ 800°C	~15 min to chill cylinder
Ramp 800°C → 875°C or 925°C	15
Dwell at reaction temperature	120 or 180 min
Ramp 875°C → 25°C	10

The second type of reactor that was investigated for synthesizing GeF_4 in a batch process was a tube reactor. The tube reactor offers a higher heat transfer rate in the high temperature zone and reduced freeboard downstream of the generation point. The first tube reactor constructed to evaluate this configuration was made of type 304L stainless steel and consisted of a 27" section of 2.75" OD pipe welded to an 11" section of 1" OD tube. The reduction in tube diameter was used to reduce void volume outside the heated reaction zone and convey the product gas out of the tube faster. The 2.75" diameter of the pipe allowed for larger amounts of reactants per batch. The tube furnace was a 3" diameter, single zone unit (*Lindberg*) possessing a 10"-12" heated bed length. This reaction tube was used for only one experiment, GeFusn-24. In this trial, a high-density alumina boat was used to shuttle a mixture of UF_4 and GeO_2 to the center of the hot zone prior to heating. A 150cc gas cylinder was fixed to the reactor effluent stream similar to the setup used to collect gas in the crucible reactor experiments. A schematic of the tube reactor configuration is shown in **Figure 4**.

An additional eight experiments were performed in a second tube reactor constructed of nickel 200 alloy. The Ni tube reactor consisted of a 1" OD section of tube 43" in length. The selection of a relatively small diameter tube for these experiments was made since it was readily available from various vendors, did not require additional fabrication techniques (welding, etc.) and used only standard compression fittings (*Swagelok*®) for connecting to the gas collection vessel. The complete list of experiments performed in the tube reactor configuration is compiled in **Table 5**. Reaction parameters and reagent specifications are listed here for each trial. In all experiments the stoichiometry of the UF_4/GeO_2 starting mixtures contained a slight excess of green salt. For the 1" OD Ni tube experiments, a small 4" long nickel boat was used to shuttle reagents into the central reaction zone. Output from the reactor was either diverted through a vent line or through a 316 stainless steel cylinder chilled using a partially filled dewar of liquid nitrogen. Starting with experiment GeFusn-28, type-K thermocouples were attached to the external surface of each collection cylinder to monitor its temperature in an effort to prevent stoppage of flow caused by GeF_4 condensing in the 0.25" diameter outage tube rather than in the cylinder interior.

Parameters investigated included temperature, reaction atmosphere (helium or helium + air) and flow rate of carrier gas. With the exception of the first two experiments (GeFusn-25

Figure 4. Schematic of the Ni tube reactor setup with gas cylinder attached to collect GeF₄.

Table 5.

Experiments Performed in the Tube Reactor Setup.

Experiment ID GeFusn -	Reaction Conditions	Motive Gas Flow Rate	Weight of Reagents	Weight Fraction GeO ₂
	Atm/Temp/Time gas / °C / hr	cc/min (He/air) = Total		
				(gms)
Experiment performed in the 304L stainless steel tube reactor				
24	He / 850 / 2.5	100	31.1941	24.236
Experiments performed in the nickel tube reactor				
25	He / 800 / 2.5	67	15.6158	24.004
26	He / 800 / 2.5	150	15.9473	24.004
27	He / 700 / 5	150 - 67	17.2200	23.991
28	He+air / 700 / 5	(67 + 9) = 76	16.0310	23.991
29	He+air / 725 / 5	(67 + 9) = 76	14.9553	23.991
30	He / 750 / 5	67	16.9337	23.991
31	He / 775 / 5	67	15.7964	23.991
32	He+air / 750 / 5	(67 + 15) = 82	17.1139	23.991

and -26), a reaction period of five hours was employed. Three experiments were performed where a small flow of dry air was added to the helium stream (for GeFusn-28,-29 and -32) after the furnace temperature reached the desired mark. The heating profile was slightly different than that listed in **Table 4**. The temperature of the furnace was raised to 500°C at 15°C/minute and maintained for 60 minutes to allow removal of adsorbed moisture from the reagents before ramping to the final reaction temperature at a rapid rate of ~100°C/minute. Upon conclusion of the reaction, the furnace temperature was lowered at 10°C/minute but the actual temperature drop tailed off after 10-15 minutes from the programmed rate to a slower pace set by heat loss from the furnace. Passage of gas through the cylinder was continued for 30 minutes following the start of cooling to harvest residual GeF₄ from the gas stream during the cool down. Data collection from the experiments was the same as that described for the crucible experiments.

Besides the gravimetric measurements collected after each reaction in both the crucible and tube reactor trials, characterization of the synthesized reaction products was also done. The powder materials recovered from the nickel beaker and boat were analyzed by x-ray powder diffraction (XRD) to qualitatively document final composition and investigate possible reaction intermediates in the cases where conversion was incomplete. The XRD analyses were performed on a *Shimadzu XRD-6000* diffractometer equipped with a copper radiation source. Data were collected over the range of 10°-150° 2-theta. The experimental data were compared to the library of reference patterns contained in the Powder Diffraction File of the *International Center for Diffraction Data*, Volumes 1-47, Release 1997 (Newtown Square, PA)¹³.

The gaseous product captured in the 150cc collection cylinders was analyzed by Fourier transform infrared spectroscopy (FT-IR) to verify the gas was indeed GeF₄ and also to evaluate

purity with respect to other foreign species such as HF and H₂O which may have been liberated during the reaction. The measurements were made using a *Nicolet Magna-IR 560* optical bench situated with a KBr beamsplitter and DTGS detector. Gas samples were contained in a gas-tight 10cm cell (*CIC Photonics, Inc.*, Albuquerque, NM) outfitted with zinc selenide windows and a programmable heater for maintaining the cell at 125°C to displace adsorbed moisture prior to data collection.

8.1.2 Materials of construction for production of GeF₄.

Fluoride gases, especially at elevated temperatures, can be very corrosive. Therefore it was necessary that the materials of construction used in building a production system be as inert and unreactive toward GeF₄ as possible when placed in demanding conditions including high temperature and strong oxidizing environments such as hydrogen fluoride vapor. Corrosion testing was performed on a number of metals and metal alloys compiled in **Table 6** below. **Table 6** also lists the constituents of the materials and their relative proportions. In the Phase II proposal task outline, *Haynes Alloy N*[®] was also selected as a potential candidate, however this alloy is being phased out by *Haynes* in favor of Alloy 242. Thus *Haynes Alloy N*[®] was not studied, as this alloy is now difficult to obtain. In place of *Haynes Alloy N*[®], copper was tested for resistance to attack by GeF₄ since some of the crucible reactor experiments used a Cu chimney over the reactor cup to minimize the freeboard within the reactor. One of the copper chimney inserts was dissected and studied for corrosion products. Monel was also included in the study since earlier work had shown that Monel reacted extensively with the product gases. Finally, 304 stainless steel (SS) was substituted for 316 SS since 304 SS was used for the tubing of the system.

Table 6.

Metals and Alloys Used in the Corrosion Studies.

Material	Composition
Ni sheet	100 % Ni
Monel	70Ni-30Cu
Inconel 600 [®]	72Ni-14Cr-6Fe-0.15C-1Mn-0.015S-0.50Si-0.50Cu
<i>Haynes 242</i> [®]	65Ni-25Mo-8Cr-2.5Co-2Fe-0.8Mn-0.8Si-0.5Al-0.5Cu-0.03C-0.006B
<i>Haynes HR-160</i> [®]	37Ni-29Co-28Cr-2.75Si-2Fe-0.5Mn-0.05C
304 Stainless Steel	Fe-18Cr-8Ni-2Mn-1Si-0.08C-0.045P-0.03S
Cu tubing	99% Cu

The metal samples were prepared by removing rough edges and polishing with 600 grit SiC paper. Two major experiments were conducted. In the first, the metal samples were exposed to pure GeF₄ gas from a commercial supplier in a tube furnace. In the second, metal samples were exposed to both the reaction mixture and the product gas produced in the crucible reactor. In addition to these experiments, materials used in other reactions that could be spared were examined. Analysis primarily consisted of scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS). In addition, x-ray diffraction (XRD) was used on some samples.

Corrosion Experiment 1

This experiment was performed in a *Mini Mite* furnace (*Blue M/Lindberg*), using an 18" section of Monel tube as the chamber. Samples tested in this experiment included 304SS, Inconel 600, *Haynes* 242, and Cu. The procedure for the experiment was as follows:

1. Purge system with dry argon for ½ hour
2. Shut off argon, and close off valves to argon side of assembly.
3. Open GeF₄ tank. Allow to flow until bubbles seen in trap.
4. Close GeF₄ tank, followed by closing each end of the reaction tube.
5. Begin heating to 900 °C at 50 °C/min.
6. Hold 1 hour
7. Cool to 300 °C. Shut off furnace
8. Open ends of reaction tube
9. Purge system for 2 hours with dry argon as it continues to cool.
10. Shut off argon.
11. Open furnace. Disconnect tube at both ends at 1" *Swagelok*[®] fitting.
12. Tilt tube to slide corrosion coupons out into beaker
13. Test coupons for pH. Wash in water, test again. Neutralize with lime solution if necessary.
14. Proceed once neutralized with metallography/microscopy.

Some difficulties were encountered during the experiment. A leak occurred at the valve after the check valve, leading to a leak at the regulator connection, which was then tightened. At the end of the experiment, when the ball valve nearest the water trap was opened, water was sucked into the reaction tube. The system was at around 200°C when this occurred. The system was purged with argon overnight to try to dry the system. The coupons needed to be neutralized as they were highly acidic.

Corrosion Experiment 2

This reaction was performed in the *Lindberg* crucible furnace used in previous experiments. A reaction mixture consisting of 194.6 g UF₄ and 67.5 g GeO₂ was made, and 172.1g of this mixture was placed into an alumina crucible. Coupons of all six metals were embedded in the reaction mixture. Additional coupons were placed in the outflow tube of the reactor. In this way, the performance of the materials in question could be studied simultaneously with exposure to the gas phase and in contact with the solids. The furnace was heated at 15°C/min to 400°C, held for 1 hour, ramped at 20°C/min to 925°C, held for 2 hours, and then cooled to room temperature. The gas produced was scrubbed out with water in a large Erlenmeyer flask.

8.1.3. Optimization of product yield.

A group of experiments was performed as part of the reactor design study in **Task 1** which explored reaction parameters that directly affected the yield of GeF₄. The parametric study included aspects such as reaction temperature, reaction atmosphere and length of reaction. As part of **Task 3**, several additional experiments were done to find conditions for maximizing both conversion and yield of GeF₄. There was also a need to increase the amount of fluoride produced per batch reaction to make sufficient quantity for analytical characterization. In order to produce more gas from each experiment using the 1" OD tube reactor setup, a larger reagent

vessel was fabricated in-house using an 8" section of 1" OD nickel 200 alloy tube. The tube was cut lengthwise, in half, and curled so that it would slide into the 0.834" internal diameter reaction tube opening. End pieces of nickel were welded to the ends of the curled section, forming a boat with a capacity of about 50 grams of combined reactants.

The first experiment to use the larger reagent boat, GeFusn-33, also incorporated a change to the gas collection hardware as recommended by *Voltaix, Inc.* personnel. The revised gas collection configuration is shown in **Figure 5**. It was suggested that the GeF_4 laden gas stream enter the cylinder through the top port and be vented through the outage tube which should be shortened to protrude into the vessel to a depth of ~2 inches. In previous trials, the outage tube delivered the incoming gas flow to the midpoint of the 9" cylinder before venting through the top port. The new gas flow pathway was instituted to reduce the likelihood of freeze-up and blockage caused by condensed product in the $\frac{1}{4}$ " outage tube. It was recommended that the coolant level remain 1-2" below the tip of the outage tube opening.

Figure 5. New cylinder configuration and gas flow pathway used in collecting GeF_4 .

After completing GeFusn-33, in which the reaction temperature was in the range between 700°-775°C and total reaction time approached 7 hours, a significant fraction on the residue remaining in the 8" boat was green in color, indicative of unreacted green salt. As a result, a probe of the internal temperature inside the nickel reaction tube was conducted. The 1" tube was

outfitted with a thermocouple to probe the internal temperature over the 12" section of heated area. A schematic of the temperature probe setup is shown in **Figure 6** depicting the four points (A, B, C, and D) along the center axis where the measurements were taken. Temperature data were recorded at five furnace set-points without the 8" boat or reagents in the reactor.

Figure 6. Schematic representation of the temperature probe within the Ni tube reactor.

A second experiment, GeFusn-35, was performed in the 1" tube reactor where the GeF_4 product stream was analyzed directly by in-line FT-IR spectroscopy using the 10cm gas cell maintained at 130°C . Multiple aliquots of gas captured at various points along the reaction timeline were examined to catalog the quality of GeF_4 with respect to moisture content and onset of gas evolution.

From the start of the experimental program, the primary germanium source to produce GeF_4 was high purity GeO_2 (99.999%). After developing the cost model for producing the gas, it became evident that there may be a competitive economic advantage to derive GeF_4 using Ge° metal as an alternative source. The alternative reaction pathway is given in equation (8.1)

This new chemistry is based on the in-situ oxidation of Ge° to GeO_2 and is analogous to the chemistry developed at *Starmet* for producing silicon tetrafluoride from the reaction between silicon metal, UF_4 and oxygen as practiced in **U.S. patent 5,901,338**.

To test the feasibility of the chemistry shown in equation (1), two milligram-scale experiments were performed using the *TA Instruments* model 2960 Simultaneous TGA/DTA (ThermoGravimetric Analyzer/Differential Thermal Analyzer). In the first trial, a small sample of Ge° metal was heated to 1000°C in a stream of dry air. In the second experiment, a mixture of UF_4 and powdered Ge° metal was heated to 850°C at $10^\circ\text{C}/\text{min}$ in a stream of dry air. In each trial the sample weight was measured as a function of time and temperature.

After completing the milligram-scale experiments, the same reaction was carried out on a larger scale using the 1" OD Ni tube reactor setup. In this trial, identified as GeFusn-39, 2.0558 grams of 99.9% pure Ge° metal powder was combined with UF_4 and reacted at temperatures in the range between 600°C - 700°C . The output from the reactor was connected to the gas-sampling

cell and multiple aliquots of reactor offgas were analyzed by FT-IR spectroscopy to characterize the purity of the product. The post-reaction solid residues were analyzed by x-ray powder diffraction.

Finally, one micro-scale experiment was performed in order to better define the temperature at which the fluoride gas was first liberated. Experiments from the reactor design trials have shown that the reaction between green salt and germanium oxide is well underway at a temperature of 650°C. A more refined determination of the reaction onset temperature is expected to impact both the purity and yield of the final product. Using the TGA instrument, a mixture of reagents was heated to 500°C at 15°C/min in a stream of air or argon. The change in the weight of the mixture was monitored during three successive heating cycles.

8.1.4. Development of analytical methodology for identifying trace uranium in GeF₄.

Analysis for uranium species, which may have carried into the GeF₄ produced by solid state reaction between UF₄ and GeO₂, was investigated previously in the Phase I SBIR program using indirect methods such as kinetic phosphorescence (KPA) involving aqueous scrubber solutions. Those results showed U content at background levels measuring in the single digit parts-per-billion (ppb) range. However, more sensitive measurements were sought employing direct methods to determine the U concentration at levels called out in specifications of other important semiconductor gases such as tungsten hexafluoride, WF₆. The value specified for uranium impurity in WF₆ offered by *Matheson Electronic Products Group / Semi-Gas Systems* is listed at 0.05 ppbwt. The goal of this task was to develop the methods and procedures that have the sensitivity to measure uranium in the range that is appropriate for products intended for use in the semiconductor industry.

To assist with meeting that challenge, a collaborative effort was undertaken with Dr. James Beitz at *Argonne National Laboratory (ANL)* to explore the applicability of using two new techniques, optical absorption spectroscopy and laser-induced photoluminescence, to measure the very low levels of U in GeF₄. The work carried out at *ANL* is compiled in four quarterly progress reports that are included in **Appendix A** of this report. Details of the experimental program and results are included there.

Two samples of GeF₄ produced at *Starmet* were sent to *ANL* for characterization by the new techniques. The first sample was made as part of the GeFusn-36 trial and contained 5.3 grams of gas in a 300cc Monel gas cylinder equipped with a shortened outage tube made from 1/4" nickel tube. The reaction conditions for this run are compiled in **Table 7**. The gas produced in this trial was collected without passing it through a filter and was considered as the most 'crude' form (worst case scenario) with regard to possible U contamination.

Table 7.

Reaction Profile for GeFusn-36.

Experiment ID:	080201-GeFusn-36	
System:	1" OD nickel tube reactor with 8" Ni boat	
Weight of reagents (gm)	34.1057	wt% GeO ₂ : 24.9847
Sweep gas:	Helium (62) + air (10) = total flow at 72 (cc/min)	
Pre-reaction drying period:	2 hours at 500°C in helium	
Total reaction time (hr):	5	
Reaction Temperature (°C)	750	
Cylinder ID:	#A1, 300cc Monel, double port, shortened Ni outage tube and Monel plug.	
Collection method:	n-propyl alcohol/liquid N ₂ bath at -62 to -72°C	
Filter:	none	

A second sample of GeF₄ was prepared as part of GeFusn-40. In this experiment, the gas stream leaving the 1" tube reactor was passed through a 0.45 μ stacked PTFE[®] membrane filter (*Osmonics, Inc.*, Westborough, MA) before collection in the 300cc Monel cylinder. Reaction conditions for GeFusn-40 are given in Table 8. By making slight changes to the pre-reaction drying period and reaction temperature profile, 8.3 grams of gas was captured for shipment to ANL.

Table 8.

Reaction profile for GeFusn-40.

Experiment ID:	011102-GeFusn-40			
Reaction:	$3\text{UF}_4 + 3\text{GeO}_2 + \text{O}_2(\text{g}) = 3\text{GeF}_4 + \text{U}_3\text{O}_8$			
System:	1" OD Nickel tube reactor with 8" nickel boat (including Ni foil spacer)			
Weight of reagents (gm):	36.4229	wt% GeO ₂ : 23.4819%		
Sweep gas:	Helium (62) + air (20) = total flow at 82 (cc/min)			
Pre-reaction drying period:	1 hour at 450°C in helium			
Total reaction time (hr):	5.33			
Reaction temperature profile		Time (hr)	at T (°C)	
		0.33	725	
		0.50	750	
		3.33	775	
		1.17	800	
Cylinder ID:	#A2, 300cc Monel, double port, Monel plug and shortened Ni			
	outage tube.			
Collection method:	n-propyl alcohol/liquid N ₂ bath at -85°C to -80°C			
Filter:	Osmonics 0.45 μ stacked PTFE® membrane / polypropylene shell			

The post-reaction solids from both GeFusn-36 and -40 were recovered and weighed to determine both reaction yield and conversion and then analyzed by x-ray powder diffraction to characterize the composition of the leftover materials.

8.1.5. Particulate filtration.

During the reactor design trials, conducted as part of **Task 1**, filtering of the gas leaving the reactor was not done in order to maximize the total amount of product captured. However, when samples of GeF₄ were made as part of the characterization of gas purity at facilities outside of *Starmet*, the gas was filtered through a 0.45 μ stacked PTFE[®] membrane filter enclosed in a polypropylene shell (*Osmonics, Inc.*, Westborough, MA). This included the material sent to *Argonne National Laboratory* and *Voltaix, Inc.*

Information about gas filtration technology was also passed along from *Voltaix, Inc.* regarding what they used for removing particulate from other semiconductor grade materials they manufacture. One filter they have experience with and recommend is the *Wafergard II F-6 In-Line Gas Filter* manufactured by *Millipore Corporation* (Bedford, MA). This unit features a teflon[®] membrane module rated for particulate removal of $\geq 0.003\mu$. This type of modular filter can be placed directly in-line within a short distance of the gas cylinder inlet. Another filter, equivalent to the unit used by *Voltaix, Inc.*, was purchased for use when the GeF₄ production-scale reaction system was built. The filter, model # TEM-811-P, was manufactured by the *T.E.M. Filter Company* (Santa Clara, CA) and purchased from *Air Products* (Allentown, PA).

8.1.6 Process scale-up.

Using what has been learned from reactor design and optimization trials (**Tasks 1 and 3**), production of GeF₄ was demonstrated at high conversion levels and reasonably good capture efficiencies. Design of a production-scale apparatus was started and conceptual drawings of a multi-station reaction manifold and gas collection station were made. The two segments of the system are depicted in **Figures 7 and 8**. The reaction hardware consisted of six individual stations linked to a common manifold for conveying GeF₄ to the collection station. The multiple reactor setup was adopted over a larger capacity single reactor apparatus to accommodate:

- improved heat transfer to the reactant bed by keeping bed dimensions to a minimum;
- adding production capacity as needed over time;
- greater control over batch purity and avoidance of lost production time;
- lower cost and time to fabricate reaction hardware;
- ease of handling reaction hardware by operators.

Each station joined to the manifold was designed to hold a reactant charge of ~1kg and produce ~0.33kg of GeF₄. With all stations in operation at once, the system would deliver ~2kg of fluoride gas per day. Pertaining to operation, the gas produced by heating each reaction tube is carried into a central manifold by introducing a sweep stream of helium (or helium+air) above the reactor charge. The GeF₄-laden stream is filtered using an in-line sintered metal (nickel) disc for snagging entrained particulate leaving the reaction zone. The combined gas flow is then directed to the collection apparatus shown in **Figure 8**, where GeF₄ is condensed into a large volume cylinder surrounded by an appropriate coolant bath such as dry ice/alcohol. Once the

Figure 7. Multi-Station Reaction System for Producing GeF_4 .

Figure 8. Gas collection system for trapping and packaging GeF_4 .

capture of GeF_4 is complete, the gas quality can be upgraded using fractional distillation procedures when transferring the product into transportable 1-liter (or larger) cylinders. It is possible to automate the transfer from the collection cylinder to the final package vessel but the automation hardware is costly and is not justified for a low production process such as this. In an effort to increase the amount of GeF_4 produced per batch and also test the merits of the reactor design put forth in **Figure 7**, a small-scale prototype of the closed-end tube reactor was constructed from a 9" section of 1"OD nickel tube to hold the reactant mixture. The sweep gas was introduced via a $\frac{1}{4}$ " tube inserted through the wall of the 90° union elbow used to cap the closed-end tube. The 1" elbow orifice was stepped down in size to a $\frac{1}{4}$ " tube connection and ultimately joined to a 300cc sample cylinder which had two ports and no outage tube. The cylinder was setup as a 'flow-through' condenser to capture GeF_4 from the gas phase as the stream exiting the reactor passed through. The details of the reaction are given in **Table 9** and the trial was identified as GeFusn-34. In this experiment, 87.84 grams of combined UF_4 and GeO_2 were loaded into the vertically oriented tube. A 6"OD x 6"long ceramic heater, controlled manually by variable potentiostat, was used to heat the tube. The 'flow-through' cylinder was positioned about 12" to the side of the reaction tube and was outfitted with a container to hold bulk dry ice pellets around the circumference of the cylinder body.

Table 9.

Reaction profile for GeFusn-34.

Experiment ID:	051501-GeFusn-34			
System:	Closed-end 1" OD nickel tube reactor			
	6" OD x 6" long ceramic heater (with manual control)			
Weight of reagents (gm):	87.84	wt% GeO ₂ : 24.1689		
Sweep gas:	Helium flow at 70 (cc/min)			
Total reaction time (hr)	5			
Reaction temperature profile		Time (hr)	at T(°C)	
		2	735-755	
		1	775	
		2	800	
Cylinder ID:	#11, 300cc volume, Monel, double port, no outage tube			
Collection method:	dry ice bath, neat			

8.1.7 Gas ultrapurification.

As part of the Phase II program to harvest GeF_4 from processing of uranium tetrafluoride, *Voltaix, Inc.* (North Branch, NJ) was subcontracted by *Starmet* to perform analytical testing of the gas to establish the purity of the "as-produced" material. *Voltaix, Inc.* agreed to partner with *Starmet* to assist with the development and commercialization of GeF_4 since they currently market this material for ion implantation applications. The material produced by the FEP™ technology requires in-depth characterization to establish what must be done at either the crude production stage or with additional purification steps to insure that this gas will be pure enough to meet or exceed the current specifications.

Under the subcontract agreement with *Voltaix, Inc.* germanium tetrafluoride produced at *Starmet* was to be characterized using three techniques, FT-IR spectroscopy (FT-IR), gas chromatography-mass spectrometry (GC-MS) and inductively coupled plasma-mass spectrometry (ICP-MS). Infrared spectra were collected using a *Nicolet Instruments MagnaIR-560* optical bench, similar to the instrumentation at *Starmet*. Analysis of gas samples by GC-MS was attempted but abandoned after experiencing problems with identifying an acceptable separatory column that did not react with GeF_4 . ICP-MS analysis of *Starmet* material was accomplished at an independent laboratory, *Applied Analytical Inc.* (Austin, TX). For this evaluation, GeF_4 , produced in laboratory trials (*GeFusn-37* and *-38*), was first hydrolyzed in deionized water at *Voltaix, Inc.* and the resultant solution, along with a similarly prepared reference sample and 'blank' specimen, were forwarded on to *Applied Analytical Inc.*. The source of the reference sample was derived using a purchased source of GeF_4 claimed to have a purity of 99.99% (vendor certified). The 'blank' sample was prepared by bubbling a known amount of nitrogen ballast gas through a set volume of deionized water.

The GeF_4 submitted for purity analysis was generated from two experiments, *GeFusn-37* and *GeFusn-38*. The material collected in both trials totaled 15.61 grams. The reaction profile for each experiment is given in **Table 10** and **Table 11** showing reaction time and temperature information.

Table 10.

Reaction Profile for GeFusn-37.

Experiment ID:	081601-GeFusn-37		
System:	1" OD nickel tube reactor with 8" Ni boat (including Ni foil spacer)		
Weight of reagents (gm)	35.1592	wt% GeO ₂ : 24.9847 (stoichiometric mixture)	
Sweep gas:	Helium (62) + air (20) = total flow at 82 (cc/min)		
Pre-reaction drying period:	1 hr at 300°C in helium		
Total reaction time (hr):	5.25		
Reaction temperature profile	Time (hr)	at T (°C)	
	0.25	700	
	1	750	
	2.75	775	
	1.25	800	
Cylinder ID:	#8, 150cc stainless steel 304, single port with shortened		
	outage tube.		
Collection method:	n-propyl alcohol/dry ice bath at -72°C		
Filter:	Osmonics 0.45μ stacked PTFE® membrane/polypropylene shell		

Table 11.

Reaction Profile for GeFusn-38.

Experiment ID:	082101-GeFusn-38		
System:	1" OD nickel tube reactor with 8" Ni boat (including Ni foil spacer)		
Weight of reagents (gm)	34.0237	wt% GeO ₂ : 24.9847 (stoichiometric mixture)	
Sweep gas:	Helium (62) + air (20) = total flow at 82 (cc/min)		
Pre-reaction drying period:	1 hr at 400°C in helium		
Total reaction time (hr):	3.75		
Reaction temperature profile	Time (hr)	at T (°C)	
	0.75	650-800	
	3	800	
Cylinder ID:	#8, 150cc stainless steel 304, single port with shortened outage		
	tube containing GeF ₄ collected in 081601-GeFusn-37.		
Collection method:	n-propyl alcohol/dry ice bath at -77°C		
Filter:	Osmonics 0.45μ stacked PTFE® membrane / polypropylene shell		

In brief, both reactions were carried out using a helium/air mixture as the sweep gas through the reactor. The material produced in both reactions was filtered using a 0.45 μ stacked PTFE[®] membrane filter (*Osmonics*, Westborough, MA) before condensation in the cylinder. FT-IR analysis of the gas stream exiting the 150cc collection cylinder was done during the GeFusn-38 trial to monitor how much product gas was escaping from the condensation zone while the cylinder was submerged in the coolant bath at -77°C. After concluding GeFusn-38, the helium/air residual was removed by vacuum processing before shipping the sample to *Voltaix, Inc.* Follow-up analysis of the reaction solids left behind after each trial was also performed using x-ray powder diffraction.

8.1.8 Product qualification.

Germanium tetrafluoride produced in laboratory trials was analyzed by several different techniques described in **Tasks 4 and 7**. The crude product was determined to be equivalent in purity to the reference material with certified purity of 99.99% (UHP grade). Additional analytical testing is required to quantify the level of impurities specifically called out in the *Voltaix, Inc.* specification for UHP grade GeF₄ such as CF₄, CO, CO₂, SO₂, N₂, Ar+O₂ and HF. Many if not all of these impurities can be measured by GC-MS, the one technique that presented the greatest challenge in obtaining useable data during the Phase II program.

However, the need for a material with higher purity than the current specification has not been established. No work was done to pursue what the next generation of electronic/semiconductor products may require with regard to material specifications.

8.1.9 Design and construction of low production rate equipment.

Due to the weak economic performance and global slump in the electronic and semiconductor sectors over the past 18 months, the decision to erect a production-scale plant for producing GeF₄ was postponed. However, conceptual drawings of a multi-station reaction system and gas collection station were made and described in **Task 6**. This system was configured to deliver up to 2kg of fluoride gas per day when operated at full capacity, making it well suited to meet the projected 100kg production plateau as forecasted by *Voltaix, Inc.*

8.2 Experimental Results for GeF₄.

8.2.1 Reactor design for producing GeF₄.

Two designs for a batch-type reaction system were tested for producing GeF₄ with good reaction yield and capture efficiency. Five experiments were performed using a crucible reactor while nine experiments were carried out using several tube reactor systems. The experimental setups and procedures were given in detail in section 8.1.1. Results for these two reactor configurations are arranged into two groups to help facilitate comparison of their performance as indicated by reaction conversion and capture efficiency values. After presenting the reaction data, results for the analyses of the reaction products (both solids and gas) by x-ray diffraction and FT-IR spectroscopy are also included.

Results for the five experiments in the crucible reactor setup are given in **Table 12**. In this table, both theoretical (calculated) and experimental (observed) values were used in deriving the "Reaction Conversion" and "Capture Efficiency" parameters. Calculations were based on gravimetric measurements collected for gaseous product and residues remaining after reaction. "Calculated" values in the table were based on 100% reaction conversion. The "Reaction Conversion" was calculated as a ratio of "Observed weight loss of reagents" to the "Calculated weight loss of reagents" expected upon complete reaction (x 100%). The "Capture Efficiency" of GeF₄ was compiled as the "Observed weight gain in cylinder" divided by the "Observed weight loss of reagents" (x 100%). Among the five trials, the Reaction Conversion ranged from a low of 84.9% (for GeFusn-20) to 95.2% (for GeFusn-23) while the Capture Efficiency ranged from 20.9% (for GeFusn-19) to a high of 38.3% (for GeFusn-21).

The reaction parameters, i.e. reaction temperature, time and flow rate of carrier gas, were varied in order to find a set of conditions which maximized both conversion and capture efficiency in this reactor configuration. As expected, when the reaction temperature was increased from 875°C to 925°C, a corresponding increase in conversion was noted. An increase in reaction time from 2 to 3 hours also helped to further conversion. It was anticipated that a faster flow of helium carrier gas would shorten the residence time of GeF₄ in the reaction zone and result in higher capture efficiency. However, this scenario was not the case when results for GeFusn-21 are compared to those of GeFusn-23. What is clearly evident from the five trials is the poor collection efficiency experienced in all experiments. Although a majority of the reaction was completed and volatile product made, it did not wind up as desired product. The use of a copper container and 'chimney' in GeFusn-22 did not result in increased recovery by minimizing effects of reactor freeboard and residence time.

It is apparent that several factors contributed to the low recovery of GeF₄. They include:

1. corrosive attack of the GeF₄ laden atmosphere on the reactor material
2. formation of Ni₂GeO₄ on the nickel beaker walls
3. less than 100% reaction conversion
4. formation of crystalline condensate (GeF₂) on cooler section of the reaction system
5. small condensing zone provided by the 150cc gas sample cylinder interior.

A more detailed explanation of factors 1-4 is provided below and is based on direct observations of similar findings during and after the disassembly of the reaction system following each experiment.

Table 12.

Experiments performed in the crucible reactor setup.

Expt. ID	Temp / Time	Helium Flow Rate	Reagent Weight	GeO ₂ Content	Calculated wt. GeF ₄ expected ^a	Calculated residue wt. expected ^a	Calculated wt. loss of reagents ^a	Observed wt. gain in cylndr	Observed wt. lost of reagents	residue wt. reclaimed ^d	Reaction ^b Convers'n	Capture ^c Efficiency
GeFusn-	°C / hr	~ cc/min	gm	wt%	gm	gm	gm	gm	gm	gm	%	%
19	875 / 2	120	30.284	0.25451	10.682	19.601	10.682	2.000	9.551	20.449	89.4	20.9
20	875 / 2	120	30.842	0.23977	10.506	20.336	10.506	2.200	8.916	21.926	84.9	24.7
21	925 / 2	75	28.691	0.23946	9.761	18.930	9.761	3.380	8.817	19.874	90.3	38.3
22	925 / 2	65-80	31.065	0.23979	10.583	20.482	10.583	2.700	9.676	21.389	91.4	27.9
copper cup/chimney												
23	925 / 3	150	32.444	0.23999	11.062	21.382	11.062	3.650	10.537	21.907	95.2	34.6
a assumes 100% reaction conversion												
b Reaction Conversion = Observed wt loss of reagents/Calculated wt loss of reagents x 100%												
c Capture Efficiency = Observed wt gain in cylinder/Observed wt loss of reagents x 100%												
d Residue weight reclaimed = Weight of boat+residue after reaction - initial weight of empty boat												

Factor 1: The inside surfaces of the reactor walls exposed to the heat of the furnace and GeF_4 atmosphere were aqua blue-green in color with formation of peeling scale. Analysis of this scale by x-ray powder diffraction showed a combination of mixed metal oxides of Ni-Cr, Cr-Co and possible oxyfluoride compounds. It was clear the HR160[®] alloy was being attacked at the reaction temperature in the presence of GeF_4 .

Factor 2: The interior wall of the nickel beaker above the solid residue was coated with a thin, flaky, light green skin which was removed easily with scraping. The light green substance was examined by both x-ray powder diffraction and energy dispersive x-ray analysis techniques in the scanning electron microscope (EDS/SEM). It was identified as Ni_2GeO_4 which obviously was produced by consuming some of the GeF_4 in the surrounding atmosphere. The weight of the empty nickel beaker at the start of each experiment was progressively higher (by as much as 0.5 gram) compared to the trial coming immediately before it. The continued formation of this skin over the course of the trials may account for the steady weight increase but it is believed the loss of GeF_4 from this interaction with the beaker represented only a small fraction of the amount not captured in the collection vessel.

Factor 3: The surface of the powder in the center of the container was varying shades of dark green and not fully blackened. The solid closer to the beaker walls was notably darker in appearance than at the center, indicative of how heat was penetrating to the vessel's core. The temperature in **Table 12** for each experiment was the furnace set point temperature. Actual temperatures inside the 4.5" diameter reactor were not profiled but were estimated to be some 60°-75°C lower than the set point temperature. The presence of color gradients in the residues is consistent with the gradients in heat transfer from the outside wall of the reactor to the center of the nickel beaker.

Factor 4: A deposit of white crystalline residue was found in varying amounts on the underside of the reaction vessel lid and sections of pipe downstream from the reaction chamber. Upon exposure to air, the solid residue became wet and eventually turned completely to liquid. A quick test of the liquid with pH test paper showed it to be extremely acidic at $\text{pH} < 1$. Because of the nature of this material to rapidly hydrolyze in air, efforts were made to quantify the amount of condensed residue by washing off reactor hardware with distilled water. When placed in water immediately following exposure to air, the surface layer turned bright yellow-orange. Over the course of 48 hours the residue was completely dissolved in water. Solutions containing dissolved residue collected after each experiment were analyzed by inductively coupled plasma (ICP) techniques to measure the amount of Ge distributed on the reactor hardware not in the form of GeF_4 . The amount of Ge lost to the buildup of this residue is summarized in **Table 13**.

Table 13.

Results showing analyses for Ge by ICP for aqueous wash solutions collected during recovery of GeF_2 residue from reactor hardware.

Experiment No.	Ge content in wash soln	Total soln. volume collected	Total Ge content	Moles Ge	equivalent amt. GeO_2	Amt. GeO_2 in reaction mixture	Fraction of GeO_2 charge recov'd from reactor hardware
	ug/ml	ml	gm	(n)	gm	gm	%
GeFusn-20	550	3000	1.650	0.0227	2.377	7.3949	32.1
GeFusn-21	355	3000	1.065	0.0147	1.534	6.8704	22.3
GeFusn-22	357	3000	1.071	0.0148	1.543	7.4491	20.7
GeFusn-23 lid	314	3000	0.942	0.0130	1.357	7.7865	17.4
- exit tube	550	50	0.0275	0.0004	0.040		0.5

The identity of the condensed crystalline residue (before exposure to moisture and water recovery) is not certain due to the lack of direct analysis. It is believed to be GeF_2 based on properties of the difluoride being a low melting solid which is rapidly hydrolyzed by moisture. Further work is required to specifically isolate the residue where it can be handled without compromising its integrity during the analytical characterization process. As shown in Table 13, and estimated 32.1% of the Ge content put into the reactor as GeO_2 for GeFusn-20 was collected from the deposited residue on the reactor hardware. This is a conservative estimate since much of the cooler surface area beyond the reactor lid not easily accessible to washing, may have contained a thin coating of residue which was not recovered. This is a very significant fraction of Ge that does not get captured as GeF_4 . A clear understanding of how the condensed residue is formed, whether it be directly by parallel side reaction or by secondary reaction which consumes GeF_4 , is lacking and requires further investigation. Additional discussion concerning a possible mechanism will be included later in the discussion section of this report.

By far, it is the formation of the GeF_2 condensate that contributes the most to the low capture yield of GeF_4 . To help understand the origin of this unwanted residue, one qualitative experiment was performed involving gaseous GeF_4 . Germanium tetrafluoride gas (purchased from *Advanced Research Chemicals, Inc.*, Catoosa, OK) was added to a stream of helium and passed through the HR160[®] alloy reactor heated at 925°C for a two-hour period. The reaction vessel contained the empty nickel beaker used in previous experiments and the same heating profile shown in Table 4 (page 13) was used. The GeF_4/He stream was introduced into the reaction zone after the reaction temperature was reached. A preweighed gas sample cylinder chilled with a liquid nitrogen bath was used to recover GeF_4 from the reactor exit stream. After completing the experiment, the cylinder contained 1.13 grams of condensed gas. Upon opening the reactor, the lid had the same crystalline residue deposited on the side exposed to the reactor interior. The residue became quickly hydrolyzed in the presence of air. Submerging the lid in a bath of distilled water produced the same yellow-orange colored solution. The inside walls of the reactor exposed to the high temperature had blue-green scale covering the surface. It is

evident from these observations that the condensed GeF_2 deposit is formed as a result of GeF_4 interaction with the HR160[®] alloy or nickel beaker. Additional discussion will be presented later after detailing experiments performed in the alternate reactor configuration, namely the tube reactor.

Investigation of the tube reactor configuration was performed by conducting nine experiments, the first using a 304L stainless steel reaction tube and eight using a nickel 200 alloy tube reactor. Results for the nine trials are given in **Table 14**, showing reaction parameters as well as "calculated" and experimental "observed" values. Again, the "Reaction Conversion" and "Capture Efficiency" values were calculated in a similar fashion to those reported for the crucible reactor experiments, thereby making it possible to compare the performance of the two reactor designs directly.

Table 14.

Reaction carried out in the tube reactor setup.

GeFusn Expt No.	Atm/T/Time gas / °C / hr	Flow Rate motive gas	Reagent Weight	GeO ₂ Content	Moles GeO ₂	Calculated wt. GeF ₄ expected ^a	Calculated residue wt expected ^a	Calculated wt loss of reagents ^a	Observed wt. loss of reagents	Observed wt. gain in cylndr	residue wt. reclaimed ^d	Reaction ^b Convers'n	Capture ^c Efficiency
		cc/min	gm	wt%	(n)	gm	gm	gm	gm	gm	gm	%	%
Experiment performed in the 304L stainless steel tube reactor.													
24	He/850/2.5	100	31.1941	0.24236	0.07228	10.7405	20.4535	10.7406	9.2584	0.560	20.0995	86.2	6.0
Experiments performed in the Ni tube reactor.													
25	He/800/2.5	67	15.6158	0.24004	0.03584	5.3252	10.2905	5.3253	5.2217	3.000	10.3941	98.1	57.5
26	He/800/2.5	150	15.9473	0.24004	0.03660	5.4383	10.5092	5.4381	5.2724	3.570	10.6749	96.9	67.7
27	He/700/5	150 - 67	17.2200	0.23991	0.03950	5.8689	11.3510	5.8690	3.2175	2.410	14.0025	54.8	74.9
28	He+air/700/5	76 (67 He+9air)	16.0310	0.23991	0.03677	5.4637	10.9595	5.0715	4.5359	4.430	11.4951	89.4	97.7
29	He+air/725/5	76 (67 He+(air)	14.9553	0.23991	0.03430	5.0971	10.2241	4.7312	4.1634	3.950	10.7919	88.0	94.9
30	He/750/5	67	16.9337	0.23991	0.03884	5.7713	11.1622	5.7715	4.3015	3.150	12.6322	74.5	73.2
31	He/775/5	67	15.7964	0.23991	0.03623	5.3837	10.4126	5.3838	5.2794	4.000	10.5170	98.1	75.8
32	He+air/750/5	82 (67He+15air)	17.1139	0.23991	0.03926	5.8328	11.6998	5.4141	4.8197	4.690	12.2942	89.0	97.3
a assumes 100% reaction conversion													
b Reaction Conversion = Observed wt loss of reagents/Calculated wt loss of reagents x 100%													
c Capture Efficiency = Observed wt gain in cylinder / Observed wt loss of reagents x 100%													
d Residue weight reclaimed = Weight of the boat+residue after reaction - initial weight of empty boat													

The first experiment carried out in a tube reactor was GeFusn-24. The reaction tube was constructed of type 304L stainless steel with a tube diameter of 2.75". The reaction parameters for this trial are given in **Table 14**. Upon concluding the run, the same set of gravimetric measurements was recorded as done in previous experiments. The residue left in the alumina boat was totally black in color indicative of a high degree of conversion. However, the weight of the boat was dramatically altered (1.8164 gram increase) by the growth of unremoveable scale on the bottom exterior surface where the boat came into contact with the stainless steel tube. Values for the "Observed weight loss of reagents" and the "residue weight reclaimed" include this artifact which compromised the accuracy of these data. Nonetheless, it is clearly evident that most of the volatile product created by the reaction never made it to the collection vessel, culminating in a capture efficiency of only 6%. Upon disassembling the reactor sections downstream from the furnace, there was clear evidence of hydrolyzed GeF_2 residue distributed on tube wall surfaces leading to the collection cylinder. From visual inspection of the heated section of the tube, most of the generated GeF_4 reacted with the 304L stainless steel. No further experimentation was performed in this apparatus due to the poor result.

A larger group of experiments was carried out using a 1" OD reaction tube constructed from nickel 200 alloy. Results for those trials are also posted in **Table 14**. In those trials, the reaction conversion ranged from a high of 98.1% (for GeFusn-25 and -31) to a low of 54.8% (for GeFusn-27). Likewise, the capture efficiency spanned a broad range from 97.7% (for GeFusn-28) down to 57.5% (for GeFusn-25). Influence of various reaction parameters can also be seen amongst the eight experiments. The influence of reaction temperature can be followed by comparing GeFusn trials 27, 30 and 31, which showed a significant increase in reaction conversion as the temperature was stepped up from 700°C (GeFusn-27) to 775°C (GeFusn-31) in a helium atmosphere. More importantly, a significant increase in capture efficiency of more than 20% was seen when the reaction atmosphere was changed from pure helium to one containing a mixture of helium and air (for GeFusn-28, -29 and -32). The GeFusn-28 trial posted the highest capture efficiency at 97.7% combined with an 89.4% reaction conversion. It is of interest to note that in the trials where air was introduced to the carrier stream (GeFusn-28, -29 and -32) it appears that the reaction conversion reached an upper limit around 89%, regardless of temperature. Additional results concerning the selection of optimum reaction parameters is included in a later section 8.2.3 dealing with optimization of product yield.

Overall, reactions conducted in the tube configuration yielded higher levels of conversion and capture efficiency. More importantly, the collection of GeF_4 increased significantly with the use of nickel 200 alloy to fabricate the reaction tube. The better performance observed during the tube trials is supported further by several key observations seen routinely across the series of eight reactions. They include:

1. onset of gas evolution
2. formation of crystalline condensate (GeF_2).

In brief:

1. Evolution of GeF_4 was confirmed by observing a stream of white vapor leaving the exit line from the reactor at a furnace temperature of 700°C. Prior to the use of the nickel tube, the reaction between UF_4 and GeO_2 was not seen until the reaction temperature eclipsed the 775°C threshold. The ability to carry out the reaction at lower temperatures will reduce the corrosive attack of the reaction atmosphere on reactor hardware and decrease the loss of GeF_4 through destructive side reactions. In all reactions prior to using the nickel material, the GeF_4 being produced (at temperatures between 775°-925°C) most likely was consumed by reacting within

the immediate vicinity of the hot zone with the vessel material. There is evidence of a fine, light green substance coating the interior surface of the nickel tube in the area of the intense heat. This is believed to be a coating of Ni_2GeO_4 generated by the reaction of GeF_4 with nickel oxide that is present as a result of moisture desorbing before and during the reaction.

2. The deposition of a white, crystalline residue at the end of the tube, just outside the body of the furnace, was seen to some extent in all eight experiments. It appeared that the residue condensed to liquid first before solidifying since most of the deposit was situated along the tube floor especially in the area where the tube diameter was reduced to $\frac{1}{2}$ ", then to $\frac{1}{4}$ " via *Swagelok*[®] reducing unions. Upon exposure to air, the same hygroscopic behavior was observed where the solid quickly became wetted. In two experiments an attempt was made to estimate how much residue collected in the area where the tube diameter narrowed. Almost all the residue was deposited on the surfaces of the reducing unions so they were quickly submerged in distilled water after dismantling the reactor after each reaction. The parts were washed clean of deposits and the resultant solutions dried to recover hydrolyzed material. Those results are shown in **Table 15**. The identity of the hydrolyzed residue was confirmed as GeO_2 by x-ray powder diffraction analysis.

Table 15.

Recovery of GeF_2 deposits from reactor hardware.

Experiment ID	Weight of material recovered (grams)	Fraction (%) of initial charge of GeO_2 used in the reaction
GeFusn-26	0.4873	12.7
GeFusn-31	0.8800	23.2

As found earlier in the crucible reactor study, a significant fraction on the order of 23.2% of the GeO_2 put in as reactant for the GeFusn-31 trial was lost to the condensed GeF_2 residue instead of being captured as GeF_4 . Quantitative results were not collected for all the reactions but two trends stand out. First, reactions carried out at lower temperature produced lesser amounts of residue downstream from the reactor hot zone. Secondly, reactions where air was included in the carrier gas stream tended to deposit lesser amounts of residue. It is clear that the formation of the Ge rich deposits is not exclusive to either of the reactor designs being evaluated. However, using suitable reaction parameters the amount of unwanted residue can be controlled and minimized.

Characterization of the reaction products synthesized during the reactor design trials was also done. The solid residues were examined using x-ray diffraction techniques while the reactor off-gas was analyzed by FT-IR spectroscopy. Results of the x-ray diffraction analyses are presented first followed by FT-IR analysis of the material collected in the 150cc gas sample cylinders.

X-ray Diffraction Analyses of Reaction Residues.

X-ray diffraction patterns for each of the residues recovered during the crucible reactor investigation (GeFusn-19, -20, -21, -22 and -23) are compiled in **Figure 9**. Reference patterns for UF_4 (pdf# 32-1401), UGeO_4 (pdf# 13-0588) and UO_2 (pdf# 41-1422) are included above the

Figure 9. XRD patterns for materials recovered from crucible reactor experiments GeFusn-19, -20, -21, -22 and -23 and reference patterns for UF₄ (pdf# 32-1401), UGeO₄ (pdf# 13-0588) and UO₂ (pdf# 41-1422).

experimental patterns. The predominant phase in each of the patterns matched well with the reference for UO_2 . Evidence for unreacted UF_4 and the presence of UGeO_4 were detected in differing amounts among the group. Patterns for residues from GeFusn-21 and -23, which were run at the 925°C temperature, showed only a trace of UF_4 in GeFusn-21 or none at all as in GeFusn-23 where the conversion was 95.2%. At the lower temperature of 875°C , lower conversion was confirmed by the appearance of more UF_4 and the formation of UGeO_4 that was apparently formed by a reaction between UO_2 and GeO_2 .

Analysis of the material recovered from the stainless steel tube apparatus, GeFusn-24, is shown in **Figure 10**. At 850°C it is clear the reaction went essentially to completion since no other phases could be identified other than UO_2 . The listed conversion of 86.2% (see **Table 14**) is remarkably low when taking into consideration the XRD result which has a limit of detection (LOD) on the order of 1-3 wt% for UF_4 .

The XRD results collected for the materials coming out of the nickel tube setup are sectioned into three groups. Analyses of samples collected from GeFusn-25 and -26 are shown in **Figure 11**. The patterns for each solid left in the reaction container matched well to UO_2 . No other phases could be detected indicating the reaction was essentially done after 2.5 hours at 800°C .

Residues reclaimed from the reactions carried out using only helium as the sweep gas are shown in **Figure 12** for GeFusn-27, -30 and -31. Included in the figure are reference patterns for UF_4 , UGeO_4 and UO_2 above those of the individual solids. It is clear that the pattern recorded for the GeFusn-31 residue showed only one phase present, namely UO_2 , which reinforces the observed conversion value of 98.1%. Reactions carried out at lower temperature (700°C and 750°C) revealed the presence of unreacted UF_4 and UGeO_4 in addition to UO_2 . The most predominant product identified in the GeFusn-27 material was not UO_2 but rather UGeO_4 . This is significant since although the conversion was only slightly greater than 50%, there was no evidence of any GeO_2 present. This observation indicates the reaction that produces GeF_4 is no longer between UF_4 and GeO_2 but instead controlled by

Lastly, the XRD patterns for the materials produced from the reactions where air was introduced into the helium carrier, i.e. GeFusn-28, -29 and -32, are shown in **Figure 13**. The multi-plot contains reference patterns for the two most abundant phases found, U_3O_8 and UO_2F_2 . Although the conversions determined from the gravimetric results were on the order of 88.0-89.4%, no evidence of unreacted UF_4 was seen. Instead, the presence of air in the reaction atmosphere resulted in the formation of U_3O_8 as the dominant uranium oxide phase. The other phase identified in all three post reaction residues was UO_2F_2 . The presence of this compound provides evidence to support the synthesis of GeF_4 may occur by a second reaction pathway given by

The *Gibbs* free energy¹⁴ for this reaction at 700°C is -19.496 kcal/mol. It is also interesting to note that no UGeO_4 was found in any of the post-reaction solids when air was included in the reactor sweep gas, irrespective of reaction temperature.

Figure 10. X-ray diffraction pattern for residue recovered from GeFusn-24 and reference pattern for UO_2 (pdf# 41-1422).

Figure 11. X-ray diffraction patterns for the solids recovered from GeFusn-25 and -26 and the reference pattern for UO₂ (pdf# 41-1422).

Figure 12. X-ray diffraction patterns for the residues recovered from GeFusn-27, -30 and -31 and reference patterns for UF₄ (pdf# 32-1401), UGeO₄ (pdf# 13-0588) and UO₂ (pdf# 41-1422).

Figure 13. X-ray diffraction patterns for the residues recovered from GeFusn-28, -29 and -32 and reference patterns for U_3O_8 (pdf# 47-1493) and UO_2F_2 (pdf# 25-1115).

FT-IR Analyses of Reaction Product Collected in the Gas Cylinder.

Infrared analysis of the gas phase product produced in the crucible and tube reactor experiments was done to verify the gas was indeed GeF_4 and also to comment on purity with respect to other foreign species such as HF and H_2O which may have been liberated during the reaction. The measurements were made using a *Nicolet Magna-IR 560* optical bench situated with a KBr beamsplitter and DTGS detector. Gas samples were contained in a gas-tight 10cm cell outfitted with zinc selenide windows and a programmable heater for maintaining the cell at 125°C to displace adsorbed moisture prior to data collection.

Infrared spectra of the gases collected from three of the five reactions performed in the crucible reactor are shown in **Figure 14** along with reference spectra for GeF_4 and SiF_4 to help with identification of constituent absorption bands. The infrared spectra for the GeFusn-19 sample and two reference materials were collected at *Voltaix* (High Springs, FL) using similar instrumentation. The data for the three trials shows that GeF_4 was produced by the reaction between UF_4 and GeO_2 . However, the gas leaving the reactor also contained a significant amount of SiF_4 that was trapped in the gas cylinder. For the GeFusn-23 sample, the fraction of SiF_4 may be greater than 50% of the gas mixture based on the ratio of intensities of each compound's major absorption band after diluting the cell contents with nitrogen to bring them onto the same absorbance scale. **Figure 15** depicts a magnified view of the absorbance scale over the wavelength region between $4000\text{--}2200\text{ cm}^{-1}$ for the three gas samples. From this view it is evident the gases also contained small amounts of substances such as HF and other unknowns (see the C-H stretch @ 2970 cm^{-1}). The peaks located between $3740\text{--}3570\text{ cm}^{-1}$ belonged to CO_2 which was present as part of the ambient atmosphere inside the instrument chamber during data collection and not as a component of the gas coming from the cylinder.

The presence of SiF_4 in all the gas generated using the HR160[®] alloy crucible reactor can be traced back to the corrosion and scaling problem observed after each trial. *Haynes* HR160[®] material contains up to 2.75 wt% silicon, which is evidently unstable in the GeF_4 at the reaction temperatures employed. A reaction between the Si component and GeF_4 to produce SiF_4 can be written as

Thermodynamic calculations¹⁴, using elemental Si as a first approximation of reaction energetics in equation (3), show that the reaction at 900°C is notably spontaneous ($\Delta G = -98.913\text{ kcal/mol}$).

The other elements making up the alloy (37Ni, 30Co, 28Cr, 3.5Fe) with the exception of nickel, all show similar spontaneous reaction ($-\Delta G$ values) when contacted with $\text{GeF}_4(\text{g})$ at such high temperatures. The HR160[®] alloy is degraded during production of GeF_4 and the purity of the gas liberated was diminished by unwanted SiF_4 . For these reasons, it is not feasible to construct the production scale reactor from this material.

Figure 14. Infrared spectra of gas samples produced in GeFusn-19, -20 and 23 and reference spectra for GeF₄, SiF₄ and BF₃.

Figure 15. Enhanced view of the spectral region between 4000-2200cm⁻¹ for samples collected in GeFusn-19, -20 and -23 and reference spectrum for GeF₄.

Analysis of the gaseous product collected from the GeFusn-24 trial using the type 304L stainless steel tube reactor is shown in **Figure 16**. As evidenced by the poor collection efficiency, most of the condensed gas from the reactor was SiF_4 with only a small amount of GeF_4 . A trace amount of BF_3 was also identified along with HF and CO_2 . The synthesis of SiF_4 was a result of the destructive attack of the GeF_4 on the tube material thereby ending any further use of the apparatus in additional experiments.

The FT-IR analyses of the gases produced in the nickel tube are grouped in a manner similar to how the XRD results were presented. Spectra of the samples drawn from GeFusn-25 and -26 trials are shown in **Figure 17** along with references for GeF_4 , SiF_4 and BF_3 . The quality of the GeF_4 was vastly improved compared to material collected in previous experiments. The trace amounts of both SiF_4 and BF_3 seen in either run may be due to desorption of these substances from the interior walls of the 1/8" tube leading to the gas cell which ran about five feet from the cylinder to the instrument. **Figure 18** represents a magnified view of the region showing absorption bands for residual HF which were also present in the reference spectrum of GeF_4 collected at *Voltaix, Inc.* Multiple bands caused by CO_2 present in the ambient atmosphere inside the spectrometer were also marked.

The second group of spectra representing gases collected where helium was used exclusively as the carrier, are illustrated in **Figure 19** for experiments GeFusn-27, -30, and -31. Reference spectra for BF_3 and GeF_4 collected at *Voltaix* are included below those for the three synthesized samples. Only a small amount of BF_3 impurity can be identified in the GeFusn-27 and -30 materials. The reaction product from GeFusn-31, which was analyzed at *Voltaix* (High Springs, FL), is essentially identical to the reference spectrum for GeF_4 . A view of the magnified scale over the 4000-2200 cm^{-1} region, drawn in **Figure 20**, shows that HF is also a trace impurity in all spectra except for the GeFusn-31 run. It is not clear why this spectrum shows only bands due to H_2O and none for HF.

Spectra from experiments where air was also included in the reaction atmosphere, i.e. GeFusn-28, -29 and -32, are displayed in **Figure 21**. Germanium tetrafluoride produced in all three trials was essentially pure when compared to the reference spectrum supplied by *Voltaix*. A small trace of BF_3 was again observed in the GeFusn-29 specimen and was attributed to the desorption off the surfaces of the sections of tubing bringing gas to the gas cell. The presence of air in the reaction environment did not alter the gas phase product made when UF_4 was reacted with GeO_2 . The introduction of air was extremely beneficial to improved collection efficiency, which was due in part to less GeF_2 being created. A magnified view of the 4000-2200 cm^{-1} region is shown in **Figure 22**. There was a small amount of HF in each of the GeF_4 spectra including the reference spectrum. Its origin in the samples made by the reactions performed here was most likely a consequence of residual adsorbed moisture being liberated during the reaction period. Using fully dehydrated UF_4 and GeO_2 reactants may help to further decrease the level of HF seen here.

Figure 16. Infrared spectrum of gaseous product collected in GeFusn-24 and reference spectra for GeF₄, BF₃ and SiF₄.

Figure 17. Infrared spectra for gases made in GeFusn-25 and -26 and reference spectra for SiF₄, BF₃ and GeF₄.

Figure 18. Enhanced view of the spectral region between 4000-2200cm⁻¹ for GeFusn-25 and -26 samples and reference spectrum for GeF₄.

Figure 19. Infrared spectra for gas samples taken from GeFusn-27, -30 and -31 and reference spectra for GeF₄ and BF₃.

Figure 20. Enhanced view of the spectral region between 4000-2200cm⁻¹ for GeFusn-27, -30 and -31 and reference spectrum for GeF₄.

Figure 21. Infrared spectra for gas samples taken from GeFusn-28, -29 and -32 and reference spectra for GeF₄ and BF₃.

Figure 22. Enhanced view of the spectral region between 4000-2200cm⁻¹ for GeF₄-28, -29 and -32 and reference spectrum for GeF₄.

8.2.2 Materials of construction for production of GeF_4 .

Results for all of the corrosion studies carried out in this program are presented next. These findings are arranged by the name of the metal or alloy tested.

Nickel

The Ni coupons were tested in Corrosion Experiment 2. The sample placed in the outlet was covered with a white residue, which liquefied on contact with air. When this was rinsed off, some scale was visible. EDS analysis showed that Ni, Ge, and O were all present on the surface of the outlet sample. Some Ca was also present, due to the lime used to neutralize the white residue.

The crucible sample had scale with varying degrees of adherence. SEM/EDS analysis showed large numbers of Al-F crystals that were quite adherent. Several smooth areas proved to be high in U. Other areas, which showed up gray in the SEM photos, proved to be Ni-Ge-O with a range of grain sizes. The scale was also examined by x-ray diffraction and matches reasonably well with both Ni_2GeO_4 and NiF_2 . Unreacted UF_4 was also found clinging tenaciously to the Ni, which was unexpected. It is not clear why the reaction was incomplete.

A Ni boat exposed to the product gas stream in a Ni reaction tube developed green residue. The SEM/EDS data shows that there are areas of Ni, Ge, and O as illustrated in **Figure 23**, and areas of Ni and F as seen in **Figure 24** and that these areas are separate. That is, there is no Ge where there is Ni and F, indicating the possibility of a protective NiF_2 scale. This occurs on the outside of the boat as well as the inside, indicating that the reaction is also occurring in the gas phase.

Figure 23. EDS pattern from the inside surface of the Ni boat.

Figure 24. EDS pattern from the outside surface of the Ni boat.

Monel

A Monel coupon was tested in the second experiment. The sample that had been embedded in the reaction mixture had a noticeable green scale. A fairly good match was made with NiGeO_4 in the x-ray diffraction pattern, but a Cu-Ni-Ge oxide was also a possible match. The scale was complex with a range of morphology, as seen in **Figure 25**. Small cubic crystals that appeared white in the backscattered image contained Al and F. Some regions were very smooth, containing large amounts of U, but no significant amount of any other elements. The Ni peak was surprisingly small in much of the area, although Ge, O, and U were present in large amounts. Some small crystals contained Ni, Ge, and O. The large amount of O was difficult to explain, since the primary source for oxygen was the GeO_2 starting material.

Figure 25. Backscattered image of Monel coupon after being embedded in the reaction mixture.

The sample placed in the outlet tube had obvious scale when viewed in the SEM. A scan of the entire area showed Ni, Cu, O and Ge. The Ge peak was definite, but slightly smaller than the crucible sample. There were also some areas containing Mn, Si, and Fe, most likely from the HR160[®] reactor. The backscattered image had black, white, and gray areas. About 40% of the surface was black and contained Ni, Cu, a large amount of O, and a definite Ge peak along with some Si and Cr. The gray areas contained Ni, Cu, O and slightly less Ge than the black regions. The white regions contained Ni, Cu, O, Mn, Fe, and just a trace of Ge.

Inconel 600

Coupons of Inconel 600 were tested both in Corrosion Experiment 1 and Corrosion Experiment 2. Information from the manufacturer indicated that the material should be acceptable at temperatures up to 1095°C, but may suffer from poor resistance to HF vapor at 48% concentration at 75°C. The coupon from Corrosion Experiment 1, which had been exposed to dry GeF_4 had fairly obvious scale. Dark regions in the backscattered image contained large amounts of F and O, and nearly equal amounts of Cr, Fe, and Ni. White regions in the image contained more Cr, O and F than Fe and Ni. No Ge was found anywhere on the coupon, and a small amount of Al was visible in one region. These results are consistent with the starting material and indicate some oxidation and fluoridation, but no gross corrosion.

The sample placed in the outlet of the crucible reactor did not look outwardly changed from the starting material and no obvious scale was visible. One small spot had a trace of Ge. The rest of the sample did not look different from the starting material except for some oxidation.

The sample exposed to the reaction mixture in the crucible had an obvious scale, as seen in **Figure 26**. Many Al-F containing crystals were present on the surface. The backscattered image contained white and gray regions. Gray areas contained Ni and Ge in large quantities along with some O. The white regions, which were highly adherent, contained large quantities of U and Ge along with Cr, Ni, Fe, O and Al. The Cr, Ni, Fe, and O were in similar ratios as in the outlet sample, but with U and Ge present as well. In addition, there was some unreacted green salt underneath some of the coupons in the crucible, which was not the case in other similar experiments without the corrosion coupons.

Figure 26. Backscattered image of Inconel 600 coupon after exposure to the reaction mixture.

The sample exposed to dry GeF_4 had light and dark regions in the backscattered image that appeared almost like striations in the SEM. An EDS scan of the entire surface showed Ni, F, Cr, O, and smaller amounts of Fe, Al, and Mo. Dark areas of the image seem to be high in Ni and F, but have a slightly larger Mo peak. White regions had Ni, F, high Cr and O peaks, but no Mo. As the starting material is 25% Mo, it is significant that many surface areas contained no Mo, suggesting that volatile MoF_6 may have been formed. Because of the suggestive surface results, the sample was sectioned and the cross section examined, as shown in **Figure 27**. The surface scale was 3-4 microns thick, and contained primarily Ni and F, with some Cu and O (spots 1 and 2). Directly underneath the scale were some spots that were very high in Mo (spot 3). By 8.5 microns into the material, the composition was that of the base material (spots 4-6). Several more spots with excess Mo were found at a depth of 13 microns (spots 7 and 10). Some Ge was found slightly beneath the surface scale (spot 3), suggesting that some Ni-Ge compound may have formed before the Ni-F scale was finished forming. However, no Ge was found at the surface, indicating that the scale was protective, and did not react with the GeF_4 product gas.

Figure 27. Cross section of *Haynes 242* coupon exposed to dry GeF_4 .

The sample tested in the crucible furnace outlet had Ni, Mo, and Cr in the expected proportions. There was also a small but significant Ge peak, along with O. Some scale was present, but in reasonably small amounts.

The sample embedded in the reaction mixture appeared to have a fine scale when viewed in the SEM. Backscattered images showed white, gray, and black regions. The white region was high in U, followed by O, Cr, Fe, and a slight trace of Ge. The gray area was high in Ni and Ge,

with a small amount of O. The black region had Cr as the primary constituent, accompanied by Fe, O, Ni, and Ge. Again, Mo was not visible on the surface, which perhaps indicates that this alloy must be pretreated before use to form a protective scale and volatilize any MoF₆ that is likely to form.

Haynes HR160[®]

Coupons of this alloy were tested in Corrosion Experiment 2. In addition, the crucible reactor itself was made of HR160[®], and some scale from the hot zone was also examined. The sample placed in the outlet tube showed significant scale. In addition, the grain boundaries were highly visible, and the surface was pitted. The backscattered image again showed black, gray, and white regions. The black areas contained a large amount of Si, along with Ge and O. The gray areas contained Cr, Ni, Co, Si, C, O and a trace of Ge. The white area contained the same elements, also with a trace of Ge.

Scale from the hot zone of the reactor was examined by Dr. Nancy Levoy using the SEM/EDS unit. The reactor surface was blue-green in color, and contained Cr, Co, F, U, and some Ni and Fe. The side of the scale that was originally not in contact with the reaction was brown. This side contained Cr, Co, F, O, Ge, Ni, and a minor Fe peak. There was less Ni than Cr or Co present. Earlier results showed Ge on both surfaces of the scale, along with Ni depletion.

The sample that had been in contact with the reaction mixture was much affected. There was a large amount of scale, some of which was adherent. The scale was very porous, as seen in **Figure 28**. A scan of the entire scale showed Co, Ni, O, a significant amount of Ge, U, Cr, and a trace amount of Fe. Some regions looked very angular in the backscattered image, and those areas were high in U, with Co, Ge, and O also present. The flat gray areas in the image were higher in Ni than other areas, with nearly equal amounts of Ge, Co, and Cr. There was an area lacking obvious scale, and this region had high Ni, high Ge, and O, with small amounts of U, Cr, and Co. There was also a thicker looking scale on the edge of the sample that contained Co, Cr, U, significant Ge, and O.

Figure 28. Haynes HR160[®] coupon exposed to the reaction mixture.

Type 304 Stainless Steel

Samples of 304 stainless steel were tested in both corrosion experiments. The sample exposed to dry GeF_4 had a fine scale over the whole sample, with some smaller surface crystals. A scan of the whole scale showed high amounts of Fe and Ge, along with Ni, Cr, O, F, and a trace of Si. One bright surface spot consisted of Cr, Si, Cl, and trace Ge. In general it seemed that even dry GeF_4 reacted substantially with 304SS.

The sample placed in the outlet of the crucible reactor did not have an enormous amount of scale, but definitely had some scale, and that scale was not particularly adherent. The most prevalent phase, which appeared gray in the backscattered image, contained Fe, Cr, a large amount of Ge, O, and Ni. There were also black chunks that were high in Ca, Fe, Ge, and O, with some Al. The white areas contained Fe, Cr, Ni, O, Ge, and a small amount of F.

The crucible samples were heavily encrusted with gray scale, including some relatively large (20 micron) crystals. The area scan showed Fe, Cr, Ni, F, O and a small but significant Ge peak. The white area in the backscattered image, shown in **Figure 29**, had high Ni, Fe, high Ge, and a small amount of F. The gray area (the primary phase) had Fe, Cr, high F, some O, nothing else. The dark area had Fe, Cr, high F, moderate O, trace U, and trace Ge. It seems that the Ge is in reasonably large particles on the surface. In general, this material behaved very poorly in these environments.

Figure 29. Type 304 Stainless Steel coupon after being embedded in the reaction mixture.

Copper

The sample exposed to dry GeF_4 in the tube reactor had very clearly visible grain boundaries and surface pits. An EDS scan of the entire area showed Cu, Ni, Ge, and O in large quantities. Some small specks on the surface contained Mg, F, and Ca, but may be from the neutralization treatment.

A copper tube assembly had been used inside the existing crucible reactor (for GeFusn-22) in order to create a chimney that would reduce the excessive internal volume of the reactor. At the conclusion of that reaction, the copper tube was sectioned for microscopy. **Figure 30** and **Figure 31** summarize the results of the EDS and visual examination of the tube sections. The inside of the tube contained large amounts of Ge everywhere but near the top, where a Ti-F-O phase was found. On the outside of the tube, Cu, Ge, and O were found, along with U in one location. Ge was always associated with Cu and O, wherever it was found.

Figure 30. Summary of the examination of the internal surface of the Copper chimney tube used in GeFusn-22.

Figure 31. Summary of the examination of the external surface of the Copper chimney tube used in GeFusn-22.

The sample located in the outlet tube of the crucible reactor had a fair amount of obvious scale. As before, the EDS showed Cu, Ge, and O, with about equal amounts of O and Ge. Multiple phases were visible in the backscattered electron image, shown in **Figure 32**. The gray region contained Cu, nearly as much Ge as Cu, along with O and some Ca. The black BEI phase contained mostly Cu, with smaller Ge and O peaks. The white phase in the backscattered image was almost completely Cu, with trace amounts of Ge and O.

Figure 32. Copper coupon exposed to GeF_4 gas in the crucible reactor outlet.

The sample that had been exposed to the reaction mixture had very large grains and some scale, along with larger adherent particles. The outside of the sample had some areas that were copper colored and some that had a silver cast, similar to the outside of some of the copper tube sections. The copper colored area contained mostly Cu, some C, trace Ni, and a very small trace of Ge. The silvery area contained a lot of Ni, a large amount of Cu, trace U, and a small amount of Cr. X-ray diffraction showed a good match with CuGe , however, this compound was very difficult to distinguish from pure Cu using x-ray diffraction.

In order to be an effective material of construction for fabricating a reactor, the alloy must be able to be structurally sound at the temperatures involved, not form extensive compounds with Ge, and not contribute gaseous impurities to the product. Although none of the materials were completely satisfactory, nickel, Inconel 600, and *Haynes* 242 performed the best according to these criteria.

Copper was not acceptable for several reasons. The reaction temperatures are near the limit of the useful range for Cu, and consequently excessive grain growth was observed. Copper and germanium formed intermetallic compounds, and although visually unchanged, the Cu samples picked up large quantities of Ge. The formation of Cu-Ge intermetallics was seen repeatedly, both in EDS and XRD analyses. In addition, literature sources indicate that Cu is highly undesirable in fluorine and fluorine containing gases¹⁵.

In this study, HR160[®] has been shown repeatedly to suffer from scale formation when exposed to GeF_4 . This is supported by the literature, which shows that alloys high in Cr and Co perform badly in fluorine environments due to the formation of Cr and Co fluorides¹⁶. In addition to the EDS data presented here, earlier work at *Starmet* showed that mixed Cr, Ni, and Co fluorides were formed after extensive exposure under reaction conditions. Monel also

showed extensive scaling and reaction between Cu in the alloy and Ge. Type 304 stainless steel, even when not visibly attacked, reacted extensively to form fluorides, and picked up a large amount of Ge on its surface. Again, the literature concurs that Fe based alloys are not effective for high temperature fluorine environments¹⁷.

Evidence suggests that Ni or a Ni-based alloy will be the best choice for a construction material. However, even these alloys seem to develop some Ni-Ge-O compounds in certain situations. To limit fluorine attack, it is standard practice to passivate Ni components by exposure to fluorine gas or HF in order to form NiF_2 in a protective layer¹⁸. This NiF_2 film has been shown to have strong resistance to both F containing gases and gas plasmas and is specifically recommended for semiconductor gases¹⁹. Examination of the *Haynes 242* coupon indicated that a layer of NiF_2 formed after exposure to the dry GeF_4 . Although *Haynes 242* formed MoF_6 on exposure to GeF_4 , which would introduce a gaseous contaminant, the alloy can be passivated by forming a protective NiF_2 layer. In addition, Mo is thought to improve the resistance of Ni alloys to fluoride attack¹⁵. Inconel and pure Ni, when properly passivated, would also form protective fluoride coatings. Evidence for this was seen when the Ni reaction boat was examined, showing no Ge present in areas high in NiF_2 .

In brief:

- Copper, type 304 stainless steel, Monel, and HR160[®] are not acceptable materials of construction;
- Nickel, inconel 600, and *Haynes 242* could be used if properly passivated;
- All materials should be passivated prior to use with GeF_4 .

8.2.3 Optimization of product yield.

In this task, several changes to the reaction system were made to improve the yield of GeF_4 . A larger reagent vessel made of nickel 200 alloy was put into service and the gas collection hardware was reconfigured by using a shorter outage tube in each cylinder. The first reaction to incorporate these changes was GeFusn-33. Results for this trial are presented in Table 16. Here, the reaction conversion was only 61.3% after 7 hours in the range between 700°C-775°C and capture efficiency for GeF_4 was 80.8%.

Table 16.

Reaction Profile for GeFusn-33.

Experiment ID:	042501-GeFusn-33		
System:	1"OD nickel tube reactor and 8" Ni boat		
Weight of reagents (gm)	41.643	wt% GeO ₂ : 24.1689	
Sweep gas:	Helium flow at 67 (cc/min)		
Pre-reaction drying period:	0.5 hour at 500°C in helium		
Total reaction time (hr):	7		
Reaction temperature profile	Time (hr)	at T (°C)	
	2	700	
	2	725	
	2	750	
	1	775	
Cylinder ID:	#10, 150cc volume, 304 stainless steel, single port with shortened outage tube		
Collection method:	liquid N ₂ bath		
Calculated weight of GeF ₄ expected (gm)	14.2983		
Observed weight loss of reagents (gm)	8.769		
Observed weight gain in the cylinder (gm)	7.09		
Reaction conversion (%)	61.3		
GeF ₄ capture efficiency (%)	80.8		

In GeFusn-33 a stepwise increase in temperature was followed in order to start the reaction off slowly without much disturbance to the near-capacity reagent bed. Ending the reaction period at the 775°C plateau was believed to be sufficient to react the UF_4 and GeO_2 completely but it was not the case. A significant fraction of the residue remaining in the boat was green in color indicative of unreacted green salt. X-ray diffraction analysis of the residue showed it to be a mixture of UO_2 , unreacted UF_4 and UGeO_4 , as shown in Figure 33. Reference patterns for the three matching phases are also included.

Figure 33. X-ray diffraction pattern for the residue recovered from GeFusn-33 and reference patterns for UF₄, UO₂ (pdf# 41-1422) and UGeO₄ (pdf# 13-0588).

Analysis of the GeF_4 collected in cylinder #10 was accomplished using FT-IR spectroscopy. A spectrum of the gas produced in the reaction is shown in **Figure 34** along with a reference spectrum of GeF_4 supplied by *Voltaix, Inc.* Comparing the *Starmet* material to the reference, the amount of HF impurity is greater in the synthesized product made by the solid state reaction. Additional in-depth analytical characterization is required to determine if the larger amount of HF is indeed a result of the reaction or an artifact of in-situ hydrolysis caused by moisture adsorbed on the walls of the line carrying the gas from the cylinder to the infrared spectrometer. As part of the routine reaction profile at the beginning of each trial, the reagent mixture is heated at a temperature just below the onset of reaction, typically 500°C , for about an hour to liberate any moisture adsorbed on the UF_4 or GeO_2 reactants. Typically, a heat gun is used to heat trace the line leaving the reactor up to the vent valve to expel any vapor from the system.

After observing the poor results obtained in the GeFusn-33 trial, where the conversion was only 61.3% after 7 hours, a probe into the temperature profile of the tube furnace was started since leftover residue at one end of the 8" boat was black while the other end contained green, essentially unreacted powder. Using an empty tube outfitted a thermocouple (see **Figure 6**), temperature data were recorded at four points along the length of the tube. Those measurements are compiled in **Table 17**, showing the spread in temperatures at five different furnace set points.

Table 17.

Internal temperature profile in the nickel tube reactor.

Furnace Set-point Temp $^\circ\text{C}$	Temperature at Indicated Points ($^\circ\text{C}$)			
	A	B	C	D
23				22
250		295	298	281
			297	280
500	527	535	538	520
		535	537	518
700	715	724	727	711
		723	726	710
775	787	795	798	782
		795	798	782
850	862	870	874	858
		870	872	857
	858	869	871	856
		867	869	

In general, within 4 inches of the midpoint of the hot zone (between points B and D) the measured temperatures were always above the furnace set-point temperatures by notable margins of $15^\circ\text{--}25^\circ\text{C}$. Measurements were made without the 8" boat or reagents in the reactor. At all the furnace set-points investigated, there was a measurable difference between temperatures at points B and D which did correlate to the approximate length of the larger nickel boat. At the 700°C

Figure 34. Infrared spectrum of GeF₄ collected from GeFusn-33 and a reference spectrum of GeF₄ supplied by *Voltaix, Inc.*

plateau and above, the margin was 13°C. This could help to explain why the left side of the boat (position B) contained fully reacted residue while the right side (position D) only partially reacted materials.

Following the probe into the temperature profile of the tube furnace, another experiment was performed in order to document two important aspects about the fusion reaction. In GeFusn-35, the gas produced by the solid-state reaction was not collected but analyzed directly by FT-IR spectroscopy at various stages during the reaction. The specific conditions for the trial are summarized in Table 18.

Table 18.

Reaction profile for GeFusn-35.

Experiment ID:	072601-GeFusn-35		
System:	1" OD nickel tube reactor with 8" Ni boat		
Weight of reagents (gm):	~22	wt% GeO ₂ : 24.9847 (stoichiometric mixture)	
Sweep gas:	Helium Flow at 68 (cc/min)		
Pre-reaction drying period:	1 hour at 350°C in helium		
Total reaction time (hr):	5.5		
Reaction temperature profile	Time (hr)	at T (°C)	
	0.75	650	
	2	700	
	2.75	725	
Cylinder ID:	none		
Collection method:	none		
Analytical method:	In-line FT-IR spectroscopy using 10cm gas cell at 130°C.		
	Multiple samples of gas were analyzed by FT-IR spectroscopy		
Calculated weight of GeF ₄ expected (gm)	~7.5		

Throughout the 5.5 hours of reaction the temperature was raised from 650°C to 700°C and finally to 725°C where it was maintained for 2.75 hours. First, the release of water vapor by the reagents during the pre-reaction drying period was cataloged. Representative spectra at temperatures between ambient and 350°C were recorded and presented in Figure 35. Compared to the baseline spectrum for helium, the liberation of moisture into the sweep gas passing over the reagent mixture can be seen beginning with the first analysis taken at room temperature. The broad bands characteristic of moisture grow steadily as the 350°C plateau is reached. After maintaining that temperature for 55 minutes, the uppermost spectrum in Figure 35 shows the sweep stream to be free of moisture vapor. It is clear that the pre-reaction period is important in clearing out adsorbed moisture from the reaction system and reactants prior to GeF₄ being generated.

Figure 35. Infrared spectra of gas samples taken during GeFusn-35 at various temperatures between ambient and 350°C.

The second observation to come out of the infrared data concerned the onset of reaction between UF_4 and GeO_2 . The liberation of GeF_4 was clearly evident at temperatures well below 700°C as seen by the group of spectra compiled in **Figure 36**. At a furnace temperature of 650°C (the actual internal temperature based on the thermal profile measurements shown in **Table 17** would be closer to 675°C), the concentration of GeF_4 in the gas stream is significant. At the 700°C and 725°C plateaus the amount of GeF_4 in the helium sweep stream was estimated to be 30 torr and 40 torr, respectively, as determined by peak area integration of numerous reference samples compiled at *Voltaix, Inc.* As seen in earlier experiments, lower reaction temperature resulted in less GeF_2 by-product formation, which is very desirable.

Upon removal of the boat from the reactor only a small portion of the residue was again blackened and a majority of the solid was varying shades of green. The 5.5-hour duration at the temperatures attained resulted in a small amount of conversion to GeF_4 . The reaction residue was analyzed by x-ray powder diffraction and the recorded diffraction pattern is shown in **Figure 37** along with reference patterns for UF_4 , UO_2 and UGeO_4 . It is most interesting to note that diffraction peaks for GeO_2 were not found and the most intense peaks matched those for the uranium germanium oxide compound. It appears at this point in the reaction scheme, the reaction dynamic is between UF_4 and UGeO_4 as shown in equation (8.5),

Formation of the UGeO_4 compound can be expressed by the reaction given in equation (8.6),

Figure 36. Infrared spectra of gas samples from GeFusn-35 at 350°C, 650°C, 700°C and 725°C.

*** Multi Plot ***

Figure 37. X-ray diffraction pattern for reaction residue from GeFusn-35 and reference patterns for UF_4 , UO_2 (pdf# 41-1422) and UGeO_4 (pdf# 13-0588).

After performing many experiments to produce GeF_4 using GeO_2 (99.999%) as the co-reagent with UF_4 , an alternative pathway was explored using Ge° metal. The new reaction scheme is shown in equation (8.7),

The new chemistry is based on the in-situ oxidation of Ge° to GeO_2 on route to forming GeF_4 . There was also a potential for this pathway to deliver a higher purity of fluoride since the metallic reagent does not contain the level of adsorbed moisture that is liberated when GeO_2 is reacted with green salt, as seen in *GeFusn-35*. Less moisture should result in a product containing less HF impurity.

For testing the pathway given in equation (8.7), two experiments were performed using the thermogravimetric analyzer (TGA) where milligram quantities of material were treated. First, the oxidation of Ge° metal was investigated by heating a small sample of powder to 1000°C in a stream of dry air. As illustrated in **Figure 38**, the sample weight increased more than 11 milligrams over the course of the heating period, providing strong indication that the metal was converted to oxide.

In a second experiment, a mixture of UF_4 and powdered Ge° metal was heated to 850°C at $10^\circ\text{C}/\text{min}$ in a stream of air. Results displayed in **Figure 39** showed the significant weight loss incurred as the temperature exceeded the 600°C range. The loss in weight is attributed to the volatilization of germanium and fluorine from the reaction mixture. Upon completion of the TGA run, the residue remaining in the TGA cup was analyzed by x-ray diffraction. Those results are given in **Figure 40**, showing that the post-reaction solid consisted of uranium oxide (U_3O_8) and a small amount of Ge° metal. These findings bolster the support for the pathway given in equation (8.7).

Sample: Germanium
Size: 38.6212 mg
Method: Ramp to 1000
Comment: metal oxidation in dry air

TGA-DTA

File: A:\082401.002
Operator: Bulko
Run Date: 24-Aug-01 14:16

Figure 38. TGA result showing the weight gain when Ge^o metal was heated to 1000°C in dry air.

Sample: Germanium
Size: 27.8128 mg
Method: Ramp to 1000
Comment: fusion reaction in dry air

TGA-DTA

File: A:\082701.002
Operator: Bulko
Run Date: 27-Aug-01 13:50

Figure 39. TGA result showing the weight loss when a mixture of UF_4 and Ge^0 metal was heated to 850°C in dry air.

Figure 40. X-ray diffraction pattern for residue recovered from the TGA reaction performed at 850°C and reference patterns for U₃O₈ (pdf# 47-1493) and Ge⁰ metal (pdf# 04-0545).

After establishing that the combination of UF_4 with germanium metal successfully liberated GeF_4 , the reaction was carried out on a larger scale using the 1"OD nickel tube reactor setup. The experiment was identified as GeFusn-39 and the details are given in **Table 19**. The source of metal was taken from a stock of 99.9% pure Ge lump which was broken up and ground to a fine powder using a mortar and pestle. The gas flow from the reactor was connected to the input of the gas-sampling cell within the FT-IR spectrometer and multiple spectra were recorded as the reaction progressed. Representative spectra recorded at 600°C and 700°C are shown in **Figure 41**. The first spectrum to show peaks for GeF_4 was taken as the reactor temperature reached 601°C. Peaks due to HF and SiF_4 impurities were also apparent. The reactor temperature was raised to 700°C and after 20 minutes, the gas flow to the gas cell ceased so the reaction was terminated. Upon disassembly of the reaction system, the 1/8"OD tube to the infrared cell was completely blocked with a white solid which over a short period of time became a tacky, wet slurry when exposed to air. The substance causing the blockage was believed to be GeF_2 , displaying similar characteristics to the white, hygroscopic solid produced in previous fusion reactions. After 30 minutes of reaction, conversion was estimated to be about 60.8% based on the weight loss of the reactants in the boat. Although the distribution of volatile fluoride between GeF_4 and GeF_2 was not measured, a significant fraction of the product appeared to be GeF_2 . Review of the literature has indicated that the difluoride compound is synthesized by passing GeF_4 over germanium metal^{20,21,22}, which in this case, is the most likely scenario occurring in this experiment. As such, further experimentation using Ge^0 metal as the reagent was curtailed.

Table 19.

Reaction profile for GeFusn-39.

Experiment ID:	083001-GeFusn-39		
Reaction:	$3\text{UF}_4 + 3\text{Ge}^0 \text{ powder} + 4\text{O}_2(\text{g}) = 3\text{GeF}_4(\text{g}) + \text{U}_3\text{O}_8$		
System:	1" OD nickel tube reactor with 4" nickel boat		
Weight of reagents (gm):	10.9761		wt% Ge^0 : 18.73
Sweep gas:	air flow at 86 (cc/min)		
Total reaction time (hr):	0.5		
Reaction temperature profile	Time (hr)	at T (°C)	
	0.17	600	
	0.33	700	
Cylinder ID:	none		
Collection method:	none		
Analytical method:	In-line FT-IR spectroscopy using 10cm gas cell at 130°C.		
	Multiple samples of gas were analyzed by FT-IR spectroscopy		
Calculated weight of GeF_4 expected (gm)	1.4028		
Calculated weight loss of reagents (gm)	3.0028		
Observed weight loss of reagents (gm)	1.8264		
Reaction Conversion (%)		60.8	defined as observ'd wt lost/calc'd wt lost

Figure 41. Infrared spectra of gas samples generated in GeFusn-39 taken at a temperature of 600°C and 700°C.

The last experiment conducted for optimizing the GeF_4 reaction concerned the determination of the reaction onset temperature (ROT). Earlier results showed that heating the reactants to 350°C was essential for sweeping away adsorbed moisture from the reaction environment before the fluoride gas was made. At 650°C the reaction was well underway. It became necessary to identify the temperature at which point the reaction commenced in earnest, yielding high quality product. To accomplish this, the TGA instrument was used in performing one experiment where a mixture of UF_4 and GeO_2 was heated to 500°C (at $15^\circ\text{C}/\text{min}$) in streams of air and argon. The weight loss curves for three successive heating cycles are displayed in **Figure 42**. The first two cycles where air was used as the sweep gas showed significant weight loss commencing about 400°C . Likewise, the third cycle, where argon was the sweep gas, the same trend was seen. As the temperature reached the 500°C plateau, the loss of weight became steady at rates in the range of 0.7% - 1.0% per hour.

In previous experiments where GeF_4 was collected in sample cylinders, the temperatures employed during the pre-reaction drying period have varied from 300°C to 500°C . From the TGA results in **Figure 42**, the production of fluoride gas was well underway at 500°C . In order to prevent significant amounts of reactants from being converted to product during the drying period, the dehydration temperature was set at 450°C when GeF_4 was collected for purity evaluation.

UF₄ + GeO₂ Heated to 500°C in Air and Argon

Figure 42. TGA results showing the temperature at which the reaction between UF₄ and GeO₂ starts producing GeF₄.

8.2.4. Development of analytical technology for identifying trace U in GeF₄.

Two samples of GeF₄, synthesized in laboratory trials, were sent to *Argonne National Laboratory (ANL)* for analysis using the two new techniques undergoing development by Dr. Beitz. The first multi-gram sample of fluoride material was made in the 1" Ni tube reactor and was packaged in a 300cc Monel gas cylinder equipped with a shortened outage tube made from 1/4" nickel tube. Details of the reaction are given in **Table 20** for GeFusn-36.

Table 20.

Reaction profile for GeFusn-36.

Experiment ID:	080201-GeFusn-36		
System:	1" OD nickel tube reactor with 8" Ni boat		
Weight of reagents (gm)	34.1057	wt% GeO ₂ : 24.9847	
Sweep gas:	Helium (62) + air (10) = total flow at 72 (cc/min)		
Pre-reaction drying period:	2 hours at 500°C in helium		
Total reaction time (hr):	5		
Reaction Temperature (°C)	750		
Cylinder ID:	#A1, 300cc Monel, double port, shortened Ni outage tube and Monel plug.		
Collection method:	n-propyl alcohol/liquid N ₂ bath at -62°C to -72°C		
Filter:	none		
Calculated weight of GeF ₄ expected (gm)	12.1056		
Calculated weight loss of reagents (gm)	11.2066		
Observed weight loss of reagents (gm)	9.1413		
Observed weight gain in the cylinder (gm)	6.46		
Reaction conversion (%)		81.6	defined as observ'd wt lost/calc'd wt lost
GeF ₄ capture efficiency (%)		65.4	defined as observ'd wt gain in cylinder / (rxn conversion) x wt GeF ₄ expected

For this reaction, the sweep gas through the reactor contained a mixture of helium and air, the pre-reaction drying period was extended to 2 hours at 500°C and the reaction temperature was maintained at 750°C for 5 hours. Under these conditions the reaction reached 81.6% conversion and 6.46 grams of GeF₄ was recovered in the sample cylinder. After completing the experiment, the residual helium/air atmosphere in the cylinder was removed using a mechanical vacuum pump while the cylinder was chilled at -70°C in an n-propyl alcohol/liquid N₂ bath. After the vacuum treatment, the cylinder contained 5.3 grams of GeF₄. The gas produced in GeFusn-36 was collected without passing it through a filter and was considered as the most 'crude' form (worst case scenario) with regard to possible U contamination.

The residue produced in GeFusn-36 was again characterized by x-ray powder diffraction. The contents of the boat were predominantly black across the length of the boat except for a small portion at one end, which was green. Samples of the black and green materials were analyzed and their diffraction patterns are shown in **Figure 43**. The black solid was clearly a match with the U₃O₈ reference pattern while the green sample contained unreacted UF₄ and

Figure 43. X-ray diffraction patterns for the black and green residues from GeFusn-36 and reference patterns for UO₂, (pdf# 41-1422), U₃O₈ (pdf# 47-1493), UGeO₄ (pdf# 13-0588) and UF₄.

peaks matching well with both UGeO_4 and UO_2 patterns. The composition of the partially reacted green solid has been consistent with diffraction results from previous experiments in that both UO_2 and UGeO_4 have been detected. Since air was added to the sweep gas in this reaction, the presence of UO_2 in the product was not expected but rather U_3O_8 . This would indicate that the gas passing over the reactant bed was deficient in oxygen when the reaction was stopped after 5 hours.

The second batch-production of GeF_4 was made as part of GeFusn-40. The same reaction system and gas collection hardware were used in preparing the second sample. The reaction profile for this operation is given in Table 21. Reaction conditions for this trial were slightly different than those for GeFusn-36.

Table 21.

Reaction profile for GeFusn-40.

Experiment ID:	011102-GeFusn-40			
Reaction:	$3\text{UF}_4 + 3\text{GeO}_2 + \text{O}_2(\text{g}) = 3\text{GeF}_4 + \text{U}_3\text{O}_8$			
System:	1" OD Nickel tube reactor with 8" nickel boat (including Ni foil spacer)			
Weight of reagents (gm):	36.4229	wt% GeO_2 : 23.4819%		
Sweep gas:	Helium (62) + air (20) = total flow at 82 (cc/min)			
Pre-reaction drying period:	1 hour at 450°C in helium			
Total reaction time (hr):	5.33			
Reaction temperature profile		Time (hr)	at T (°C)	
		0.33	725	
		0.50	750	
		3.33	775	
		1.17	800	
Cylinder ID:	#A2, 300cc Monel, double port, Monel plug and shortened Ni			
	outage tube.			
Collection method:	n-propyl alcohol/liquid N_2 bath at -85°C to -80°C			
Filter:	Osmonics 0.45 μ stacked PTFE® membrane / polypropylene shell			
Calculated weight of GeF_4 expected (gm)	12.1505			
Calculated weight loss of reagents (gm)	11.2782			
Observed weight loss of reagents (gm)	9.9823			
Observed weight gain in cylinder (gm)	8.33			
Reaction Conversion (%)		88.5	defined as observ'd wt lost/calc'd wt lost	
GeF_4 capture efficiency (%)		77.5	defined as observ'd wt gain in cylinder / (rxn conversion) x wt GeF_4 expected	

Notably, the pre-reaction drying period was changed to 1 hour at 450°C while the reaction temperature was ramped in steps over the range between 725°C-800°C during the 5.33 hour reaction period. Using this profile, reaction conversion was 88.5% and 8.3 grams of GeF_4 was captured in the sample cylinder after removing the residual helium/air carrier gas with vacuum

pump. In contrast to the first sample of gas sent to *ANL*, during the preparation of this sample, the gas was passed through a 0.45 μ stacked PTFE[®] membrane filter (*Osmonics, Inc.*, Westborough, MA) before collection in the 300cc Monel cylinder. The post-reaction residue from GeFusn-40 was not analyzed by x-ray diffraction but visual inspection showed a small portion of the material had the characteristic green color of unreacted green salt at one end of the reagent boat.

Detailed results from the program to develop analytical methodology to measure trace uranium in GeF₄ produced by the new fluoride extraction technology are contained in four interim progress reports provided by Dr. Beitz at *ANL*. Those reports describe the methods, equipment, procedures and results learned during that investigation and are included at the end of this report in **APPENDIX A**. Included below are the abstracts and/or summary for the interim reports highlighting the accomplishments of the program in chronological order.

March 12, 2001 Progress Report (J.V. Beitz and C.W. Williams)

We are developing two methods for ultratrace determination of uranium in germanium tetrafluoride (GeF₄) gas. Both methods are designed primarily for determination of uranium based on its most probable volatile chemical compound, namely uranium hexafluoride (UF₆). The first method relies on detection and measurement of UF₆ via its characteristic and very strong ultraviolet optical absorption spectrum. The scientific basis for this method is well established, although it is technically challenging to implement. Most of our work to date has been carried out to establish the scientific basis for our second method, which relies on laser-induced fluorescence of uranyl ions in glassy germanium dioxide (GeO₂). Hydrolysis of GeF₄ that contains UF₆ and subsequent treatment with ammonium hydroxide is expected to generate hydrated germanium dioxide (GeO₂) that contains uranyl hydroxo complexes. Thermal fusion of this material and rapid cooling should produce glassy GeO₂ that contains uranyl ions. Although this is a plausible scheme for ultratrace determination of uranium in GeF₄, it rests on the presumption that uranyl ions are chemically stable in molten GeO₂. We now have carried out studies on uranyl-doped glassy GeO₂ that have shown that 1) uranyl ions are stable for hours in molten GeO₂, 2) uranyl ions in glassy GeO₂ at ambient temperature are strongly luminescent, and 3) the likely limit of detection for uranium in GeF₄ using this method is 50 ppt (parts per trillion), or better, on a weight basis. Using our present non-optimized apparatus, we have achieved signal-to-noise ratios for uranyl ion luminescence in glassy GeO₂ that are equivalent to a limit of detection of 500 ppt.

October 23, 2001 Progress Report (J.V. Beitz and C.W. Williams)

One approach that we are investigating to improve analytical methods for quantifying uranium hexafluoride (UF₆) in germanium tetrafluoride (GeF₄) is hydrolysis of impure GeF₄ gas to generate GeO₂ and uranyl fluoride. Subsequent heating produces uranyl ions embedded in glassy GeO₂. In our earlier work, we showed that laser-induced fluorescence analysis for uranyl ion had the potential to detect less than 0.5 parts per billion of uranium in glassy GeO₂. We also noted difficulty in reproducibly creating visually clear, bubble-free glassy GeO₂ on the one gram scale. Bubble-free GeO₂ is required to achieve reproducible measurement of luminescence intensity. Such reproducibility is essential for quantitative measurement of uranium impurity content in analyzed samples via the standard addition method.

Based on a parametric study, we now have identified a simple means of producing visually clear, bubble-free glassy GeO₂ on the gram scale. However, this method creates an

impurity that, following excitation at 355nm, luminesces such that its emission spectrum and luminescence decay overlap those of uranyl ion in glassy GeO_2 . The impurity species likely is the result of thermal reduction of some tetravalent Ge in GeO_2 to divalent Ge. The impurity species grows in with increased sample residence time in the high temperature zone of the furnace. This impurity interference is present to varying degrees in all other methods that we investigated to minimize the presence of small bubbles in GeO_2 glass produced by melt processing in air. Given difficulties in producing glassy GeO_2 of acceptable quality for quantitative uranyl luminescence analysis, we began a search for alternate, but related methods of achieving our goal of improved ultratrace analysis for UF_6 in GeF_4 gas. We have identified a promising method that does not require high temperature processing and so is likely to be more easily and economically implemented in a quality assurance laboratory.

Our new approach retains the same initial step, namely, hydrolysis of GeF_4 gas in water to generate GeO_2 , H_2GeF_6 , and HF, and the same second processing step, namely sub-boiling point distillation of volatile species. Our new approach then dissolves the resulting non-volatile residue (GeO_2 and uranyl fluoride, if any UF_6 was present in the GeF_4) in concentrated hydrochloric acid. This converts GeO_2 to volatile GeCl_4 that is removed, along with excess hydrochloric acid, by a second sub-boiling point distillation. The residue (uranyl chloride and trace amounts of GeO_2) is taken up in dilute phosphoric acid solution. The uranium content of the resulting solution is quantified by laser-induced fluorescence and the standard addition method. This new approach will permit use of 266 nm excitation which has the advantage of being more strongly absorbed by uranyl in dilute phosphoric acid than is light at 337nm (nitrogen laser) or 355nm (tripled Nd:YAG laser). In consequence, limits of detection for uranyl comparable to the best reported in the literature (1 to 40 ppt) are expected. The primary interference that we anticipate in our germanium chloride volatilization process is luminescence from trace level organic contaminants leached from the perfluoropolymer distillation vessel. We expect to eliminate such interference by 185nm photolysis that should photochemically destroy such contaminants. In our initial studies of this new approach, we have hydrolyzed GeF_4 gas and verified volatilization of the resulting GeO_2 from concentrated hydrochloric acid.

Using a 9.3cm path length nickel-bodied, elastomer-free cell equipped with single crystal aluminum oxide windows, we have recorded the ultraviolet absorption spectrum of Starmet-produced GeF_4 gas. Based on those spectra and literature values for the molar absorptivity of uranium hexafluoride gas, Starmet-produced GeF_4 contains less than 0.75 parts per million (by volume) of UF_6 . Based on an observed small decreases in pressure upon contact of Starmet-produced GeF_4 gas with a clean, passivated vacuum system and subsequent FT-IR analysis of that GeF_4 gas using our nickel-bodied cell, we have concluded that the sample of Starmet-produced GeF_4 that we analyzed contains approximately 0.8% hydrogen fluoride (HF) gas by volume.

May 11, 2002 Progress Report (J.V. Beitz and C.W. Williams)

In lieu of a formal abstract for this report, a brief summary of the results is outlined below.

Work began on the alternative approach to determine U (as UF_6) in GeF_4 , termed 'chloride volatility'. In testing the new approach, a sample of fluoride was hydrolyzed in a small volume of water, contacted with concentrated HCl and subjected to a sub-boiling point distillation treatment. Solid residue recovered from the distillation treatment was analyzed by FT-IR spectroscopy using CsI powder to make a transparent pellet. The infrared spectrum of the

solid showed bands consistent with GeO_2 and bands correlating to CsGeF_6 produced by interaction of H_2GeF_6 and CsI . Further steam hydrolysis treatments were successful in converting the H_2GeF_6 fraction to GeO_2 . However, in subsequent steam hydrolysis trials, it took a total of 400ml of water and approximately 80 hours of contact with steam at slightly above 100°C to completely hydrolyze the combined $\text{GeO}_2/\text{H}_2\text{GeF}_6$ solids to GeO_2 . The steam hydrolysis apparatus was modified to enable vapor phase hydrochlorination of GeO_2 produced by the steam hydrolysis procedure. After three hours of reflux at 115°C the hydrochloric acid vapor treatment was not effective in converting GeO_2 to volatile GeCl_4 .

March 17, 2003 Progress Report (J.V. Beitz)

Our primary focus was evaluation of our proposed "chloride volatility" process for analysis of the uranium content of hydrolyzed GeF_4 gas. The basis of this process is detailed in our May 11, 2002 progress report. The process requires conversion of "particulate GeO_2 " into volatile germanium tetrachloride (GeCl_4). The "particulate GeO_2 " of interest is that which arises from repeated steam hydrolysis of the solids that result from reaction (hydrolysis) of GeF_4 with water. As noted in our May 11, 2002 report, the GeO_2 of interest is of the hexagonal structure type based on its infrared absorption spectrum. Standard reviews of germanium chemistry state that hexagonal GeO_2 reacts with concentrated hydrochloric acid to form GeCl_4 . We carried out extensive tests of the reactivity of our particulate GeO_2 with hydrochloric acid solutions. Our particulate GeO_2 failed to react with concentrated (analytical reagent grade) hydrochloric acid (HCl) solution at ambient temperature over a period of several months contact. It did not react at temperatures up to and including the boiling point of concentrated HCl . Particulate GeO_2 was held in the refluxing vapor above constant boiling point hydrochloric acid and in the refluxing vapor above concentrated hydrochloric acid. Portions of the refluxing vapor were collected for analysis and no evidence of GeCl_4 was found. To maximize the solution acidity, dry hydrogen chloride gas was passed through a stirred slurry of particulate GeO_2 and concentrated HCl at ambient temperature. No formation of liquid GeCl_4 was observed in the slurry container. The vapor exiting the reaction vessel was passed through a trap held at 273°K . Analysis of the trap contents did not reveal any GeCl_4 . We conclude that our particulate GeO_2 , although of the hexagonal structure type, exhibits a negligible reaction rate with hydrochloric acid under our experimental test conditions. For this reason, our proposed "chloride volatility" process is not suitable for high sensitivity analysis for the presence of uranium in hydrolyzed GeF_4 gas. Reaction of particulate GeO_2 with dry HCl gas at moderately high temperature (e.g., 400°C) was not attempted due to concern about chemical reduction (due to the presence of small amounts of hydrogen gas in HCl). Such reduction of trace levels of uranyl would result in lower valent uranium chlorides whose volatility likely would compromise analytical accuracy.

In a final effort to quantify uranium in hydrolyzed GeF_4 gas, we contacted an aliquot of particulate GeO_2 with 22% hydrofluoric acid solution and found that the particulate GeO_2 readily dissolved to give a clear, colorless solution. This solution was transferred to a single crystal aluminum oxide cell that consisted of a single crystal aluminum oxide rod into which a hole that had been drilled coaxial with the cylinder axis of the rod to create a flat-bottomed "test tube" shape. A polished disk of single crystal aluminum oxide capped the cavity in the rod and prevented escape of significant amounts of HF vapor from the contained solution. Laser-induced fluorescence analysis of the solution in this cell was carried out using 355nm excitation with the apparatus described in our March 12, 2001 progress report. Luminescence from the solution was observed throughout the visible spectral range and exhibited complex, non-exponential decay.

The luminescence initially peaked in the blue. With increasing time following an excitation pulse, the peak luminescence intensity wavelength shifted to longer wavelength. An aliquot of a solution of uranyl ion in dilute nitric acid was added to the solution in the cell in an amount sufficient to give approximately 6 parts per million of uranyl on a weight basis. The characteristic luminescence emission bands of uranyl ion could not be discerned in the recorded emission spectra due to the much more intense broadband, complex luminescence of the solution. This interfering luminescence likely arises from low molecular weight polymers that had leached from the Kel-F and perfluoroalkoxy (PFA) Teflon[®] containers that we used to generate the particulate GeO₂. Such luminescence was not observed from our HF stock solution nor was it present in solutions of commercial GeO₂ dissolved in our HF stock solution. We conclude that the sensitivity of luminescence analysis for uranyl in hydrofluoric acid solutions of particulate GeO₂ is significantly hindered by the presence of interfering luminescing species that likely are low molecular weight polymers that leached from the walls of Kel-F[®] and Teflon[®] containers.

Absorbance Analyses of GeF₄ Gas using ultraviolet absorption spectroscopy

An aliquot of germanium tetrafluoride (GeF₄) gas from Starmet Sample Reference Number "GeFusn-40" (Starmet preparation date 1/11/02) underwent analysis by ultraviolet absorption spectroscopy for the presence of uranium hexafluoride gas (UF₆). This analysis and an infrared analysis were carried out using the methods, equipment, and procedures noted in our October 23, 2001 progress report to Starmet with one exception. That exception was the averaging together of ten spectral scans, which resulted in slightly improved sensitivity. No absorbance attributable to UF₆ gas was observed. If one uses three times the observed standard deviation of the measurement as the "limit of detection" criterion, then the sample of Starmet-produced GeF₄ gas contained less than 0.64 parts per million of UF₆ gas on a volume basis relative to GeF₄. The sample also underwent infrared absorbance analysis in the 2000 to 5000 wavenumber (cm⁻¹) spectral region in the same sample cell used for ultraviolet absorption analysis. The characteristic fundamental vibration-rotation bands of hydrogen fluoride gas (HF) were observed in the 3700 to 4200cm⁻¹ spectral range with nearly the same optical density as was the case for our previous analysis of an aliquot of GeF₄ from Starmet Sample Reference Number "GeFusn-36" (Starmet preparation date 8/06/0). In addition, weak absorption bands (peak absorbance: 0.002 absorbance units) of the ν_3 fundamental absorption bands of carbon dioxide gas (CO₂) were observed in the 2310 to 2375cm⁻¹ spectral range.

8.2.5 Particulate filtration.

Information concerning effective gas filtration technology for semiconductor grade materials was supplied by *Voltaix, Inc.* It was recommended that a *Wafergard II F-6 Inline Gas Filter* (Millipore Corporation, Bedford, MA) or equivalent be used when processing and packaging the final fluoride product. The *Wafergard* product featured a teflon[®] membrane module rated for particulate removal of $\geq 0.003\mu$. An equivalent filter, model # TEM-811-P manufactured by *T.E.M. Filter Company* (Santa Clara, CA), was purchased from *Air Products* (Allentown, PA) and was to be integrated into the production-scale reaction system when built. A description of the TEM-800 Series Gas Filter is included in **Figure 44** along with a picture and schematic diagram of the flow rating.

TEM-800 Series Gas Filters

- 99.9999999% Efficient @ 0.003 Microns
- PTFE[®] Membrane
- 0.5 square foot Effective Filtration Area
- 316L, 10Ra finish, electro-polished stainless steel housing
- 750 psig operation pressure at 250°F
- Helium leak tested to 1×10^{-9} cc/sec
- Available with Compression, Face Seal, and N.P.T. fittings
- Interchangeable with all Pall and Millipore Filters
- Compatible with all Semiconductor Grade Gases

TEM-800 Series filters are specifically designed for filtration of critical semiconductor gases where flow rates of more than 20 liters per minute are required. The filters use a PTFE[®] membrane in a small pleated cartridge form to provide .003 micron absolute filtration. The teflon[®] membrane cartridge is encapsulated in a 316L stainless steel housing that is electro-polished and totally welded. The final assembly is purged at a high flow rate with filtered nitrogen for initial cleanliness.

Figure 44. Description and illustration of the TEM- 800 Series Gas Filter.

From the results gathered in section 8.2.4, uranium carryover into the laboratory-synthesized samples of gas was not detected above the minimum detection limits of the analytical instrumentation even for the unfiltered batch from GeFusn-36. None the less, filtering of the gas is essential for producing a clean, high purity product for use in the semiconductor industry.

8.2.6 Process scale-up.

Preliminary drawings of a six-station reaction system and gas collection station were made to begin the process of scaling-up production of GeF_4 to ~2kg of gas per day. In order to prove-out the design concept, a small prototype of a closed-end tube reactor was fabricated from a 9" section of 1" Ni tube. The basic setup was shown in Figure 7 (section 8.1.6) where the sweep gas was piped close to the surface of the reaction mixture to convey the emerging fluoride gas out of the reaction zone and toward the collection vessel. Leaving the reaction tube, the gas was passed into a 300cc double-ported, Monel cylinder setup as a 'flow-through' condenser. Results for this trial, identified as GeFusn-34, are given in Table 22. After 5 hours of reaction with the temperature in the range between 735°C-800°C, the reagent mixture lost only 3.07 grams, representing only 10.2% of the expected weight loss. Of greater significance was the fact that none of the synthesized GeF_4 was captured in the collection vessel maintained at dry-ice temperature.

Table 22.

Results for GeFusn-34.

Experiment ID:	051501-GeFusn-34			
System:	Closed-end 1" OD nickel tube reactor			
	6" OD x 6" long ceramic heater (with manual control)			
Weight of reagents (gm):	87.84	wt% GeO ₂ : 24.1689		
Sweep gas:	Helium flow at 70 (cc/min)			
Total reaction time (hr)	5			
Temperature profile		Time (hr)	at T(°C)	
		2	735-755	
		1	775	
		2	800	
Cylinder ID:	#11, 300cc volume, Monel, double port, no outage tube			
Collection method:	dry ice bath, neat			
Calculated weight of GeF ₄ expected (gm):		30.1603		
Observed weight loss of reagents (gm)		3.07		
Observed weight gain in cylinder (gm)		none		
Reaction conversion (%)		10.2		
GeF ₄ capture efficiency (%)		0		

The low conversion witnessed in GeFusn-34 was most likely a result of poor heat transfer through the wall of the vertically mounted tube from the ceramic heater. The reaction temperature of 800°C was measured outside the nickel tube and must have been substantially below that within the reaction mixture. The fact that no GeF₄ was collected in the cylinder was, in part, a result of foregoing the pre-reaction drying step that allowed adsorbed moisture to migrate and condense in cooler sections of the tubing and hydrolyze some fluoride before reaching the intended collection area. Some GeF₄ was also lost to passivating the nickel surfaces of the new reaction tube, forming a Ni₂GeO₄ film as seen in previous experiments. Collection was also hampered by the low concentration of fluoride gas in the stream passing through the chilled cylinder. At dry ice temperature (-78°C) the equilibrium vapor pressure of GeF₄ is ~26 torr or ~3.4% by volume. The short condensation zone (~6" length of the chilled cylinder wall) was obviously not sufficient to capture measurable amounts of GeF₄.

In light of the poor results observed in GeFusn-34 using the vertical tube configuration, design plans for a production scale apparatus were reviewed by the staff at *Voltaix, Inc.* Based on their recommendations and expertise with semiconductor grade materials, a new set of drawings for a multi-station reaction system and gas collection apparatus were drafted. The revised designs are shown in **Figures 45 and 46**. In brief:

- The closed-end reaction tube was switched to a 'pass-through' reaction tube similar to the tube reactor used in the design trials.
- The use of sintered metal disc filters was to be avoided since they clog easily and are not easily cleaned. Multi-membrane canister filters are recommended and they can be placed anywhere in the system as long as the gas has cooled to ambient.
- Capture of GeF₄ using a 'flow-through' condenser approach is more efficient as the concentration (partial pressure) increases to atmospheric pressure or above. For low concentration environments the use of a closed-end vessel equipped with a short outage tube is preferred.
- For low level production, automating the transfer of gas into the product cylinder is a costly add-on to equipment. Manual transfer using alternating vacuum/pressurization cycles to move GeF₄ into transportable carbon steel cylinder is recommended.

In conjunction with plans to increase the scale of GeF₄ production, a Process Hazards Review (PHR) was conducted involving both the reaction and collection systems illustrated in **Figures 45 and 46**. The first draft of the PHR is presented in **Table 23** and includes sections concerning the reactor, the gas collection cylinder, final transport cylinder and support system. In the review, various 'what If . . .' scenarios are presented along with the effect they would have on operations, the consequences stemming from the effect and what remedial actions/resources are available to manage the situation to a satisfactory outcome.

Figure 45. Revised design of the multi-station reaction system.

Figure 46. Revised design of the condensation zone in the collection system.

Table 23.

Process Hazards Review for GeF₄ Production.

System/Question	Instrument(s)	Effect	Consequence	Remediation	Issues
1. Reactor system					
a. What if reactor temperature too high?	Reactor temperature sensor	GeF ₄ produced faster than expected	GeF ₄ may not condense completely, overpressure situation may exist	Vent to scrubber system, pressure relief device engaged.	none
b. What if reactor temperature too low?	Reactor temperature sensor	Reagents may not react at all or very slowly	No safety consequence. Fluoride is not made.		
c. What if reactor outlet plugs?	---	No outlet for gas	Overpressure in reaction tube.	Shutdown reactor furnace on high pressure. Vent excess pressure to scrubber system	Venting excess pressure may cause exposure.
d. What if reactor inlet plugs	---	No sweep gas flow	Difficult to purge reactor of GeF ₄ -laden atmosphere after reaction is completed	Residual GeF ₄ vented into hood system	Disassembly may cause exposure.
e. What if sweep gas stops flowing (supply tank is depleted)?	---	No helium/air sweep gas flow	Difficult to purge GeF ₄ from reactor after completing reaction. May not get full reaction	Replace the sweep gas cylinder.	Replacing sweep gas supply could cause exposure if done improperly
f. What if reactor leaks?	---	GeF ₄ escapes into ventilation hood.	Potential exposure	Shutdown process and repair leak. Gas vented into hood is scrubbed.	Potential exposure to operator.
g. What if manifold plugs?	---	Over pressure in all active reactors.	Reactor overpressure	Shutdown reactor furnace on high pressure. Vent excess pressure to scrubber system	none
h. What if manifold filter plugs		Over pressure in all active reactors.	Reactor overpressure	Shutdown reactor furnace on high pressure. Vent excess pressure to scrubber system	none
2. Gas Collection System					
a. What if primary cooling bath is too warm?	Bath temperature sensor	Gas will not be captured.	Gas goes to scrubber system.	Adjust coolant bath temperature – not a safety issue except potential for small release to scrubber.	none
b. What if the cooling bath is too cool?	Bath temperature sensor	Components and impurities in the sweep gas may be captured.	Captured GeF ₄ contains impurities.	Raise the coolant bath temperature to stop carryover of unwanted impurities.	Condensation cylinder may fill with liquefied air.
c. What if collection cylinder plugs during filling?	---	Could cause overpressure in system or stop gas flow, depending on where plug occurs.	Reactor overpressure	Shutdown reactor furnace on high pressure. Vent excess pressure to scrubber system	none

Table 23 (cont.)					
System/Question	Instrument(s)	Effect	Consequence	Remediation	Issues
d. What if the collection cylinder plugs during transfer?		Over pressure in all active reactors.	Reactor overpressure	Shutdown reactor furnace on high pressure. Vent excess pressure to scrubber system.	none
3. Final Transport Cylinder					
a. What if filter plugs?		No flow of GeF4 from condensation cylinder to final packaging cylinder.	Pressure in condensation cylinder and filter increases	Pressure relief device engaged or GeF4 recondensed by applying coolant bath around collection cylinder.	Filter can be bypassed and transfer completed to lower system pressure.
b. What if bath is too cold?		No effect			
c. What if bath is too warm?		Transfer cylinder may not condense fluoride gas	Condensation cylinder and filter overpressurize.	Pressure relief device engaged or GeF4 recondensed by applying coolant bath around collection cylinder.	none
d. What if vacuum not sufficient?	Pressure gauge	High pressure in transfer cylinder	GeF4 is comingled with impurities.	no safety effects	
e. What if vacuum is still on when transfer is initiated?		Vacuum pump still pumping on transfer cylinder when condensation vessel is opened.	Some GeF4 may be pumped out through the vacuum pump.	Vacuum pump outlet vented through the scrubber.	
f. What if the flowmeter fails low?	Flowmeter	Flowmeter fails to indicate flow of gas.	No indication of gas flow may make operator think that transfer to packaging vessel is complete.	Transport cylinder is weighed to check transferred amount of gas.	Condensation cylinder may contain more GeF4 than expected on startup of next condensation cycle.
g. What if the flowmeter fails high?	Flowmeter	Flowmeter reads high	Operator may think gas flow is proceeding when there is no or little flow.	Operator may continue gas transfer longer than needed. No safety implications.	none
h. What if pressure gauge fails high? fails low?	Pressure gauges	Operator stops transfer of gas prematurely. Operator continues transfer of gas longer than necessary.	Transfer of GeF4 less than expected. Transfer of more GeF4 than expected.	System evacuated using vacuum pump. System evacuated using vacuum pump.	Transport cylinder contains less than desired amount. Transfer cylinder contains more than desired amount.
4. Support Systems					
a. What if ventilation hood fails during operation?	Hood velocity sensor	Ventilation surrounding reactor(s) ceases.	Potential for exposure to process gases and GeF4 increases dramatically.	Immediate shutdown of operations, evacuate.	Evacuation may include personnel in surrounding areas.
b. What if scrubber fails during operation?		Scrubber stops working	Environmental discharge of gas less than 2 kg maximum	Significant residual trapping in scrubber packing, HF sensor in discharge.	

8.2.7 Gas ultrapurification.

Voltaix, Inc. was subcontracted to characterize the purity of GeF_4 made by the new *Starmet* process. Material synthesized in two lab trials, GeFusn 37 and 38, was shipped to them in order that the purity of the "as-produced" gas be established and to determine if further purification steps were needed to upgrade the quality to meet current specifications. Results of the two lab runs are included in **Table 24**, which yielded a 15.61 gram sample of fluoride.

Table 24.

Profile and results for GeFusn-37 and 38.

Experiment ID	081601-GeFusn-37		082101-GeFusn-38	
Reaction system	1" nickel tube reactor with 8" nickel boat			
Weight of reagents	35.1592 grams		34.0237 grams	
Weight % GeO ₂ (%)	24.9847		24.9847	
Sweep gas	Helium (62) + air (20) = total flow at 82 (cc/min)			
Pre-reaction drying period	1 hr @ 300°C		1 hr @ 400°C	
Reaction temperature profile	Time (hr)	at T (°C)	Time (hr)	at T (°C)
	0.25	700	0.75	650-800
	1	750	3	800
	2.75	775		
	1.25	800		
Total reaction time (hr)	5.25		3.75	
Cylinder ID	#8, 150cc type 304 SS, single port with shortened outage tube			
Collection method	n-propyl alcohol/dry ice bath maintained at			
	-72°C		-77°C	
Filter	Osmonics 0.45μ stacked PTFE® membrane/polypropylene shell			
Calculated weight of GeF ₄ expected (gm)	12.4796		12.0765	
Calculated weight loss of reagents (gm)	11.5843		11.2096	
Observed weight loss of reagents (gm)	10.9961		10.8304	
Observed weight gain in the cylinder (gm)	6.87		8.89	
Reaction conversion (%)	94.9		96.6	
GeF ₄ capture efficiency (%)	58.0		76.2	

In brief, both reactions were carried out using a helium/air mixture as the sweep gas. A high degree of conversion was observed in both cases (94.9% and 96.6% for GeFusn-37 and 38, respectively), with the latter run yielding the larger amount of captured product (8.89 grams). The material produced in both reactions was filtered using a membrane filter placed immediately before the condensation cylinder. After concluding GeFusn-38, the helium/air residual was removed by vacuum processing before capping the gas container.

Follow-up analyses of the reaction solids by x-ray powder diffraction and gas analysis by FT-IR spectroscopy of the stream leaving the stainless steel cylinder in GeFusn-38 were also done. Those results are shown in **Figures 47** and **48**, respectively. X-ray diffraction results in **Figure 47** indicate the black, post-reaction residue was solely U_3O_8 . It can be seen in **Figure 48** that the gas stream exiting the condensation cylinder, while submerged in coolant at -77°C , contained measurable GeF_4 on the order of 3.4% (by volume). Peaks due to several impurities seen throughout the experimental program were also marked in the sample spectrum. Evidence of the BF_3 and SiF_4 species has been difficult to flush out of the gas sample cell and lines to the FT-IR instrument from prior sample analyses.

After being received at *Voltaix, Inc.*, the "as-produced" fluoride was also analyzed using FT-IR spectroscopy in their laboratory. Spectra were collected for the *Starmet* material along with two GeF_4 samples from other vendors. The spectra were collected at a cell pressure of 200 torr and arranged on a common set of axes to facilitate comparison between scans. Those results are shown in **Figure 49**. Locations of increased absorbance due to the presence of impurities have been marked in the spectra. It is clear the *Starmet* GeF_4 had the least number and lowest intensity peaks due to impurities compared to the two other samples. The GeF_4 material from *Advance Research Chemical* possessed a purity of 99.99%.

*** Multi Plot ***

Figure 47. X-ray diffraction patterns for the solids recovered from GeFusn-37 and -38 and reference pattern for U_3O_8 (pdf# 47-1493).

Figure 48. Infrared spectrum of the gas stream leaving the collection cylinder in GeFusn-38 with the furnace at 800°C and a reference sample of GeF₄ at 10 torr. Peaks due to known impurities such as CO₂, BF₃, SiF₄ and H₂O have been marked.

Figure 49. Infrared spectra for GeF₄ produced at *Starmet* in GeFusn-37&38 and two samples obtained from other vendors.

Finally, the purity of the lab-synthesized sample of GeF_4 was characterized using ICP-MS (inductively coupled plasma-mass spectroscopy) analysis. Three test specimens were prepared at *Voltaix, Inc.* and sent to *Applied Analytical, Inc.* (Austin, TX) for quantitative assessment for 37 elemental impurities including uranium. The test solutions were prepared by hydrolyzing the gas in deionized water with assistance of a nitrogen ballast. Solutions for the *Starmet* gas, a reference material ("Voltaix") claimed to have a purity of 99.99% and a "blank" consisting of deionized water treated with ballast gas were analyzed under similar conditions.

Results of the ICP-MS analysis for the three test solutions are arranged in **Table 25**. For the 'as-produced' *Starmet* material, only boron and niobium could be detected above their detection limits while uranium **could not be detected** at a detection limit of 0.019ppm-wt. In comparison, the *Voltaix, Inc.* material also showed detectable levels of boron and niobium and also a third impurity, namely titanium. It is clear the *Starmet* GeF_4 had fewer detectable impurities than the reference supplied by *Voltaix, Inc.*

Based on the series of FT-IR and ICP-MS analyses that the GeF_4 material was subjected to, both at *Voltaix, Inc.* and at the outside analytical laboratory, the *Starmet* material has been shown to be of superior quality. Additional analyses by gas chromatography to quantitatively assess the impurity levels of HF , CO_2 , CO , SO_2 , Ar , O_2 and N_2 are required before stating, with certainty, that the "as produced" fluoride gas meets the most demanding specifications put forth by *Voltaix, Inc.* for their UHP grade - 99.99% material. The current specifications for UHP grade GeF_4 , as put forth by *Voltaix, Inc.*, are compiled in **Table 26**.

From the investigations conducted thus far concerning the production of GeF_4 using *Starmet's* new fluoride extraction process (FEP™), the quality of gas produced in laboratory trials is of sufficient purity for use in the semiconductor industry.

Table 25.
Results for ICP-MS analysis of 'as-produced' GeF₄ received from *Voltaix, Inc.*

The following germanium fluoride solutions were analyzed by ICP-MS. Results are expressed in terms of the original gas sampled using the sample weight provided. Units are ppm weight.				The following "Blank" Sample of germanium fluoride solution was analyzed by ICP-MS. Results are based on the solution as it was received. Units are ppm weight. nd = not detected	
Sample from:	<i>Starmet</i>	<i>"Voltaix"</i>		"Blank"	
			Detn.		Detn.
Element	253-35	253-36	Limit	253-34	Limit
Aluminium	nd	nd	0.240	nd	0.005
Antimony	nd	nd	0.029	nd	0.001
Barium	nd	nd	0.054	nd	0.001
Beryllium	nd	nd	0.018	nd	0.001
Bismuth	nd	nd	0.019	nd	0.001
Boron	0.475	0.370	0.087	nd	0.002
Cadmium	nd	nd	0.058	nd	0.001
Chromium	nd	nd	0.136	nd	0.003
Cobalt	nd	nd	0.008	nd	0.001
Copper	nd	nd	0.040	nd	0.001
Gallium	nd	nd	0.067	nd	0.001
Gold	nd	nd	0.015	nd	0.001
Hafnium	nd	nd	0.009	nd	0.001
Iron	nd	nd	9.6	nd	0.21
Lanthanum	nd	nd	0.005	nd	0.001
Lead	nd	nd	0.019	nd	0.001
Lithium	nd	nd	0.019	nd	0.001
Magnesium	nd	nd	0.067	nd	0.001
Manganese	nd	nd	0.006	nd	0.001
Mercury	nd	nd	0.037	nd	0.001
Molybdenum	nd	nd	0.048	nd	0.001
Nickel	nd	nd	0.219	nd	0.005
Niobium	<2.69	<2.02	0.019	nd	0.001
Platinum	nd	nd	0.019	nd	0.001
Silver	nd	nd	0.029	nd	0.001
Sodium	nd	nd	0.173	nd	0.004
Strontium	nd	nd	0.048	nd	0.001
Tantalum	nd	nd	0.081	nd	0.002
Thallium	nd	nd	0.013	nd	0.001
Thorium	nd	nd	0.010	nd	0.001
Tin	nd	nd	0.019	nd	0.001
Titanium	nd	0.719	0.104	0.095	0.002
Tungsten	nd	nd	0.039	nd	0.001
Uranium	nd	nd	0.019	nd	0.001
Vanadium	nd	nd	0.019	nd	0.001
Zinc	nd	nd	0.106	nd	0.002
Zirconium	nd	nd	0.024	nd	0.001

Table 26.

Specifications for UHP grade - 99.99% GeF₄ established by *Voltaix, Inc.*

Impurity	Maximum Concentration	Impurity	Maximum Concentration
HF	35ppm	N ₂	10ppm
CO ₂	5ppm	CF ₄	10ppm
CO	10ppm	Fe	0.08ppm-wt
SO ₂	10ppm	Cr	0.05ppm-wt
Ar + O ₂	20ppm	Mn	0.01ppm-wt

8.3 Discussion - GeF₄.

8.3.1 Producing the Gas

In the batch-type operation, the tube reactor setup was shown to be the better design for harvesting GeF₄. The highest Capture Efficiency (CE) amongst the crucible reactor trials was 38.3% as determined in the GeFusn-21 run while a CE of 97.7% was recorded during the GeFusn-28 trial conducted in the tube reactor system. The better efficiency was realized as a result of manipulating reaction parameters and using materials of construction that held up well under the preferred reaction conditions. The most significant factor compromising the collection of GeF₄ was the formation of crystalline GeF₂ residue. It was found that the unwanted by-product could be controlled and minimized by maintaining the reaction temperature in the range between 700°C-800°C and using a reactor sweep stream containing a small fraction (10-12 vol.%) of dry air. The selection of nickel 200 alloy as a construction material also helped to improve collection of product by lessening the extent of destructive side-reactions at the surface of the metal. Some interaction between GeF₄ and the nickel material was noted by the formation of a Ni₂GeO₄ residue. It is anticipated that this side-reaction can be eliminated by properly passivating all nickel surfaces in and around the heated reaction zone with a protective layer of NiF₂ before beginning the production of GeF₄.

Reaction conversion during the tube reactor trials was determined to be at least 88% or greater except for two experiments (GeFusn-27 and -30). Those experiments performed using a 100% helium sweep gas (GeFusn-25, -26 and 31) showed higher conversion levels than the trials where air was added to the sweep stream (GeFusn-28, -29 and 32). However, the higher conversions were achieved in those runs where the reactor temperature was the highest (775°C-800°C). In two trial-to-trial comparisons where the same reactor temperature was reached, the greater conversion was attained when the reaction environment contained a small amount of air in the sweep gas as shown in **Figure 50**.

Likewise, when the reaction conversion was plotted against reaction temperature for the eight trial series (see **Table 14**), experiments carried out using a pure helium sweep stream showed a significant increase in conversion with rise in temperature. In contrast, those runs where the helium/air sweep gas was employed showed almost no change in conversion as the temperature was stepped up between 700°C-750°C. These trends are demonstrated in **Figure 51** below. In subsequent runs where GeF₄ was produced for purity characterization (GeFusn-37 and -38), conversion levels of 94.9% and 96.6% were attained when a reaction temperature of 800°C was employed while using the helium/air sweep stream. Additional discussion concerning reaction mechanism and kinetic issues will be included after discussing the quality of the gas produced by the solid-state reaction.

Effect of Sweep gas on the Reaction Conversion

Figure 50. Comparison of reaction conversions using either 100% helium or a mixture of helium + air as the sweep gas at 700°C and 750°C.

Conversion vs Temperature

Figure 51. Reaction conversion charted as a function of temperature for the series of tube reactor experiments where pure helium and helium/air sweep streams were employed.

8.3.2 Quality of the Gas

The quality of the GeF_4 produced throughout the development program was constantly monitored by FT-IR spectroscopy and routinely compared to several commercial GeF_4 sources both at *Starmet* and *Voltaix, Inc.* Laboratory synthesized samples made during the reactor design and parameter optimization trials routinely contained low levels of impurities such as SiF_4 , BF_3 , CO_2 , HF and moisture that were formed by side reaction between GeF_4 and the system hardware components (i.e., HR160[®] alloy reactor, silicone-based valve lubricant, etc.). Traces of boron trifluoride in the gas produced in the crucible reactor experiments could be tracked back to prior use of the reactor hardware for making BF_3 by similar technology reacting UF_4 with B_2O_3 . Likewise, GeF_4 produced in the nickel tube reactor showed a similar pattern of impurities which, in the case for BF_3 , probably diffused off the interior walls of the 10cm gas cell, which was used repeatedly to analyze several other fluoride gases made by *Starmet's* fluoride extraction process. Varying traces of CO_2 were observed in many infrared scans and was caused by changing atmospheric conditions in the infrared spectrometer's sample compartment since the cell compartment could not be totally enclosed and purged due to input and exhaust lines connecting the cell to the reaction system.

However, the levels of HF and moisture could be managed through implementation of the pre-reaction drying period where the UF_4/GeO_2 reaction mixture was first heated to $\sim 450^\circ\text{C}$ under a helium purge. Removal of moisture from the system prior to generating GeF_4 was successful in lowering the level of HF impurity by minimizing the amount of GeF_4 consumed by hydrolysis with H_2O .

After completing the tube reactor trials and optimization runs, GeF_4 produced for analytical characterization at *Argonne National Laboratory* and *Voltaix, Inc.* proved to be superior in quality when compared to other GeF_4 sources. Lab synthesized GeF_4 from GeFusn-37 and -38 analyzed at *Voltaix, Inc.* showed it to contain the least amount of infrared-detectable impurities as illustrated in **Figure 49**. The benchmark reference material supplied by *Advanced Research Chemicals, Inc.* was claimed to have a purity of 99.99%. In addition to the analysis by FT-IR spectroscopy, the *Starmet* material was found to contain only two of the 37 elements analyzed for by ICP-MS. The benchmark reference gas had three detectable impurities. More importantly, uranium could not be detected in the fusion-derived gas at the detection limit of 0.019ppm-wt.

Trace level detection of uranium in GeF_4 samples sent to *ANL* also proved to be a challenge. The two techniques being developed to detect U at low levels, i.e., laser-induced photoluminescence spectrometry and UV optical absorption spectroscopy, could not detect uranium in the *Starmet* product. The luminescence method for detecting uranyl species (UO_2^{2-} ions) in glassy GeO_2 met with unexpected interferences preventing further analyses. Alternative procedures to convert hydrolyzed GeO_2 to GeCl_4 met with resistance in chlorinating precipitated GeO_2 thereby hindering the analysis for uranyl species. Analysis for U (as UF_6) using optical absorption spectroscopy was accomplished on both samples of lab synthesized material produced in GeFusn-36 and GeFusn-40 . Using a 9.3cm gas cell, no uranium could be detected in either the unfiltered or filtered batch of GeF_4 , although the detection limits (0.75 and 0.64ppm-vol., respectively) were slightly higher than what was achieved in the ICP-MS analysis. To enhance the detection limit for U as UF_6 , a longer pathlength cell on the order of 1 meter in length was considered as an option but not pursued due to both excessive fabrication costs and limited time concerns. The goal of attaining a uranium detection sensitivity in the parts-per-trillion range was

not achieved. However, it is believed that additional development of the laser photoluminescence technique to measure uranyl species in glassy GeO_2 may prove successful with continued research to overcome the noted interferences.

8.3.3 Mechanistic Considerations

It was previously shown (in section 8.2.3) that the onset of reaction between UF_4 and GeO_2 begins to take place around 400°C when air is included in the sweep stream (refer to Figure 42). By 500°C the conversion to GeF_4 is well underway and at temperatures between 700°C - 750°C conversions near 90% have been documented. In contrast, when the reaction was run without air in the sweep stream, conversion was very much dependent on reaction temperature. Review of TGA data collected during the Phase I SBIR program showed that the onset of reaction, when conducted in an argon atmosphere, was delayed until $\sim 600^\circ\text{C}$. From this data and the x-ray diffraction results of the residues left behind at various stages of completion, it is clear that the reaction mechanism to liberate GeF_4 is different for the air-laden sweep gas environment versus a pure inert stream. One pathway to make GeF_4 in an inert sweep stream, which is supported by the x-ray diffraction data from many trials including GeFusn-27, -30, -31, -33 and -35, is given below:

Helium sweep stream -

In this scenario, UO_2 being formed in equation (A) is subsequently combined with available GeO_2 to form a stable compound with the formula UGeO_4 . This compound was identified in residues collected from GeFusn-33 and GeFusn-35 in which there was only partial conversion. No traces of GeO_2 could be detected in the diffraction patterns of either residue. Once all GeO_2 is consumed, the reaction cross-section is between UF_4 and UGeO_4 , which leaves behind UO_2 as the only solid remaining after complete conversion.

In studying the kinetic behavior of the GeF_4 reaction as part of the Phase I SBIR program²³, a mathematical expression was developed to model the rate of gas production for engineering a larger reaction system. Data for the GeF_4 reaction carried out in argon was fitted to a version of the *Avrami* equation for a solid-solid transformation process^{24,25}. This was one of several known kinetic models for a solid-solid reaction to be applied for approximating the rate of gas evolution and the only one that fit the experimental data well.

When air is added into the reactor sweep stream the above scenario changes. Diffraction data for post-reaction residues made in environments containing air (such as GeFusn-28, -29 and -32) showed UO_2F_2 and U_3O_8 were the only identifiable constituents (see Figure 13). A reaction sequence can be written which involves these species:

Helium + Air sweep stream -

The sum of the four simultaneous equations results in the net reaction (I) for producing GeF_4 . Early attempts to apply the *Avrami* equation for modeling the data derived in Phase I trials was unsuccessful. Correlation to other standard kinetic models was found to be poor as well. Additional work will be necessary in order to model the kinetics of process when air is included in the reaction atmosphere.

Kinetic issues notwithstanding, it is clear that inclusion of air in the sweep stream is advantageous during production since the reaction is initiated at a lower temperature and conversion is greater at intermediate temperatures (700°C-750°C) where the amount of GeF_2 by-product can be controlled. Although the rate-determining step amongst the 4-step mechanism may not be certain, this description offers three parallel pathways in which GeF_4 can be formed. At this time it is the preferred scenario over that for the inert gas synthesis scheme.

9 WF₆ PRODUCTION

9.1 Experimental Procedures - WF₆.

9.1.1 Bench-scale process development for WF₆ from WOF₄.

The goal of this task was to establish a pathway for making WF₆ using the intermediate compound, WOF₄, formed in the reaction between UF₄ and tungsten oxide. The first series of experiments carried out to investigate the chemistry involved milligram quantities of material and the *TA Instruments* TGA/DTA setup as the reaction apparatus. The use of the TGA facilitated the study of several reaction parameters including selection of tungsten oxide reactant, i.e. WO₂ or WO₃, reaction stoichiometry and reaction temperature. The list of 14 micro-scale experiments is given in **Table 27** below.

Table 27.

Micro-scale experiments performed using the thermogravimetric analyzer.

Mixture	Stoichiometric Ratio UF ₄ :WO _x	Reaction cup	Heat rate (°C/min)	Reaction Temperature (°C)
UF ₄ + WO ₂	1.014 : 1	alumina	15	600
UF ₄ + WO ₂	1.014 : 1	Pt	15	600
UF ₄ + WO ₂	1.014 : 1	Pt	20	600
UF ₄ + WO ₂	1.014 : 1	Pt	20	700
UF ₄ + WO ₂	1.844 : 1	Pt	20	700
UF ₄ + WO ₂	1.844 : 1	Pt	20	800
UF ₄ + WO ₂	2.013 : 1	Pt	20	700
UF ₄ + WO ₃	1 : 1.025	Pt	20	700
UF ₄ + WO ₃	1.908 : 1	Pt	20	800
UF ₄ + WO ₃	1.908 : 1	Pt	20	700
UF ₄ + WO ₃	1.908 : 1	Pt	20	750
WO ₂		Pt	15	600
WO ₂		alumina	15	600
WO ₂		Pt	20	800

For these trials, mixtures of UF₄ with WO₂ and UF₄ with WO₃ were made up in varying proportions to explore various stoichiometric ratios between the reactants. Three different combinations of UF₄ and WO₂, ranging between 1.014:1 to 2.013:1 (UF₄:WO₂), were examined. Likewise, two compositions between UF₄ and WO₃ were investigated. Three trials were performed to follow the conversion of WO₂ to WO₃ under oxidizing conditions. Reaction temperatures in the range between 600°C to 800°C were employed with all experiments being run in a flow of dry air. With the exception of several trials, the reactions were conducted in platinum cups following a procedure where the reagents were first held under isothermal conditions at room temperature for up to 15 minutes. The temperature was then ramped to the desired maximum at the specified rate and held there for a period of either 45 or 90 minutes. For

each experiment, the change in weight of the reagents was recorded as a function of temperature and/or time. At the conclusion of each run, the residue remaining in the cup was subjected to analysis by x-ray diffraction to identify the material composition.

After concluding the study involving milligram quantities of reagents and the thermogravimetric analyzer, experimentation using gram-scale quantities of material commenced using several variations of the tube reactor design. A total of 11 trials were performed, 10 using a 24" long, horizontal, 1"OD nickel tube and one using a 10" long, vertically oriented 1"OD tube (closed at one end) described earlier in section 8.1.6 (refer to **Figure 7**) for producing GeF_4 . This group of experiments is shown in **Table 28** listing experiment ID, tungsten reagent used, reactor configuration, stoichiometry and ultimate reaction temperature.

Table 28.

Experiments performed in the bench-scale reaction system.

Experiment ID	Primary Tungsten Reagent	Second Stage Reactants	Configuration	$\text{UF}_4 : \text{WO}_x$ (mol)	Reaction Temperature ($^{\circ}\text{C}$)
WFusn-7	WO_2		Vertical	2.013 : 1	800
WFusn-8	WO_2		Horizontal	2.013 : 1	775
WFusn-9	WO_2		Horizontal	2.013 : 1	780
WFusn-10	WO_2		Horizontal	2.013 : 1	790
WFusn-11	WO_3		Horizontal	2.001 : 1	790
WFusn-12	WO_3		Horizontal	2.001 : 1	750
WFusn-13	WO_2	$\text{WOF}_4, \text{UF}_4$	Horizontal	2.013 : 1	750
WFusn-14	WO_2		Horizontal	2.013 : 1	800
WFusn-15	WO_2	$\text{WOF}_4, \text{SiO}_2$	Horizontal	2.013 : 1	800
WFusn-16	WO_2		Horizontal	2.013 : 1	780
WFusn-17	WO_2	$\text{WOF}_4, \text{TiF}_4$	Horizontal	2.013 : 1	800

A brief summary of pertinent data, reaction parameters and experimental details is included below for each of the eleven experiments along with the respective reaction profile chart.

The first bench-scale experiment, WFusn-7, was conducted using a 10" long section of 1" OD nickel tube, closed at one end, oriented vertically and heated with a *Minimite*[®] tube furnace (*Lindberg/Blue M*). The furnace was supported so that the ~4" hot zone overlapped the reagent mixture at the bottom of the tube. A stream of dry air was introduced to the tube via a 1/4" feed tube passed through the wall of the vessel's top closure fitting and brought to a level about 1" above the reactant bed. The reaction conditions are shown in **Table 29**. A 250ml 2-neck round bottom flask was used as the collection vessel, which was maintained at ambient temperature for trapping the WOF₄ product.

Table 29.

Reaction Profile for WFusn-7.

Experiment ID:	022502-WFusn-7		
Reagent used:	WO ₂		
Reaction:	4UF ₄ +2WO ₂ +3O ₂ (g)=2WOF ₄ (g)+4UO ₂ F ₂		
System:	Closed-end 1" OD Nickel tube reactor		
	MiniMite [®] tube furnace mounted vertically		
	250ml round bottom flask used as the collection vessel		
	The 1" OD section of exit line was heated using heat tape.		
Weight of reagents (gm):	34.9769	wt% WO ₂ =25.4526	
Reagent stoichiometry (moles)	UF ₄ :WO ₂ = 2.013:1		
Sweep gas:	Air flow at ~100 (cc/min)		
Pre-reaction drying period:	None		
Total reaction time (hr):	~ 32 min.		
Reaction temperature profile:	Time	at T (°C)	heat rate (°C/min)
	22 min.	700	20
	10 min.	800	max.
Collection method:	Collection vessel was kept at ambient (no coolant).		

The vertical tube configuration was used for just one experiment. It was replaced with a 24" long, horizontally mounted 1" OD nickel tube using the same *Minimite*® furnace. A 4" long nickel boat was used to hold reactants and the same pyrex® collection flask as before was connected to the exit stream through a series of *Swagelok*® reducing unions (1" to 1/2" and 1/2" to 1/4"). For the WFusn-8 trial the flask was submerged in an ice-water bath to aid in condensing the product vapor cloud. Details of WFusn-8 are compiled in **Table 30**.

Table 30.

Reaction Profile for WFusn-8.

Experiment ID:	022802-WFusn-8		
Reagent used:	WO ₂		
Reaction:	4UF ₄ +2WO ₂ +3O ₂ (g)=2WOF ₄ (g)+4UO ₂ F ₂		
System:	Horizontal 1" OD Ni tube reactor with 4" nickel boat		
	MiniMite tube furnace with ~4" hot zone; integral		
	temperature programmable controller.		
	250ml round bottom flask used as the collection vessel		
Weight of reagents (gm):	13.3549	wt% WO ₂ =25.4526	
Reagent stoichiometry (moles)	UF ₄ :WO ₂ = 2.013:1		
Sweep gas:	Air flow at ~100 (cc/min)		
Pre-reaction drying period:	None		
Total reaction time (hr):	46 min.		
Reaction temperature profile:	Time	at T (°C)	heat rate(°C/min)
	10 min.	725	20
	36 min.	775	50
Collection method:	short 1/4" OD ss tube carried flow into glass flask.		
	Flask was chilled with ice/water bath		

The post-reaction solids were analyzed by x-ray powder diffraction.

For the third experiment, the reaction system was assembled as in the previous setup (WFusn-8) with the addition of wrapping the sections of tubing, from where the tube left the furnace to the point where the collection flask was joined at the 1/4" reducing union, with heat tape and insulation. This was done to prevent condensation of WOF₄ and blockage of flow to the flask. During the heating of the UF₄/WO₂ mixture to 780°C, the exit line from the furnace was heated to 209°C. The individual details for the WFusn-9 reaction are given in Table 31.

Table 31.

Reaction Profile for WFusn-9.

Experiment ID:	030702-WFusn-9		
Reagent used:	WO ₂		
Reaction:	4UF ₄ +2WO ₂ +3O ₂ (g)=2WOF ₄ (g)+4UO ₂ F ₂		
System:	Horizontal 1" OD Ni tube reactor with 4" nickel boat		
	MiniMite [®] tube furnace with ~4" hot zone; integral temperature programmable controller.		
	250ml round bottom flask collection vessel with ss tube		
	carrying flow into glass flask.		
	Exit line was wrapped w/ heat tape from elbow to 1/4" ss tube.		
Weight of reagents (gm):	14.0759	wt% WO ₂ =25.4526	
Reagent stoichiometry (moles)	UF ₄ :WO ₂ = 2.013:1		
Sweep gas:	Air flow at ~100 (cc/min)		
Pre-reaction drying period:	2 hr at 150°C in air		
Total reaction time (hr):	30 min.		
Reaction temperature profile:	Time	at T (°C)	heat rate(°C/min)
	10 min.	750	20
	20 min.	780	50
Collection method:	Flask was chilled with ice/water bath		

Collection of post-reaction data included weight measurements of the solid residue in the boat and x-ray diffraction analysis to determine material composition. Solids generated when the condensed vapor in the flask and clogged exit lines were hydrolyzed with water were also examined using x-ray diffraction.

In light of the trouble experienced during trials WFusn-8 and 9, where the lines to the collection flask became blocked with condensed product, the pathway to the condensation vessel was redesigned. For WFusn-10, the 250ml round bottom flask was replaced with a 10" long section of 1" OD tube connected at a 90° angle to the reactor out flow via a union elbow fitting modified with a 1/4" outage tube welded through the wall to direct flow from the tube. In this configuration, the diameter of the line from the reaction zone to the condensation zone was preserved at 1" diameter. Details of this trial are compiled in **Table 32** for WFusn-10.

Table 32.

Reaction Profile for WFusn-10.

Experiment ID:	031302-WFusn-10		
Reagent used:	WO ₂		
Reaction:	4UF ₄ +2WO ₂ +3O ₂ (g)=2WOF ₄ (g)+4UO ₂ F ₂		
System:	Horizontal 1" OD Ni tube reactor with 4" nickel boat		
	MiniMite [®] tube furnace with ~4" hot zone; integral temperature		
	programmable controller.		
	Collection vessel was 1"OD Monel tube w/1/4" outage tube exit.		
Weight of reagents (gm):	14.5138	wt% WO ₂ =25.4526	
Reagent stoichiometry (moles)	UF ₄ :WO ₂ = 2.013:1		
Sweep gas:	Air flow at ~100 (cc/min)		
Pre-reaction drying period:	None		
Total reaction time (hr):	2hr-5min.		
Reaction temperature profile:	Time	at T (°C)	heat rate(°C/min)
	5 min.	750	20
	2 hr	790	50
Collection method:	1"OD Monel tube was chilled in ice/water bath		

Samples of the residue remaining after reaction and also after hydrolyzing the condensed product in the collection tube were isolated for characterization by x-ray diffraction.

After completing three trials using WO₂ as the tungsten oxide source, a bench-scale reaction between UF₄ and WO₃ [UF₄:WO₃=2.001:1] was investigated. The profile for WFusn-11 is shown in Table 33. Here, the reagent mixture was heated to 790°C for 3 hours and the volatile reaction product captured in the 1" OD collection tube described in the previous trial.

Table 33.

Reaction Profile for WFusn-11.

Experiment ID:	041702-WFusn-11		
Reagent used:	WO ₃		
Reaction:	2UF ₄ +WO ₃ +O ₂ (g)=WOF ₄ (g)+2UO ₂ F ₂		
System:	Horizontal 1" OD Ni tube reactor with 4" nickel boat		
	MiniMite [®] tube furnace with ~4" hot zone; integral temperature		
	programmable controller.		
	Collection vessel was 1"OD Monel tube w/1/4" outage tube		
	elongated to bottom of Monel tube.		
Weight of reagents (gm):	11.8572	wt% WO ₃ =26.9519	
Reagent stoichiometry (moles)	UF ₄ :WO ₃ = 2.001:1		
Sweep gas:	Air flow at ~100 (cc/min)		
Pre-reaction drying period:	None		
Total reaction time (hr):	3hr-10min.		
Reaction temperature profile:	Time	at T (°C)	heat rate(°C/min)
	5 min.	725	20
	5 min.	750	50
	3 hr	790	50
Collection method:	1"OD Monel tube was chilled in ice/water bath		

Data collection included measurement of the weight of captured product and post-reaction residue. Specimens of the residue created after hydrolyzing the solid captured in the condenser as well as the reaction product remaining in the nickel boat were analyzed by x-ray diffraction.

After reviewing the information collected from WFusn-11, a second reaction, similar to the previous run, was performed using the same parent UF_4/WO_3 stock mixture with the 2.001:1 molar stoichiometry. For this experiment, identified as WFusn-12, the 250ml round bottom flask was joined to the exit stream via a $\frac{1}{4}$ " 316 stainless steel tube and the line wrapped with heat tape back to where the reaction tube emerged from the furnace. The flask was again submerged in an ice-water bath. In this reaction, volatile product was collected for about 100 minutes while the reactor was at 750°C . The exit stream was maintained at 204°C during the reaction. Full details of this experiment are given in **Table 34** below.

Table 34.

Reaction Profile for WFusn-12.

Experiment ID:	042402-WFusn-12		
Reagent used:	WO ₃		
Reaction:	2UF ₄ +WO ₃ +O ₂ (g)=WOF ₄ (g)+2UO ₂ F ₂		
System:	Horizontal 1" OD Ni tube reactor with 4" nickel boat		
	MiniMite [®] tube furnace with ~4" hot zone; integral temperature		
	programmable controller.		
	250ml round bottom flask w/ 1/4" ss tube connection		
	Exit line wrapped w/ heat tape from elbow to joint at 1/4" tube.		
Weight of reagents (gm):	10.3506	wt% WO ₃ =26.9519	
Reagent stoichiometry (moles)	UF ₄ :WO ₃ = 2.001:1		
Sweep gas:	Air flow at 120 (cc/min)		
Pre-reaction drying period:	None		
Total reaction time (hr):	2 hr		
Reaction temperature profile:	Time	at T (°C)	heat rate(°C/min)
	10 min.	700	20
	10 min.	725	50
	1 hr-40min.	750	50
Collection method:	Flask was chilled in ice/water bath		

As done before, gravimetric measurements and x-ray diffraction analysis were collected for the condensed product and bulk residue, respectively.

After completing the two trials using WO₃, further experimentation with WO₂ as the tungsten source was resumed. In this trial, the experimental plan was to first react UF₄ and WO₂ to produce WOF₄, then react the condensed product with more UF₄. The profile for the 2-step reaction is given in Table 35. Thermodynamic considerations¹⁴ for the step (2) reaction shown in Table 35 indicate favorable reaction energetics for converting WOF₄ to WF₆(g), as illustrated in Table 36.

Table 35.
Reaction Profile for WFusn-13.

Experiment ID:	050102-WFusn-13		
Reagent used:	WO ₂		
Reaction	Step (1):	4UF ₄ +2WO ₂ +3O ₂ (g)=2WOF ₄ (g)+4UO ₂ F ₂	
	Step (2):	2UF ₄ +2WOF ₄ +O ₂ (g)=2UO ₂ F ₂ +2WF ₆ (g)	
System:	Horizontal 1" OD Ni tube reactor with 4" nickel boat		
	MiniMite [®] tube furnace with ~4" hot zone; integral temperature programmable controller.		
	500ml round bottom flask w/ 24/40 glass to Swagelok		
	adapter joined to 1/2" ss tube.		
	Exit line wrapped from elbow to adapter joint w/ insulation.		
Weight of reagents (gm):	10.4865	wt% WO ₂ =25.4526	
Reagent stoichiometry (moles)	UF ₄ :WO ₂ = 2.013:1		
Sweep gas:	Air flow at 120 (cc/min)		
Pre-reaction drying period:	None		
Total reaction time (hr):	2 hr-20min.		
Reaction temperature profile:	Time	at T (°C)	heat rate(°C/min)
	10 min.	700	20
	10 min.	725	50
	2 hr	750	50
Collection method:	Flask was chilled in ice/water bath		

Table 36.
Thermodynamic calculations for reacting UF₄ with WOF₄.

2UF ₄ + 2WOF ₄ + O ₂ (g) → 2UO ₂ F ₂ + 2WF ₆ (g)				
Temperature °C	delta H (kcal)	delta S (cal)	delta G (kcal)	K
0.00	-25.540	24.223	-32.157	5.381E+025
100.0	-27.508	18.049	-34.243	1.142E+020
200.0	-33.092	4.160	-35.061	1.570E+016
300.0	-35.993	-1.410	-35.185	2.616E+013
400.0	-38.682	-5.738	-34.820	2.022E+011
500.0	-41.241	-9.283	-34.063	4.262E+009
600.0	-43.714	-12.292	-32.981	1.802E+008
700.0	-46.128	-14.910	-31.618	1.263E+007
800.0	-48.498	-17.229	-30.009	1.294E+006
900.0	-50.836	-19.312	-28.180	1.779E+005
1000.0	-53.149	-21.205	-26.153	3.089E+004

The experimental setup was similar to previous trials. Here, a 500ml 2-neck round bottom flask was used as the condensation vessel. To the flask was added ~2.17 grams of UF_4 while the mixture of $\text{UF}_4 + \text{WO}_2$ (2.013:1 $\text{UF}_4:\text{WO}_2$) was added to the nickel boat. The first stage of the reaction was carried out for two hours and attained a temperature of 750°C . During this time volatile product was captured on top of the UF_4 layer in the flask maintained at 0°C in the ice-water bath. After concluding the high temperature stage of the reaction, the reactor was allowed to cool to ambient. The flask containing the WOF_4/UF_4 powder was then swirled to mix the solids thoroughly and then connected to a flow of dry air and heated to carry out the second step to produce WF_6 .

Upon concluding both steps of the scenario, routine gravimetric and x-ray diffraction data were collected.

In the eighth trial, WFusn-14, a group of reaction parameters was selected with the intent to optimize and deliver the maximum yield of oxyfluoride intermediate. The specific details for Wfusn-14 are compiled in **Table 37**. As in previous runs, the exit line downstream from the furnace to the condenser was wrapped with heat tape and insulation and maintained at $\sim 205^{\circ}\text{C}$ to keep the WOF_4 vapor trail flowing to the collection vessel. For this reaction, an accelerated heating profile was implemented where the furnace temperature was first raised to 750°C at $20^{\circ}\text{C}/\text{min}$ during the initial heating step and maintained there for only 5 minutes. This was followed by a rapid temperature jump (at $50^{\circ}\text{C}/\text{min}$) to 775°C and similar dwell time of 5 minutes. In the final step, the furnace temperature was raised to 800°C (at $50^{\circ}\text{C}/\text{min}$) where it was held for 3 hours.

Table 37.

Reaction Profile for WFusn-14.

Experiment ID:	061902-WFusn-14		
Reagent used:	WO ₂		
Reaction	4UF ₄ +2WO ₂ +3O ₂ (g)=2WOF ₄ (g)+4UO ₂ F ₂		
System:	Horizontal 1" OD Ni tube reactor with 4" nickel boat		
	MiniMite tube furnace with ~4" hot zone; integral temperature programmable controller.		
	500ml round bottom flask w/ 24/40 glass to Swagelok®		
	adapter joined to 1/2" stainless steel tube.		
	Exit line from elbow to 24/40 adapter joint was wrapped with		
	heat tape under the insulation.		
Weight of reagents (gm):	11.4094	wt% WO ₂ =25.4526	
Reagent stoichiometry (moles)	UF ₄ :WO ₂ = 2.013:1		
Sweep gas:	Air flow at 120 (cc/min)		
Pre-reaction drying period:	None		
Total reaction time (hr):	3 hr-10 min.		
Reaction temperature profile:	Dwell Time	at T (°C)	heat rate to T(°C/min)
	5 min.	750	20
	5 min.	775	50
	180 min.	800	50
Collection method:	Flask was chilled in ice/water bath		
Exit line temperature (°C)	205		

Upon concluding the trial, x-ray diffraction analysis of the product residue from the boat and material coating the reactor walls was performed. A gravimetric measurement of the resultant end product was also gathered.

Experiment WFusn-15 consisted of a two-step reaction scheme in order to probe the reactivity of WOF_4 . Tungsten oxyfluoride generated in the first step was reacted with SiO_2 in the second step. Details of this scenario are included in Table 38 while the thermodynamic calculations¹⁴, showing a favorable and spontaneous reaction (negative *Gibbs* free energy change, $-\Delta G$) between WOF_4 and SiO_2 , are tabulated in Table 39.

Table 38.

Reaction Profile for WFusn-15.

Experiment ID:	071102-WFusn-15		
Reagent used:	WO ₂		
Reaction	Step (1):	4UF ₄ +2WO ₂ +3O ₂ (g)=2WOF ₄ (g)+4UO ₂ F ₂	
	Step (2):	WOF ₄ + SiO ₂ = WO ₃ + SiF ₄ (g)	
System:	Horizontal 1" OD Ni tube reactor with 4" nickel boat		
	MiniMite tube furnace with ~4" hot zone; integral temperature		
	programmable controller.		
	500ml round bottom flask w/ 24/40 glass to Swagelok [®]		
	adapter joined to 1/2" stainless steel tube.		
	Exit line from elbow to 24/40 adapter joint was wrapped with		
	heat tape under the insulation.		
Weight of reagents (gm):	13.4509	wt% WO ₂ =25.4526	
Reagent stoichiometry (moles)	UF ₄ :WO ₂ = 2.013:1		
Sweep gas:	Air flow at 120 (cc/min)		
Pre-reaction drying period:	None		
Total reaction time (hr):	3 hr.		
Reaction temperature profile:	Dwell Time	at T (°C)	heat rate to T (°C/min)
	5 min.	725	20
	10 min.	750	50
	65 min.	780	50
	100 min.	800	50
Collection method:	Flask was chilled in ice/water bath		
Exit line temperature (°C)	202		

Table 39.

Thermodynamic calculations for reacting WOF_4 with SiO_2 .

$\text{WOF}_4 + \text{SiO}_2 \longrightarrow \text{WO}_3 + \text{SiF}_4(\text{g})$				
Temperature °C	delta H (kcal)	delta S (cal)	delta G (kcal)	K
0.00	-36.289	34.475	-45.706	3.739E+036
100.0	-37.072	32.037	-49.027	5.212E+028
200.0	-39.838	25.161	-51.743	7.982E+023
300.0	-41.327	22.303	-54.110	4.310E+020
400.0	-42.748	20.017	-56.222	1.799E+018
500.0	-44.142	18.085	-58.125	2.702E+016
600.0	-45.661	16.240	-59.842	9.543E+014
700.0	-46.814	14.990	-61.402	6.176E+013
800.0	-47.590	14.222	-62.853	6.328E+012
900.0	-49.265	12.713	-64.179	9.060E+011
1000.0	-50.424	11.764	-65.402	1.690E+011

For the first step of WFusn-15, a mixture of UF_4 and WO_2 (2.013:1 mole ratio) was heated, again to a reaction temperature of 800°C using a less aggressive heating program compared to the previous experiment. After two short dwell periods at 725°C and 750°C (totaling 15 minutes), the heating program raised the reaction temperature to 780°C where it was held for 65 minutes before climbing to the plateau temperature of 800°C for the final 100 minutes. In similar fashion, the exit line from the furnace to the collection vessel was maintained at ~202°C to maximize the collection of WOF_4 . In preparation for the reaction in step (2), approximately 0.5 gram of SiO_2 (99.5% purity, -325 mesh powder from *Alfa Aesar*, Ward Hill, MA) was added to the 500ml condensation flask before the start of the experiment. During the collection of WOF_4 , the condensation flask was maintained at 0°C in an ice/water bath. Upon conclusion of the reaction, the ice/water bath was removed and the flask warmed to ambient temperature while maintaining a flow of air through the vessel. A heating mantle was placed around the flask with a thermocouple situated near the bottom where the bulk of the residue had deposited. The mixture of condensed residue and SiO_2 was then slowly heated to explore the step (2) reaction in **Table 38**.

Following the completion of the second reaction step, the post-reaction solids in the Ni tube were recovered and analyzed by x-ray diffraction. The final weight of the reacted solids was also measured.

For the next experiment, WFusn-16, several changes were made to the experimental plan. First, a clean nickel boat was used to contain the UF_4/WO_2 mixture. Again, the furnace-heating program was adjusted by starting the reaction at a lower temperature, 700°C , and lengthening the dwell periods to reach the plateau temperature of 780°C . A new condenser vessel, consisting of a 10.5" x 2.5" OD pyrex[®] cylinder with 0.5" entry and exit ports, was attached to the exit line from the reactor. The new collection vessel provided a larger surface area for condensing product vapors and allowed direct connection to the 0.5" stainless steel tube section immediately adjacent to the reaction tube. The complete list of experimental parameters for WFusn-16 is given in the profile listed in **Table 40**. During the three-hour reaction period the exit line to the condenser was maintained at 210°C while the collector was submerged in an ice-water bath.

Table 40.
Reaction Profile for WFusn-16.

Experiment ID:	080102-WFusn-16			
Reagent used:	WO ₂			
Reaction	4UF ₄ +2WO ₂ +3O ₂ (g)=2WOF ₄ (g)+4UO ₂ F ₂			
System:	Horizontal 1" OD Ni tube reactor with 4" nickel boat			
	MiniMite tube furnace with ~4" hot zone; integral temperature			
	programmable controller.			
	10"x2.5"OD pyrex [®] condenser fitted with a 1/2" stainless steel			
	inlet tube & exit stopcock.			
	Exit line was wrapped with heat tape from elbow to the			
	reducing union connection.			
Weight of reagents (gm):	12.9059	wt% WO ₂ =25.4557		
Reagent stoichiometry (moles)	UF ₄ :WO ₂ = 2.013:1			
Sweep gas:	Air flow at 120 (cc/min)			
Pre-reaction drying period:	None			
Total reaction time (hr):	3 hr			
Reaction temperature profile:	Dwell Time	at T (°C)	heat rate to T (°C/min)	
	10 min.	700	20	
	10 min.	725	50	
	25 min.	760	50	
	135 min.	780	50	
Collection method:	Condenser tube was chilled in ice/water bath			
Exit line temperature (°C)	210			

Routine x-ray diffraction analysis was conducted on the recovered residue from the reactor.

The last experiment in the series listed in **Table 28** was WFusn-17. This trial was performed in order to add to the amount of WOF₄ contained in the pyrex[®] condenser synthesized in the WFusn-16 run. The reaction system setup was similar to that used previously with the exception that the exit line to the collection vessel was only wrapped with insulation (from the elbow to the reducing union connection) and not heated by heat tape. The reaction between WO₂ and UF₄ was the first step in another two-step scenario where the oxyfluoride material was reacted further with TiF₄. This two-step reaction scenario is shown in the reaction profile for WFusn-17 given in **Table 41** below.

Table 41.

Reaction Profile for WFusn-17.

Experiment ID:	082002-WFusn-17		
Reagent used:	WO ₂		
Reaction (Step 1)	4UF ₄ +2WO ₂ +3O ₂ (g)=2WOF ₄ (g)+4UO ₂ F ₂		
(Step 2)	TiF ₄ +2WOF ₄ =2WF ₆ (g)+TiO ₂		
System:	Horizontal 1" OD Ni tube reactor with 4" nickel boat		
	MiniMite tube furnace with ~4" hot zone; integral temperature		
	programmable controller.		
	10"x2.5"OD pyrex [®] condenser fitted with a 1/2" stainless steel		
	inlet tube & exit stopcock. Condenser contained the residue		
	from WFusn-16. Exit line was wrapped with insulation from		
	elbow to the 1"to1/2" reducing union connection.		
Weight of reagents (gm):	14.1475	wt% WO ₂ =25.4557	
Reagent stoichiometry (moles)	UF ₄ :WO ₂ = 2.013:1		
Sweep gas:	Air flow at 120 (cc/min)		
Pre-reaction drying period:	None		
Total reaction time (hr):	3 hr.		
Reaction temperature profile:	Dwell Time	at T (°C)	heat rate to T (°C/min)
	10 min.	700	20
	10 min.	725	50
	25 min.	760	50
	135 min.	800	50
Collection method:	Condenser tube was chilled in ice/water bath.		
Exit line temperature (°C)	N/M		

The reaction between WOF_4 and TiF_4 displayed favorable thermodynamic parameters¹⁴ (negative *Gibbs* free energy change, $-\Delta G$) for producing WF_6 , as indicated by the tabulated values in **Table 42**. The selection of TiF_4 as the fluorinating agent has the noted distinction that it too can be produced when ilmenite or other titanium-bearing ores are reacted with UF_4 . This chemistry has been demonstrated at *Starmet* as part of a DOE Phase I SBIR grant (grant no. DE-FG02-99ER82893) conducted by M.D. Stephens²⁶.

Table 42.

Thermodynamic calculations for reacting WOF_4 with TiF_4 .

$\text{TiF}_4 + 2\text{WOF}_4 \longrightarrow \text{TiO}_2 + 2\text{WF}_6(\text{g})$				
Temperature °C	delta H (kcal)	delta S (cal)	delta G (kcal)	K
0.00	12.472	60.994	-4.189	2.247E+003
100.0	10.314	54.258	-9.932	6.571E+005
200.0	4.282	39.315	-14.320	4.119E+006
300.0	0.765	32.567	-17.901	6.706E+006
400.0	-2.699	26.996	-20.872	5.982E+006
500.0	-6.210	22.135	-23.323	3.922E+006
600.0	-9.840	17.722	-25.313	2.170E+006
700.0	-13.650	13.592	-26.877	1.088E+006
800.0	-17.696	9.636	-28.038	5.133E+005
900.0	-22.028	5.779	-28.808	2.329E+005
1000.0	-26.694	1.965	-29.195	1.028E+005

To qualitatively explore the reaction between WOF_4 and TiF_4 , the pyrex[®] condenser containing the oxyfluoride intermediate was placed in an argon-filled glovebag along with the source of TiF_4 purchased from *Advanced Research Chemicals, Inc.*, (Catoosa, OK). About 1.0636 grams of TiF_4 was weighed out in a separate container and then added to the condenser while being kept in the inert atmosphere. The sealed condenser was then taken out of the glovebag and connected to two traps placed in series at the sidearm port of the cylinder. The first trap contained a solution of NaOH to neutralize and capture any WF_6 gas while the second trap consisted of distilled water and used as an in-line scrubber. The $\text{WOF}_4/\text{TiF}_4$ mixture was heated slowly using a heat gun to bring about reaction. After heating the condenser vessel once, it was allowed to cool to ambient temperature and was put back into the argon-filled glovebag where the material deposited in the upper sections was dislodged and recombined with the bulk solids. The pyrex[®] condenser was then heated a second time using the heat gun.

After completing the reaction, the residue was transferred to a storage container while being handled in the glovebag. However, x-ray diffraction analysis of the residue was not done due to the potential for release of hazardous hydrogen fluoride vapors should there be any unreacted materials leftover that would interact with moisture in the air to produce HF.

Based on the results of the qualitative reaction performed in step (2) of WFusn-17, the chemistry to use TiF_4 as a fluorinating agent was targeted for further investigation. Another reaction to form WF_6 directly from WO_2 , using TiF_4 as the fluorine source, was put forth after considering the results from the previous trial. The new pathway for producing WF_6 is given in equation (9.1),

Thermodynamic calculations¹⁴ for this reaction are compiled in Table 43 and show favorable *Gibbs* free energy changes ($-\Delta G$ values) over a wide temperature range. To explore the feasibility of this pathway, the first reaction between these two materials was performed using a small amount of each substance in the thermogravimetric analyzer (TGA).

Table 43.

Thermodynamic calculations for reaction WO_2 with TiF_4 .

$3\text{TiF}_4 + 2\text{WO}_2 + \text{O}_2(\text{g}) \longrightarrow 2\text{WF}_6(\text{g}) + 3\text{TiO}_2$				
Temperature °C	delta H (kcal)	delta S (cal)	delta G (kcal)	K
0.00	-35.434	31.572	-44.058	1.794E+035
100.0	-37.370	25.529	-46.897	2.945E+027
200.0	-39.358	20.814	-49.207	5.378E+022
300.0	-41.529	16.660	-51.078	3.008E+019
400.0	-44.019	12.665	-52.544	1.150E+017
500.0	-46.965	8.593	-53.608	1.429E+015
600.0	-50.505	4.295	-54.255	3.812E+013
700.0	-54.779	-0.332	-54.456	1.701E+012
800.0	-59.925	-5.358	-54.175	1.081E+011
900.0	-66.081	-10.835	-53.369	8.774E+009
1000.0	-73.387	-16.805	-51.992	8.427E+008

For this micro-scale experiment, the reactants were premixed in a glass vial under an argon atmosphere using 0.1850 gram of WO_2 and 0.1501 gram of TiF_4 . After thoroughly mixing the materials, a small amount (~8.549mg) was transferred to a tared platinum cup and quickly mounted onto the TGA balance pan and isolated under a flow of dry air. The TGA was programmed to maintain the reaction mixture at room temperature for 15 minutes followed by ramping the temperature at $15^\circ\text{C}/\text{min.}$ to 500°C where it was held for 15 minutes. The weight change of the reactants was recorded over the course of the thermal treatment.

After completing the micro-scale experiment, two additional trials were conducted using gram-scale quantities of reactants and a different reaction system than used in previous runs. For these last two trials, WFusn-18 and 19, the reaction vessel consisted of a Series 4566 Bench-top Mini-Reactor from *Parr Instruments, Co.* (Moline, IL) featuring 316 stainless steel construction and ~100cc internal volume. The two-piece vessel, when assembled with a teflon[®] gasket, was capable of staging a reaction up to a 350°C temperature maximum and pressure maximum of 3000psi. The temperature of the reactor was controlled by a Model 4842 PID controller, which

was also capable of stirring the contents of the vessel. However, for the two experiments between TiF_4 and WO_2 , the stirring capability was not included in the reactor setup. A schematic diagram of the new reaction system is shown in **Figure 52**. Here, the exit port on the reactor was connected to a 3-way valve to direct flow of gas either through an aqueous scrubber or through a 10cm gas cell equipped with ZnSe windows for analysis of the product stream by FT-IR spectroscopy. The attached pressure gauge was used to monitor the internal pressure while the thermocouple was inserted to sense and regulate the reaction chamber temperature.

Experiments WFusn-18 and WFusn-19 are presented together as a result of a technical glitch during the execution of WFusn-18. During that trial a computer malfunction caused the loss of accumulated FT-IR data and was terminated prematurely so a second experiment, WFusn-19, was performed. The reaction profiles for both experiments are included in **Table 44**.

Figure 52. Schematic diagram of the reaction system used for conducting WFusn-18 and 19.

Table 44.

Reaction Profiles for WFusn-18 and WFusn-19.

Experiment ID:	091802-WFusn-18	
Reagent used:	TiF ₄ , WO ₂	
Reaction	$3\text{TiF}_4 + 2\text{WO}_2 + \text{O}_2(\text{g}) = 2\text{WF}_6(\text{g}) + 3\text{TiO}_2$	
System:	Parr Instrument Co. Model 4566C T316 stainless steel reactor with teflon [®] gasket, 100ml internal vol. and integrated PID temperature controller. Exit stream from reactor connected to 10cm gas cell for analysis by FT-IR spectroscopy.	
Weight of reagents (gm):	7.6389	wt% WO ₂ = 52.7157
Reagent stoichiometry (moles)	TiF ₄ :WO ₂ = 1.563:1	
Sweep gas:	Air flow at 120 (cc/min)	
Pre-reaction drying period:	None	
Total reaction time (hr):	1 hr.	
Reaction temperature profile:	Reaction vessel heated slowly, stopping periodically to capture an aliquot of gas for analysis by FT-IR.	
	Maximum temperature reached - 155°C	
Collection method:	10cm gas cell equipped with ZnSe windows	
Exit line temperature (°C)	N/M	
Experiment ID:	110502-WFusn-19	
Reagent used:	TiF ₄ , WO ₂	
Reaction	$3\text{TiF}_4 + 2\text{WO}_2 + \text{O}_2(\text{g}) = 2\text{WF}_6(\text{g}) + 3\text{TiO}_2$	
System:	Parr Instrument Co. Model 4566C T316 stainless steel reactor with teflon [®] gasket, 100ml internal vol. and integrated PID temperature controller. Exit stream from reactor connected to 10cm gas cell for analysis by FT-IR spectroscopy.	
Weight of reagents (gm):	7.6916	wt% WO ₂ = 52.9539
Reagent stoichiometry (moles)	TiF ₄ :WO ₂ = 1.548:1	
Sweep gas:	Air flow at 100 (cc/min)	
Pre-reaction drying period:	None	
Total reaction time (hr):	2.5 hr.	
Reaction temperature profile:	Reaction vessel heated slowly from ambient to 265°C over a 2.5 hour period, stopping periodically to capture an aliquot of reactor off-gas for analysis by FT-IR spectroscopy.	
	Maximum temperature reached - 265°C	
Collection method:	10cm gas cell equipped with ZnSe windows	
Exit line temperature (°C)	N/M	

To begin WFusn-18, the given amounts of WO_2 and TiF_4 reagents were weighed out in such a manner where the fluoride compound was added to the oxide material (1.563:1 mole ratio $\text{TiF}_4:\text{WO}_2$) contained in a small plastic bottle kept in the argon-filled glovebag. The combined solids were mixed thoroughly before being transferred to the *Parr* mini-reactor also maintained under the inert atmosphere. Before heating the reaction vessel, a set of background infrared scans was collected with the gas cell containing dry air for use as a reference. The first sample scans were collected after beginning the flow of air through the reactor at 25°C and diverting gas through the cell for a five minute period. The reactor was then heated, raising the temperature in stages. Samples of the reactor effluent were isolated in the gas cell after sweeping through the cell for 2 minutes each at various temperatures along the heat-up. It was prior to the analysis of the sample captured at 96°C that the computer controlling the FT-IR spectrometer faulted, making it impossible to analyze more samples or retrieve previously recorded data files. The temperature of the reactor climbed to 155°C before the experiment was terminated.

The reaction vessel was cleaned and reassembled to conduct the same reaction over again in WFusn-19. In this trial, the exit line leaving the top of the *Parr* vessel was changed to a 1/4" line from the previous 1/8" OD tubing. The closure valve on the exit line from the reactor was switched to a *Swagelok*® 1/4" ball valve compared to the 1/8" stem valve used in WFusn-18. The larger diameter lines downstream from the reactor were inserted to address the near stoppage of flow observed during the last reaction. The setup downstream from the 3-way valve was the same as that shown in **Figure 52** with the option to direct flow through the 10cm gas cell or through the aqueous scrubber.

For WFusn-19, 7.6916 grams of combined reagents were heated slowly from room temperature to 265°C over a 2.5 hour period, stopping periodically to capture an aliquot of reactor off-gas for analysis by FT-IR spectroscopy. As before, the sweep period for the off-gas through the cell was 2 minutes before closing the cell to flow. A set of background scans was collected with air passing through the reactor at room temperature. Sample scans were collected for aliquots of gas when the temperature reached 85°C, 185°C, 187°C, 190°C and 245°C.

After completing the trial, the post-reaction solid from WFusn-19 was not analyzed by x-ray diffraction due to the potential for release of HF vapors during the analysis. However, residue formed from the hydrolysis of material found coating the internal surfaces of the reactor was examined further by x-ray diffraction after drying the aqueous solution to recover the solid.

9.1.2 Selection of suitable materials of construction for producing WF_6 .

The experimental program to investigate the chemistry to produce WF_6 was conducted using a reaction system made of nickel 200 alloy. The material performed well during the trials for producing GeF_4 so it was put to the test in carrying out the WF_6 program. Along with the 1" OD tube reactor, the boat used to hold the reactant mixture was also made of nickel. After performing the many experiments to produce WOF_4 , the nickel boat showed significant signs of corrosion and deterioration. An investigation into the corrosion was begun in order to learn what effects the high temperature fusion chemistry would have on a reaction system constructed of nickel.

The corrosion on the nickel boat was documented through a series of images. Much of the boat's exterior and interior walls were covered with a green-brown layer of flaky solid. A large piece of this corrosion layer was removed and divided into two specimens for characterization by x-ray diffraction. One piece of the corrosion solid was mounted exposing the outward-facing surface to the x-ray beam while the other sample was prepared with the interfacial side (side oriented against the wall of the boat) facing the analysis beam. X-ray diffraction patterns were collected for each specimen in order to identify the composition of the corrosion layer.

Rigorous testing of other materials besides nickel was not pursued in light of the information gathered during the materials compatibility studies performed for GeF_4 production (refer to section 8.1.2).

9.1.3 Reactor design.

Two reactor configurations were used in conducting the experimental program to derive WF_6 . Both of these lab-scale systems were batch-type operations suitable for exploring the chemistry in small bench-top equipment. Since a pathway to the final product was not deduced, no effort was put into designing a production scale apparatus until the process was worked out where WOF_4 was fluorinated to WF_6 .

9.1.4 WF_6 product characterization.

In preparation for characterizing the purity of WF_6 generated by the high temperature fusion process, a small quantity (250 grams) of WF_6 was purchased from *Advanced Research Chemicals, Inc.* (Catoosa, OK). This material was certified at 99.99% purity. Using the *Nicolet Instruments* Magna-IR 560 infrared spectrometer and 10cm gas cell with ZnSe windows, several aliquots of fluoride gas were analyzed to record a reference spectrum for this material.

Since the pathway to tungsten hexafluoride from WOF_4 remained unresolved, no further work could be performed on this task.

9.2 Experimental Results for WF_6 .

9.2.1 Bench-scale process development for WF_6 from WOF_4 .

The first experimental efforts to develop the chemistry to make WF_6 began by investigating a group of reaction parameters including the selection of a tungsten oxide reagent (WO_2 or WO_3), the reaction temperature and the reagent stoichiometry (between UF_4 and tungsten species). A series of 14 experiments was performed using milligram quantities of material and the thermogravimetric analyzer (TGA). A description of the reaction mixture and specific test conditions for each trial was compiled in **Table 27** in section 9.1.1. Results for the 14 TGA runs have been clustered into groups sharing the same parent reaction mixture. Examination of each of the post-reaction residues by x-ray diffraction was done in order to identify the leftover material. After presenting the findings for the five combinations of UF_4 with tungsten oxide, trending between the various groups will be addressed.

The first group of reactions involved a mixture of UF_4 and WO_2 in a 1.014:1 stoichiometric ratio. The maximum reaction temperature was either 600°C or 700°C . One of the reactions in this group was carried out in an alumina cup. Although no abnormalities were observed during the reaction at 600°C , this data set was not evaluated due to possible interference caused by material incompatibilities. As illustrated in **Figure 53**, when the reactants were heated to 600°C in air, there appeared to be two events occurring. At about 400°C , the sample weight started to decrease, suggesting the start of the fusion reaction. However, at about 500°C the weight of the sample started to increase at an accelerated rate as the maximum temperature was reached. The dominant weight increase observed here was similar to that seen in the oxidation of WO_2 to WO_3 , which is also plotted in **Figure 53**.

In contrast, when this combination of reagents was heated to 700°C in air, the results were dramatically different as illustrated in **Figure 54**. Beginning at a temperature around 660°C the sample weight dropped on the order of 30 weight percent as a result of the fusion between UF_4 and WO_2 and release of WOF_4 as a gas. The reaction happening at 700°C is given in equation (9.2)

As further evidence to support equation (9.2), the residue from the platinum cup was analyzed by x-ray powder diffraction. The diffraction pattern for that material is shown in **Figure 55** along with a reference pattern for UO_2F_2 (pdf # 27-0933). With the exception of several unassigned small peaks, the sample and reference patterns were an excellent match.

UF₄ + WO₂ and WO₂ Heated to 600°C in Air

Figure 53. TGA results showing the weight change during the reaction between UF₄ and WO₂ [UF₄:WO₂=1.014:1] in air at 600°C and the oxidation of WO₂ in air at 600°C.

UF₄ + WO₂ Heated to 600°C and 700°C in Air

Figure 54. TGA result comparing the weight change during the reaction between UF₄ and WO₂ [UF₄:WO₂=1.014:1] at 600°C and 700°C in air.

Figure 55. X-ray diffraction pattern of the residue from $\text{UF}_4 + \text{WO}_2$ [$\text{UF}_4:\text{WO}_2=1.014:1$] reacted at 700°C in air and the reference pattern for UO_2F_2 (pdf# 27-0933).

In contrast, the diffraction pattern for the residue from the reaction carried out at 600°C supported the conclusion that reaction between components had not proceeded very far. In **Figure 56**, the reaction product matched well to the reference pattern for UF_4 (pdf # 32-1401) and to a fluoride exchanged tungsten oxide compound with the formula $\text{WO}_{2.96}\text{F}_{0.04}$ (pdf # 22-0960). The presence of a fluorine-doped oxide is one indication the interaction between UF_4 and WO_2 had started.

From a quantitative perspective, results for the four micro-scale experiments are presented in **Table 45** below.

Table 45.

TGA results for the reactions using UF_4+WO_2 [$\text{UF}_4:\text{WO}_2=1.014:1$].

Reaction	Temperature	Sample Weight	Observed Weight Change	Calc'd Wt. Change for $\text{WO}_2 \rightarrow \text{WO}_3$ Only	Calc'd Weight Change for $\text{UO}_2\text{F}_2+\text{WOF}_4$
	(°C)	(mg)	(mg)	(mg)	(mg)
UF_4+WO_2	600	25.0164	0.252	0.7489	-5.0409
UF_4+WO_2	600	34.7404	0.4097	1.0400	-7.0003
UF_4+WO_2	700	46.2571	-13.14		-9.3210
WO_2+O_2	600	19.3901	1.463	1.4370	----

Included in the table are "calculated" weight changes based on either complete reaction of the UF_4 with WO_2 to UO_2F_2 and $\text{WOF}_4(\text{g})$ or the oxidation of WO_2 to WO_3 only. For the trial where WO_2 was heated to 600°C by itself, the observed weight gain was on par with the predicted increase. For those runs using the combined reactants, at 600°C, the observed weight changes fell in-between the two calculated values. As one would expect, the smaller than predicted weight gains signaled the fusion process and release of gaseous product was beginning to offset the effects of the oxidation process. The weight loss observed for the reaction carried out at 700°C was larger than that predicted by equation (9.2) (page 133). Explanation of the excessive weight loss will be discussed after presenting the results for the other TGA experiments.

Figure 56. X-ray diffraction pattern of the residue from $\text{UF}_4 + \text{WO}_2$ [UF₄:WO₂=1.014:1] reacted at 600°C in air and reference patterns for $\text{WO}_{2.96}\text{O}_{0.04}$ (pdf# 22-0960) and UF_4 (pdf# 32-1401).

The second set of experiment using WO_2 as the oxide source consisted of two trials encompassing a stoichiometric ratio of 1.844:1 $\text{UF}_4:\text{WO}_2$. Here, one reaction was done at 700°C while the other at 800°C , both using a $20^\circ\text{C}/\text{min}$ heating profile and a 45 minute dwell period at their respective temperatures. The TGA results are shown in **Figure 57** for both trials. The dominant feature again was the weight loss caused by the release of WOF_4 starting around 660°C - 680°C . For the mixture reacted at 700°C , the observed weight loss was 10.58mg, which was the exact loss predicted by the scheme in equation (9.2) (page 133). For the trial at 800°C , the mixture lost weight at a faster rate initially but took longer to achieve a steady weight. As seen in other reactions, the actual weight loss of 28.34mg was considerably greater than the calculated loss of 17.04mg.

X-ray diffraction analyses of both residues were collected. Patterns are shown in **Figure 58** along with the reference for UO_2F_2 (pdf # 27-0933). Both products were similar to each other and matched well with the reference. Within each of the experimental patterns, there were small peaks in the range between 21° - 28° 2-theta indicating the presence of other phases in very low concentration. In the material made at 700°C , there was evidence of UF_4 left over along with U_3O_8 . The 800°C residue had several peaks matching well with the U_3O_8 reference pattern (pdf # 47-1493). Visual inspection of the solids in the platinum cups revealed the surface of each powder had discolored from the typical pale yellow color found in the bulk. The top layer of the 800°C material was charcoal gray-black while the 700°C residue had a less intense gray-brown surface. The specimens collected and mounted for x-ray analysis were representative of the bulk reaction product in each case. Examination of the undisturbed discolored surface layers could not be done easily using the x-ray equipment in-house.

UF₄ + WO₂ Heated in Air

Figure 57. TGA results showing the weight change during the reaction between UF₄ and WO₂ [UF₄:WO₂=1.844:1] at 700°C and 800°C in air.

Figure 58. X-ray diffraction patterns for the residues from $\text{UF}_4 + \text{WO}_2$ [$\text{UF}_4 : \text{WO}_2 = 1.844 : 1$] reacted at 700°C and 800°C in air and reference patterns for UO_2F_2 (pdf# 27-0933), UF_4 (pdf# 32-1401) and U_3O_8 (pdf# 47-1493).

The third mixture between UF₄ and WO₂ to be investigated had the stoichiometric ratio of 2.013:1 UF₄:WO₂. Only one experiment was performed with this combination of reagents. The material was heated at 20°C/min to 700°C and held there for 90 minutes. The dwell time was lengthened to evaluate the stability of the reaction product under thermal stress. The TGA result is shown in **Figure 59**. As before, there was a significant weight loss as the temperature crested at 700°C and continued at a steady rate for about 15 minutes before subsiding at the 80-minute point into the run. From that point on until the end (~59 minutes) there was a very gradual loss amounting to 0.77mg. The weight loss during the first 80 minutes totaled 16.41mg. The residue in the Pt cup again had a brown-black top layer covering a fine, pale yellow powder. X-ray diffraction analysis of the material, pictured in **Figure 60**, showed it to be UO₂F₂ along with a second phase matching that of U₃O₈ (pdf # 47-1493). The gradual weight loss over the last 60 minutes coupled with the presence of an increased amount of U₃O₈ are attributed to the decomposition of UO₂F₂ said to begin around 300°C²⁷.

In addition to the reactions carried out using WO₂, a parallel investigation into reacting WO₃ with UF₄ was undertaken because it became evident that some of the WO₂ reactant in the previous trials was converted to WO₃ beginning at temperatures as low as 400°C (see **Figure 53**). The oxidation of WO₂ to WO₃ could impede the desired reaction to liberate WOF₄(g) should the trioxide compound be non-reactive or produce an unwanted by-product. From a thermodynamic viewpoint, the reaction between UF₄ and WO₃ to produce WOF₄(g) and UO₂F₂ as written in equation (9.3)

is not spontaneous at temperatures below 1000°C according to the calculations¹⁴ shown in **Table 46**.

Table 46.

Thermodynamic calculations for the reaction between UF₄ and WO₃.

2UF₄ + WO₃ + O₂(g) → 2UO₂F₂ + WOF₄(g)				
Temperature °C	delta H (kcal)	delta S (cal)	delta G (kcal)	K
0	12.607	5.851	11.008	1.553E-009
100	11.918	3.674	10.547	6.641E-007
200	11.454	2.566	10.240	1.861E-005
300	11.084	1.856	10.021	1.509E-004
400	10.754	1.324	9.863	6.276E-004
500	10.436	0.884	9.753	1.749E-003
600	10.115	0.493	9.684	3.765E-003
700	9.779	0.129	9.654	6.790E-003
800	9.095	-0.532	9.666	1.075E-002
900	8.833	-0.765	9.730	1.539E-002
1000	8.544	-1.001	9.818	2.063E-002

$\text{UF}_4 + \text{WO}_2$ Heated to 700°C in Air

Figure 59. TGA result showing weight change during reaction between UF_4 and WO_2 [$\text{UF}_4:\text{WO}_2=2.013:1$] at 700°C in air.

Figure 60. X-ray diffraction pattern for the residue from $\text{UF}_4 + \text{WO}_2$ [$\text{UF}_4:\text{WO}_2=2.013:1$] and reference patterns for UO_2F_2 (pdf# 27-0933) and U_3O_8 (pdf# 47-1493).

With that knowledge in hand, a mixture of UF_4 and WO_3 was prepared where the stoichiometric proportions were 1:1.025 UF_4 : WO_3 . This mixture was heated at $20^\circ\text{C}/\text{min}$ to 700°C and held there for 30 minutes. The result is shown in **Figure 61**. The mixture began losing weight beginning around 655°C . After the 30 minute period there was a weight loss of 3.57mg. Using the scenario in equation (9.3) (page 141), the calculated weight loss, assuming complete reaction, was 5.80mg. The residue remaining in the platinum cup was yellow with just a trace of gold and brown discoloration on the surface of the powder. The reaction product was characterized by x-ray diffraction and that result is included in **Figure 62**. It was clear that the reacted solid did contain a sizeable amount of UO_2F_2 as indicated from the match with the corresponding reference pattern (pdf # 27-0933). However, additional diffraction peaks associated with one or more phases were present but could not be matched with much certainty to any materials containing any combination of U, W, O and F in the ICDD database¹³. A diffraction pattern recorded for WO_3 is also included in **Figure 62** since the final residue should contain ~27.5% (by weight) WO_3 left behind due to stoichiometric excess. The pattern for the reaction product does not correlate well with that for the starting tungsten oxide material.

The last group of TGA experiments to be completed were done using a mixture possessing a 1.908:1 mole ratio of UF_4 : WO_3 . Reactions at temperatures of 700°C , 750°C and 800°C were performed, all using a similar heating rate of $20^\circ\text{C}/\text{min}$ and 45 minute dwell at the indicated maximum. The weight loss curves for the three runs are pictured in **Figure 63**. In all three cases, weight loss began about 650°C . The mixture heated to 700°C lost 6.40mg over the course of the reaction. A total of 21.03mg was lost in the 750°C reaction while a decrease of 13.52mg was observed during the first 68 minutes of the run carried out at 800°C . During the last 30 minutes of the 800°C fusion, an additional loss of 0.44mg was recorded. These weight loss results are compiled in **Table 47** below

Table 47.

Weight loss results for the reactions between UF_4 + WO_3 [UF_4 : WO_3 =1.908:1].

Reaction Temperature	Sample Weight	Observed Weight Loss	Calculated Weight Loss	Ratio Obsv'd/Calc'd
($^\circ\text{C}$)	(mg)	(mg)	(mg)	(%)
700	32.61	6.40	9.13	70.1
750	54.27	21.03	15.19	138
800	32.31	13.96	9.05	154

$\text{UF}_4 + \text{WO}_3$ Heated to 700°C in Air

Figure 61. TGA result showing the weight change during the reaction between UF_4 and WO_3 [$\text{UF}_4:\text{WO}_3=1:1.025$] at 700°C in air.

Figure 62. X-ray diffraction patterns for the residue from $\text{UF}_4 + \text{WO}_3$ [UF₄:WO₃=1:1.025] reacted in air at 700°C, WO_3 reagent from *Alfa Aesar* and the reference pattern for UO_2F_2 (pdf# 27-0933).

$\text{UF}_4 + \text{WO}_3$ Heated to 700°C, 750°C and 800°C in Air

Figure 63. TGA results showing weight change during the reaction between UF_4 and WO_3 [$\text{UF}_4:\text{WO}_3=1.908:1$] at 700°C, 750°C and 800°C in air.

When compared to the calculated weight change using equation (9.3) (page 141), the reaction at 700°C was only partially complete while the other two fusions produced a greater than expected loss. Visual inspection of each residue showed a progressively darker surface layer beginning with a tan coloring over the 700°C material and transitioning to a gray-black overlayer covering the 800°C powder. Material at the core of each platinum cup was pale yellow. Characterization of two residues by x-ray diffraction is shown in **Figure 64** along with the matching references for UO_2F_2 (pdf # 27-0933), U_3O_8 (pdf # 47-1493) and UF_4 (pdf # 32-1401). The detection of UF_4 peaks in the pattern of the 700°C residue was consistent with the TGA result showing incomplete reaction. The correlation of peaks in the 800°C product matching those for U_3O_8 confirmed the decomposition of UO_2F_2 was contributing to and was most likely responsible for the 0.44mg loss observed during the last 30 minutes of that experiment. The dominant phase in both sample patterns was that of UO_2F_2 .

Now that all TGA results have been summarized, comparisons and trending across the groups can be highlighted with respect to the three parameters of interest. First off, with regard to selection of a tungsten oxide reagent, it is apparent that both WO_2 and WO_3 reacted with UF_4 to liberate a volatile tungsten oxyfluoride compound and in the process leave behind UO_2F_2 . Based on the thermodynamic calculations in **Table 46**, the reaction between WO_3 and UF_4 was not predicted to be spontaneous with a *Gibbs* free energy (ΔG) of +9.654 kcal at 700°C. Yet, a reaction between substances did take place suggesting that: 1) the pathway to WOF_4 may be more complex than the one-step reaction shown in equation (9.3) and 2) the data calculated by the software program be considered an estimate containing some degree of uncertainty.

In the presence of air, it has been shown that WO_2 was oxidized to WO_3 beginning below 500°C so some WO_3 was already present when the fusion reaction with UF_4 kicked off around 660°C. It is not certain what influence the exotherm from the $\text{WO}_2 \rightarrow \text{WO}_3$ may exert on the reaction dynamic. From an economic viewpoint, using WO_3 as the starting reagent would lower production costs in making the WOF_4 intermediate. There is about a factor of ten price difference between WO_2 and WO_3 for kilogram quantities of reagent (source: *Alfa Aesar* catalog).

The second parameter studied using the TGA apparatus was that of stoichiometry between reagents. Weight loss and temperature difference curves for the three combinations of $\text{UF}_4 + \text{WO}_2$ are depicted in **Figure 65**. The 1.014:1 $\text{UF}_4:\text{WO}_2$ mixture showed the largest weight increase before dropping at the fastest rate amongst the three data sets. This trend is mimicked in the temperature difference curves where the greatest change was observed in the reaction with equi-molar amounts of reactants. At this stoichiometric ratio, there is almost a 100% excess of WO_2 above what is required for reaction with UF_4 . It is probable that the exotherm generated in converting excess WO_2 to WO_3 supplied additional thermal energy beyond the external heat input thereby increasing the rate of reaction and evolution of WOF_4 vapor. The 2.013:1 composition, possessing the ratio closest to theoretical stoichiometry, tracked along at a somewhat slower rate of weight loss where the exotherm was marginally perceptible in the temperature difference curve.

The weight loss and temperature difference curves for the two compositions of $\text{UF}_4 + \text{WO}_3$ are shown in **Figure 66**. Here, the difference in reagent stoichiometry appeared to have little impact on liberation of the gaseous intermediate as viewed from the weight loss curves. Beyond the 60 minute point into the reaction profile, the curves showed some divergence with respect to weight loss which was most likely due to the presence of excess WO_3 in the 1:1.025 $\text{UF}_4:\text{WO}_3$

Figure 64. X-ray diffraction patterns for the residues from the reactions between $\text{UF}_4 + \text{WO}_3$ [$\text{UF}_4:\text{WO}_3=1.908:1$] and reference patterns for UO_2F_2 (pdf# 27-0933), U_3O_8 (pdf# 47-1493) and UF_4 (pdf# 32-1401).

UF₄ + WO₂ Heated to 700°C in Air

Figure 65. TGA results showing weight loss and temperature difference for three stoichiometric mixtures of UF₄ with WO₂ heated to 700°C in air.

UF₄ + WO₃ Heated to 700°C in Air

Figure 66. TGA results showing weight loss and temperature difference for two stoichiometric mixtures of UF₄ with WO₃ heated to 700°C in air.

experiment. From the temperature difference curves, the reaction exotherm is minimal compared to that seen in the UF_4/WO_2 trials.

The third variable to be examined involved the reaction temperature. The two experiments utilizing the 1.844:1 $\text{UF}_4:\text{WO}_2$ reagent combination and the three trials involving the 1.908:1 $\text{UF}_4:\text{WO}_3$ mixtures are plotted in **Figure 67** displaying the weight change during the $20^\circ\text{C}/\text{min}$ heating cycle and 45 minute dwell period at temperature. Within either parent mixture, the higher the reaction temperature the faster the weight loss. At 800°C , there was little difference in the rate of weight loss observed whether the co-reagent was WO_2 or WO_3 . In both experiments, the loss trailed off to a slow but steady decline attributed to the decomposition of UO_2F_2 . A more significant difference emerged when the reaction temperature was lowered to 700°C . At that temperature, the weight loss for the UF_4/WO_2 mixture was notably faster than that for the UF_4/WO_3 combination and went essentially to 100% completion while the latter reaction yielded only 70% of the expected loss.

The last point of discussion addressing the micro-scale experiments concerns the composition of the post-reaction residue. For all reactions performed at 700°C and above, the solid, end-product was similar, being predominantly UO_2F_2 . Several diffraction patterns of materials synthesized under different conditions are pictured in **Figure 68**. The presence of small peaks caused by small amounts of UF_4 and U_3O_8 has been pointed out in previous discussion of x-ray data. What is of interest to note is the absence of diffraction peaks for any tungsten oxide species where stoichiometric conditions are not satisfied. As an example, the reaction between UF_4 and WO_2 at 700°C for the 1.014:1 UF_4/WO_2 mixture should have left behind approximately half the supplied tungsten oxide as WO_3 if the proposed reaction pathway in equation (9.2) (page 133) was followed. Based on calculation, the residue composition would contain ~27 wt% WO_3 , yet none was detected. One plausible explanation would be that the excess WO_3 reacted with UF_4 and/or the UO_2F_2 product. The diffraction pattern of the residue from the 700°C fusion between UF_4 and WO_3 (1:1.025 $\text{UF}_4:\text{WO}_3$) did show a second phase in addition to UO_2F_2 as a result of the excess WO_3 in the final material. However, the identity of this second phase could not be matched to anything in the x-ray database.

[UF₄+WO₂] and [UF₄+WO₃] Mixtures Heated to 700°C, 750°C and 800°C in Air

Figure 67. TGA results showing the weight change during reactions between mixtures of UF₄ with WO₂ and WO₃ at 700°C, 750°C and 800°C in air.

Figure 68. X-ray diffraction patterns for several residues from reactions between UF₄ with WO₂ and WO₃ at 700°C and 800°C and the reference pattern for UO₂F₂ (pdf# 27-0933).

Following the parameter study using the TGA apparatus, bench-scale trials began. The reactor configuration was explored briefly by performing one experiment in a vertically oriented, closed-end tube setup (WFusn-7) similar to the GeFusn-34 run. For the other ten experiments listed in

Table 28 (p.112), a horizontally mounted, flow-through tube reactor was used as the reaction apparatus. Experimental details for each run were provided in section **9.1.1**. Results for the first six reactions, WFusn-7 to WFusn-12, are compiled in **Table 48** and provide feedback on the effect of reaction temperature and choice of tungsten oxide reagent for producing WOF₄. A brief review of each of these trials is presented below including the analysis of the post-reaction solids by x-ray diffraction.

Table 48.

Summary of results for trials WFusn-7 to WFusn-12.

Experiment ID WFusn-	7	8	9	10	11	12
Reactor Configuration	Vertical closed-end tube	Horizontal flow-throu tube	Horizontal flow-throu tube	Horizontal flow-throu tube	Horizontal flow-throu tube	Horizontal flow-throu tube
Tungsten Reactant	WO ₂	WO ₂	WO ₂	WO ₂	WO ₃	WO ₃
Reaction Temperature (°C)	800	775	780	790	790	750
Calculated weight WOF ₄ expected (gm)	11.3769	4.3439	4.5785	4.7209	3.8022	3.3190
Calculated weight loss by reagents (gm)	9.3974	3.5881	3.7820	3.8994	3.3612	2.9339
Observed weight loss by reagents (gm)	N/M	1.5897	1.9596	5.1143	4.2912	2.8975
Observed weight gain in condenser flask (gm)	Trace	N/M	N/M	3.17	2.44	1.61
Reaction Conversion ^a (%)	Trace	44.3	51.8	131.2	127.7	98.8
Capture Efficiency ^b (%)	N/M	N/M	N/M	67.1	64.2	48.5

^a [Observed weight loss by reagents/Calculated weight loss by reagents] x 100%

^b [Observed weight gain in flask/Calculated weight of WOF₄ expected] x 100%

N/M = Not Measured

The first bench trial, WFusn-7, was performed in the 1"OD closed-end, nickel tube reactor which was oriented in a vertical position and heated by the *MiniMite*[®] tube furnace. After raising the furnace temperature to 800°C and holding for 30 minutes, only a very faint stream of vapor was observed entering the flask. A short time later it ceased so the experiment was terminated. It was obvious that heat transfer into the tube was poor using the vertical orientation since prior TGA experiments showed considerable reaction between reagents occurred even at 700°C. Visual inspection of the material in the reaction tube showed it was still green like the starting mixture.

The vertically oriented tube configuration was again abandoned and replaced with a horizontally mounted 1"OD flow-through tube reactor heated by the same *MiniMite*[®] tube furnace. In WFusn-8, the 250ml collection flask was submerged in an ice-water bath to enhance the condensation of product vapor. After 36 minutes at a reaction temperature of 775°C, the flow of white vapor into the flask came to a halt, suggesting either the reaction was complete or a blockage was restricting flow to the receiver. Again, the reaction was terminated after trapping only a very small amount of white solid. Upon disassembling the flow path from the flask back to the 1" tube, a white solid had deposited along the interior section of the ½" to ¼" reducing union, causing the interruption in flow. The white solid was removed to a ceramic dish where it slowly changed to a wet, green yellow mass. This residue was analyzed by x-ray diffraction but no discernable diffraction pattern was found after scanning several times, suggesting it was amorphous.

The post-reaction solid remaining in the nickel boat was recovered and analyzed. During the short reaction period, the UF₄/WO₂ mixture lost 1.5897 grams, presumably WOF₄. The resulting powder was pale yellow toward one side of the container where the volume of material had more than doubled. The powder closer to the bottom of the boat was a lighter shade of green. An x-ray diffraction pattern of this yellow powder is displayed in **Figure 69** along with the reference pattern for UO₂F₂ (pdf # 27-0933). As seen in the TGA experiments, the pale yellow residue was essentially UO₂F₂ and only very small peak intensities associated with UF₄ were present.

For WFusn-9, the reaction system was assembled as in the previous set-up. In order to prevent the condensation of white solid in the line to the flask, the sections of tubing from where the 1" tube left the furnace to the point where the collection flask was joined at the ¼" reducing union were wrapped with heat tape and insulation. During the run, this section of tubing was kept at 209°C. As the furnace temperature passed through the 700°C point, a white fume was seen passing into the flask being chilled in the ice-water bath. After 30 minutes into the reaction, the vapor stream stopped so the operation was terminated. Once again a blockage in the line formed in the 3" section of ¼" stainless steel tubing carrying product into the flask. This section of tube was the only section not heated because the connection to the flask was made using a viton o-ring and could not withstand the heat stress. As before, only a small amount of white fume was captured.

Assessment of post-reaction data included weight lost by the reactants (1.9596 grams) and x-ray analyses of the hydrolyzed solid causing the blockage, the residue remaining in the boat and the hydrolyzed solid trapped in the flask. The x-ray diffraction patterns for the three samples are included in **Figure 70** along with reference patterns identifying their compositions. When the solid causing the blockage in the tube was contacted with H₂O, it turned bright yellow. The same occurred when H₂O was added to the flask containing the white condensate. After removing the water in each sample, the yellow precipitate was analyzed and matched to a combination of hydrated WO₃ compounds, namely WO₃•2H₂O (pdf # 18-1419) and WO₃•H₂O (pdf # 43-0679). The partially reacted residue in the boat was matched to UO₂F₂ (pdf # 27-0933) and unreacted UF₄ (pdf # 32-1401).

Figure 69. X-ray diffraction pattern for residue from Wfusn-8 and the reference pattern for UO_2F_2 (pdf# 27-0933).

Figure 70. X-ray diffraction patterns for the hydrolyzed residue causing the blockage in the tube, the hydrolyzed solid captured in the flask and residue in the boat from WFusr-9 and reference patterns for $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ (pdf# 18-1419), $\text{WO}_3 \cdot \text{H}_2\text{O}$ (pdf# 43-0679), UF_4 (pdf# 32-1401) and UO_2F_2 (pdf# 270933).

Using the weight loss data, the conversion of WO_2 to WOF_4 was estimated by ratioing the "Observed weight lost by the reagents" to the "Calculated weight loss by the reagents" predicted according to equation (9.2) (page 133) given earlier. In WFusn-9 the estimated reaction conversion was 51.8%.

Since the previous two experiments were terminated prematurely because of blocked lines, the pathway to the condensation zone was redesigned in the next trial, WFusn-10. The flask used for capturing the white fume was replaced with a 1"OD tube approximately 10" long. The tube was connected at a 90° angle to the reactor outflow via a union elbow modified with a ¼" outage tube welded through the wall to direct flow from the tube. In this configuration, the diameter of the line from the reaction zone to the condensation zone was maintained at 1"OD.

The reaction in WFusn-10 was carried out for two hours at 790°C with the condensation tube submerged in ice-water. Approximately 3.17 grams of condensed product was trapped while a loss of 5.1143 grams was recorded for the contents of the boat. Upon retrieving the boat from the reaction zone, it was observed that the volume of residue had expanded so much so that it overflowed the confines of the vessel. A sample of the bulk residue was taken for x-ray analysis. The condensed solid in the tube was contacted with H_2O , forming the familiar yellow precipitate, which was also isolated for characterization by x-ray diffraction. The experimental patterns are shown in **Figure 71** along with matching reference patterns. When dried, the yellow precipitate matched the reference for hydrated WO_3 . For this reaction, a capture efficiency of 67.1% was reported. It was defined as the ratio between "Observed weight gain in condensation flask" compared to the "Calculated weight of WOF_4 expected" for the complete reaction.

Figure 71. X-ray diffraction patterns for the residue recovered after WFusn-10, the hydrolyzed residue from the condensation tube and reference patterns for UO_2F_2 (pdf# 27-0933) and $\text{WO}_3 \cdot \text{H}_2\text{O}$ (pdf# 43-0679).

After completing three trials using WO_2 as the oxide source, a bench-scale reaction between UF_4 and WO_3 [$\text{UF}_4:\text{WO}_3 = 2.001 : 1$] was investigated. The combination of reagents was heated at 790°C for 3 hours and a volatile reaction product was captured in the 1"OD collection tube as in the previous trial. During the reaction, 4.2912 grams was lost from the starting mixture while 2.44 grams was captured in the chilled tube. Capture efficiency was determined to be 64.2%. The residue recovered from the reactor was pale yellow and had swelled in volume but remained within the boat. There was evidence of a light coating of residue along the interior surfaces of the elbow union and upper section of the collection tube where it was not chilled by the ice-water bath.

The solid from WFusn-11 was analyzed by x-ray diffraction along with a hydrolyzed sample of material captured in the tube. Patterns for those specimens are displayed in **Figure 72** and **Figure 73**. The residue from the boat shown in **Figure 72**, did contain the familiar UO_2F_2 but another phase(s) was present which did not match well to any reference compound in the x-ray database. The solid residue made between UF_4 and WO_3 when reacted at 800°C in the TGA apparatus is also included for comparison. Patterns for the white fume after being hydrolyzed by H_2O and dried are presented in **Figure 73**. The bright yellow precipitate was matched to a combination of hydrated WO_3 species similar to what was seen after hydrolyzing the condensed material from WFusn-10 where WO_2 was the co-reagent.

Since the residue left behind in WFusn-11 contained a phase not seen before, a second reaction was performed using the same parent UF_4/WO_3 stock mixture with the 2.001:1 molar stoichiometry. In WFusn-12, the receiver vessel was changed to the 250ml round bottom flask and the line wrapped with heat tape back to where the reaction tube emerged from the furnace. During the trial, white fume was collected for about 100 minutes at 750°C . At that point the reaction was stopped since no fume was seen entering the flask. That observation was a strong indication the line might be blocked again. The heated section of the line to the flask did reach 204°C during the run. Upon cooling and disassembly, no blockages or restrictions were found in the pathway to the round bottom flask. The powder in the boat had swelled in volume and was pale yellow over the surface but took on a greenish tint as the bulk was probed. An x-ray diffraction pattern of this residue is shown in **Figure 74** along with matching reference patterns for UO_2F_2 (pdf # 27-0933) and UF_4 (pdf # 32-1401). The unidentified phase produced in WFusn-11 was not observed in the WFusn-12 product but rather the same two phases seen in many of the trials.

The overall reaction conversion for WFusn-12 was 98.8% based on the observed weight loss by the reagents while the capture efficiency was only 48.5% of the expected amount of WOF_4 . From inspection of the interior walls of the line from the reactor exit to the flask, there was a coating of a deep blue colored residue evenly deposited over the surface. The intense blue color is consistent with a tungsten oxide phase with the formula $\text{W}_2\text{O}_5^{28}$, which obviously developed through deposition and decomposition of WOF_4 as it passed through the heated line to the flask.

Figure 72. X-ray diffraction patterns for the residue recovered after WFusn-11, the residue produced by the reaction between UF_4 and WO_3 at 800°C in the TGA apparatus and the reference pattern for UO_2F_2 (pdf# 27-0933).

Figure 73. X-ray diffraction patterns for hydrolyzed samples of condensed solid produced in WFusn-10 and WFusn-11 and reference patterns for $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ (pdf# 18-1419) and $\text{WO}_3 \cdot \text{H}_2\text{O}$ (pdf# 43-0679).

Figure 74. X-ray diffraction patterns for the bulk reaction residue recovered from WFusn-12 and reference patterns for UO_2F_2 (pdf# 27-0933) and UF_4 (pdf# 32-1401).

After completing WFusn-12, five additional bench trials were performed, all using WO_2 as the primary tungsten source. Of the five, three runs consisted of two reaction steps in order to probe the reactivity of the WOF_4 compound and explore pathways to produce WF_6 . As before, the experimental details for each of the trials were given in section 9.1.1. Results for WFusn-13, -14, -15, -16 and -17 are arranged below in Table 49. A brief review of each run, including material characterization of the post-reaction residues is presented here.

Table 49.

Summary of results for WFusn-13 to WFusn-17.

Experiment ID WFusn-	13	14	15	16	17
Reaction step (1)	$\text{UF}_4 + \text{WO}_2$	$\text{UF}_4 + \text{WO}_2$	$\text{UF}_4 + \text{WO}_2$	$\text{UF}_4 + \text{WO}_2$	$\text{UF}_4 + \text{WO}_2$
(2)	$\text{WOF}_4 + \text{UF}_4$	—	$\text{WOF}_4 + \text{SiO}_2$	—	$\text{WOF}_4 + \text{TiF}_4$
Reaction Temperature ($^{\circ}\text{C}$)	750	800	800	780	800
Calculated weight WOF_4 expected (gm)	3.4109	3.7112	4.3751	4.1984	4.6023
Calculated weight loss by reagents (gm)	2.8172	3.0655	3.6138	3.4677	3.8015
Observed weight loss by reagents (gm)	3.3090	4.2125	4.1800	4.1181	4.5586
Observed weight gain in condenser flask (gm)	N/M	1.80	N/M	2.19	2.44
Reaction Conversion ^a (%)	117.5	137.4	115.7	118.8	119.9
Capture Efficiency ^b (%)	N/M	48.5	N/M	52.2	53.0

^a [Observed weight loss by reagents/Calculated weight loss by reagents] x 100%

^b [Observed weight gain in flask/Calculated weight of WOF_4 expected] x 100%

N/M = Not Measured

The first of the 2-step experiments to be performed was WFusn-13. Here, the plan was to first react UF_4 with WO_2 to make WOF_4 , then react that material with more UF_4 , as shown in the step (2) reaction given in Table 35 (p.119). The reaction was setup as in previous trials using a 2-neck 500ml round bottom flask as the condensation vessel. About 2.17 grams of UF_4 was added to the flask before the $\text{UF}_4 + \text{WO}_2$ reaction was started. During the two-hour reaction period at 750°C , white fume was deposited over the bed of green salt maintained at 0°C in the flask submerged in the ice-water bath. There were no signs of spontaneous reaction between the condensed fume and UF_4 . After concluding the reaction, the flask was removed from the line and sealed. The white fume was thoroughly mixed with the green salt by gently swirling the

flask and the combination allowed to stand overnight at ambient temperature. After finding no change in appearance of the mixed materials, the flask was then connected to a flow of dry air and heated to 196°C where very little change was observed after one hour.

Upon conducting the post-reaction assessment, contents of the nickel boat lost 3.3090 grams compared to the 2.8172 grams expected by calculation using the reaction in step (1) shown in **Table 35** (page 119). As seen earlier, the powdery residue was pale yellow and had swelled in volume across the right half of the boat. The left side surface and subsurface materials contained a notably greener tint. All was recovered for analysis by x-ray diffraction. Those results are shown in **Figure 75**. The solid product was consistent with previous experiments where UO_2F_2 and a small amount of unreacted green salt were the only constituents present.

The amount of condensed white fume was not determined although it was sufficient to investigate if the equation given in **Table 36** is a viable pathway to WF_6 . X-ray analysis of the green material recovered after heating the condensed fume/ UF_4 mixture is shown in **Figure 76**. Here the sample pattern matched well with the pattern collected for untreated UF_4 . The reference pattern for UO_2F_2 is also included since detection of any amount in the residue would be a signal that the conversion to $\text{WF}_6(\text{g})$ listed in **Table 36** had gotten underway. The small diffraction peak observed at $\sim 17^\circ$ 2- θ in the middle pattern of **Figure 76** may be the first indication that UO_2F_2 was indeed produced by the reaction of UF_4 with WOF_4 . However, from the observations and data collected, evidence for that reaction was not clearly established.

Figure 75. X-ray diffraction patterns for the residue recovered from WFusn-13 and untreated UF_4 and the reference pattern for UO_2F_2 (pdf# 27-0933).

Figure 76. X-ray diffraction patterns for the residue recovered after heating the UF_4/WO_4 mixture to 196°C in air, untreated UF_4 and the reference pattern for UO_2F_2 (pdf# 27-0933).

After completing the first two-step reaction using UF_4 , another single-step reaction, WFusn-14, was performed with the intent to optimize the yield of oxyfluoride intermediate. During this trial, the line from the reaction tube to the collection flask was heated and an accelerated heating profile (shown in **Table 37** (p.121)) was tested. Upon concluding the run, approximately 1.80 grams of residue was collected in the condenser which represented ~48.5% of the calculated yield. Along with the white residue, there was also evidence of a fine green residue in the collection vessel. During disassembly of the reactor to recover the reacted solids, the interior walls of the exit line leading back to the Ni tube were dusted with a green powdery film. The contents of the Ni boat were completely yellow on the surface and throughout the bulk and had expanded in volume filling the boat to capacity without spillover.

Both the pale yellow solid from the boat and the fine green powder found on the interior walls downstream from the reactor were analyzed by x-ray powder diffraction. Those results are shown in **Figures 77, 78 and 79**. As in previous trials, the pattern for the pale yellow solid matched the reference pattern for UO_2F_2 (pdf# 27-0933), depicted in **Figure 77**. However, there were additional peaks of low intensity in the pattern that proved a challenge to index. As seen in **Figure 78**, the residual peaks in the pattern for the post-reaction solid indexed well with several hydrated species of UO_2F_2 , namely $\text{UO}_2\text{F}_2 \cdot 1.5\text{H}_2\text{O}$ (pdf# 24-1154) and $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$ (pdf# 24-1153). The diffraction pattern for the green powder coating the interior walls of the exit line is shown in **Figure 79**. It is clearly evident the green solid is UF_4 when compared to the pattern recorded for the virgin reagent. The conveyance of UF_4 throughout the exit line down to the condenser must be a direct result of the accelerated heating profile to 800°C which lead to the rapid and disruptive evolution of WOF_4 vapor entrained with green salt. The loss of UF_4 from the reaction vessel would also help to explain the larger weight loss by the reagents (4.2125gm) when compared to the calculated weight loss expected (3.0655gm).

Following the completion of WFusn-14, all components of the reaction system from the Ni tube to the condenser vessel were thoroughly cleaned to remove any UF_4 deposited downstream during the reaction. The 1" Ni tube was heated to 150°C for 4 hours to thoroughly dry the reaction chamber. The cleaned components were re-assembled for use in the next experiment, WFusn-15.

Figure 77. X-ray diffraction pattern for the residue from WFusn-14 and the reference pattern for UO_2F_2 (pdf# 27-0933).

Figure 78. X-ray diffraction pattern for the WFusn-14 residue and reference patterns for two hydrated analogs of UO₂F₂ formed by adsorption of moisture from the air, UO₂F₂•1.5H₂O (pdf# 24-1154) and UO₂F₂•2H₂O (pdf# 24-1153).

Figure 79. X-ray diffraction pattern for the green powder coating the interior walls of the reaction tube and reference pattern for untreated UF₄.

For the WFusn-15 trial, a two-step reaction scenario was undertaken. Details of this scheme were given in **Table 38** (p.122). A less aggressive heating program was implemented in an attempt to prevent the expulsion of green salt from the reagent boat while the line to the condenser was heated and maintained at $\sim 202^{\circ}\text{C}$. In preparation for the reaction in step (2), approximately 0.5 gram of SiO_2 was added to the WOF_4 condenser. Initially and throughout the reaction period, as WOF_4 accumulated in the flask, there was no visible sign of reaction between WOF_4 and SiO_2 at the 0°C temperature of the surrounding ice/water bath.

Upon conclusion of the step (1) reaction, the ice/water bath surrounding the collection flask was removed and the flask warmed to ambient temperature while maintaining a flow of air through the vessel. A heating mantle was placed around the flask with a thermocouple situated near the bottom where the bulk of the residue had deposited. The mixture of condensed residue and SiO_2 was slowly heated to explore the reaction in step (2). After reaching $\sim 100^{\circ}\text{C}$, the WOF_4 component began to melt, showing no signs of reaction. At $\sim 187^{\circ}\text{C}$, the tungsten oxyfluoride began to vaporize and re-crystallize on the upper sections of the flask which were not heated, again without displaying any signs of color change or evolution of SiF_4 gas. The anticipated product, WO_3 , is bright yellow but no hint of color change was observed. It might well be that the reaction requires a higher temperature than what was attained here for significant conversion to occur.

Following the completion of the second reaction step, the post-reaction solids in the Ni tube were recovered and analyzed. The UF_4/WO_2 reagent mixture lost 4.18 grams, which was slightly more than the calculated loss of 3.6138 grams. Again, the contents of the boat were completely pale yellow and the volume of solids expanded to maximum capacity. During the weight measurement, a slow but steady weight gain was observed as the boat sat on the balance, most probably as a result of the adsorption of moisture from the air. An x-ray diffraction pattern of the pale yellow residue is shown in **Figure 80** along with the reference patterns for UO_2F_2 (pdf# 27-0933) and a hydrated analog, $\text{UO}_2\text{F}_2 \cdot 1.5\text{H}_2\text{O}$ (pdf# 24-1154). Similar to WFusn-14, a coating of green powder was detected on the walls of the Ni tube downstream from the reaction zone but to a lesser extent. It appears the rapid rise in temperature from 725°C to 780°C over a 15 minute span was too severe for keeping the reagent bed from losing UF_4 .

After completing WFusn-15, it was observed that the nickel boat used in the majority of reactions conducted in the tube reactor between UF_4 and WO_2/WO_3 showed evidence of significant corrosion. The used boat was set aside for more detailed examination and analysis. A discussion of those results is included in section 9.2.2 as part of the investigation into suitable materials of construction for the WF_6 production system. Another clean nickel boat was used for the remainder of the program.

As done previously, the nickel reaction tube was cleaned again due to the expulsion of green salt from the reagent mixture. The reaction apparatus was re-assembled and heated to insure it was free from moisture.

Figure 80. X-ray diffraction pattern for the pale yellow solid recovered from WFusn-15 and reference patterns for UO₂F₂ (pdf# 27-0933) and UO₂F₂•1.5H₂O (pdf# 24-1154).

Before starting WFusn-16, a single-step reaction, several changes to the experimental procedure and apparatus were instituted. The furnace heating cycle was adjusted in order to control the displacement of UF_4 from the reagent mixture and a larger collection vessel was inserted into the exit stream to enhance product capture. During the three-hour reaction period the exit line to the condenser was maintained at 210°C while the condenser was submerged in an ice/water bath. The 780°C maximum temperature was held for 135 minutes before concluding the run. Under these conditions, 2.19 grams of WOF_4 was collected which was about 52.2% of the theoretical yield. The condensed solid was completely white with no sign of contamination by displaced UF_4 .

Upon recovery of the post-reaction solids, the material in the boat had a green tint on the surface off to one end. Approximately 80% of the reagent mixture expanded to maximum capacity while leaving the green-tinted area undisturbed. As the solid was transferred to a storage container, the powder adjacent to the bottom of the boat had the familiar green tint of partially reacted material. It did not appear that any material was expelled from the boat. It was also evident that the exterior surfaces of the boat changed from metallic gray to green, similar to the exterior color of the previous boat.

As in previous trials, the solid produced in WFusn-16 was analyzed by x-ray diffraction. The pattern for the recovered residue is shown in **Figure 81** along with matching reference patterns for UO_2F_2 (pdf# 27-0933) and $\text{UO}_2\text{F}_2 \cdot 1.5\text{H}_2\text{O}$ (pdf# 24-1154). There were also low intensity peaks indexed to the pattern collected for unreacted green salt. Similarly, during the transfer of the pale yellow solid to the storage container, the residue appeared to adsorb moisture and form a sticky, wet mass.

In regard to the changes implemented for WFusn-16, use of the larger collection vessel did not appear to greatly improve the efficiency of capturing WOF_4 . However, the attenuated heating program did appear to curtail the liberation of UF_4 from the reagent bed but may have contributed to the presence of unreacted material left behind.

Figure 81. X-ray diffraction pattern for the residue reclaimed from WFusn-16 and reference patterns for UO_2F_2 (pdf# 27-0933), $\text{UO}_2\text{F}_2 \cdot 1.5\text{H}_2\text{O}$ (pdf# 24-1154) and unreacted UF_4 .

The last trial conducted in the horizontal tube reactor setup was WFusn-17, which was planned as a two-step scenario. The reaction system was setup similar to that for the WFusn-16 run with the exception that the exit line to the condenser was not heated but wrapped only with insulation. The same condenser containing the 2.19 grams of WOF_4 collected in WFusn-16 was put in place to receive the output from step (1) of this trial. Details of the WFusn-17 experiment were given in **Table 41** (p.125) in section **9.1.1**. Using a duplicate set of heating parameters and reaction times, the reaction between UF_4 and WO_2 produced an additional 2.44 grams of WOF_4 , which was about 53.0% of the expected amount. As before, the post-reaction solids in the boat were green-tinted at one end while completely yellow at the other. Weight lost by the reagents during the reaction amounted to 4.5586 grams compared to the theoretical loss of 3.8015 grams calculated. The residue was split into two samples, separating the pale yellow solid from the green-tinted material. It is interesting to note that before removing the powder from the boat, there were many fragments of dark-colored scale scattered across the surface of the powder as seen below in **Figure 82**.

Figure 82. Post-reaction residue in the nickel boat after WFusn-17 showing many pieces of scale scattered across the surface of the UO_2F_2 powder.

A detailed discussion of the origin of the scale is included in the next section concerning the selection of appropriate materials of construction for the reaction system.

The two samples of residue collected from the boat were analyzed by x-ray diffraction. Those results are shown in **Figure 83** and **Figure 84** for the green-tinted and pale yellow powders, respectively. The green-tinted material was indexed to three phases including UO_2F_2 (pdf# 27-0933), $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$ (pdf# 24-1153) and a small amount of unreacted UF_4 (see **Figure 83**). The pale yellow fraction, representing a majority of the bulk, was indexed to UO_2F_2 and a small amount of the hydrated analog, $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$ (**Figure 84**).

Figure 83. X-ray diffraction pattern for the green-tinted portion of residue from WFusn-17 and reference patterns for UO_2F_2 (pdf# 27-0933), $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$ (pdf# 24-1153) and unreacted UF_4 .

Figure 84. X-ray diffraction pattern for the pale yellow residue from WFusn-17 and reference patterns for UO_2F_2 (pdf# 27-0933) and $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$ (pdf# 24-1153).

After completing the first stage of WFusn-17, the total amount of WOF_4 contained in the pyrex[®] cylinder climbed to 4.63 grams. This material was then used as a reactant for the reaction shown in **Table 42** (page 126), that being the reaction with TiF_4 . When TiF_4 was added to the WOF_4 powder, there were no visible changes observed as the two compounds were mixed. The combined powder mixture was then heated slowly using a heat gun. Gas bubbles began to pass through the in-line traps and at one point a vapor cloud appeared above the liquid NaOH trap. After 5-7 minutes of heating, it appeared the temperature reached the vaporization point for WOF_4 ($\sim 187^\circ\text{C}$) which lead to a buildup of condensed film on the upper sections of the cylinder. Throughout the heating period, the white color of the mixture did not appear to change. However, no color change was expected since the TiO_2 product is also white.

After cooling the cylinder to ambient temperature, it was put back into the argon-filled glovebag where the material deposited in the upper sections was dislodged and recombined with the bulk solids. The pyrex[®] condenser was then heated a second time using the heat gun. After 10 minutes of applied heat, there was no sign of further reaction or sublimation of components so the experiment was terminated. The post-reaction solid was transferred to a storage container while being handled in the glovebag. X-ray diffraction analysis of the residue was not done due to the potential release of hazardous hydrogen fluoride vapors from any leftover unreacted materials.

Based on the observation of bubble formation and a vapor cloud in the NaOH trap, it was concluded that there was at least partial reaction between TiF_4 and WOF_4 and that further experimentation using TiF_4 as the fluorinating agent was warranted. The new chemistry proposed for making WF_6 is based on the reaction of TiF_4 with WO_2 , as presented in **Table 43** (p.127). To explore this scenario, milligram quantities of reactants were combined and reacted in the thermogravimetric analyzer (TGA).

For this micro-scale experiment, 8.549 milligrams of combined reactants were heated to 500°C in a stream of dry air. The results of the prescribed treatment are shown in **Figure 85**, displaying the weight change of the reactants over the course of the thermal treatment. During the first 15 minutes at ambient temperature, the contents of the cup gained weight ($\sim 0.1\text{mg}$), most likely as a result of moisture adsorption. Then, as the temperature rose to the 500°C plateau, there were three weight loss events clearly delineated before the sample weight stabilized at the peak temperature. Overall, the starting materials lost a total of 1.61mg during the experiment. The first significant weight loss event began around 44°C and carried out to a temperature of $\sim 321^\circ\text{C}$, accounting for a loss of $\sim 0.8\text{mg}$. A second, smaller weight loss of $\sim 0.3\text{mg}$ occurred between 321°C and 441°C followed by a third decline of $\sim 0.5\text{mg}$ as the 500°C plateau was reached. A complete explanation of each event is not possible without performing additional trials and supplemental analytical data gathering. However, the first weight loss (representing $\sim 50\%$ of the total loss) strongly suggests that a reaction did occur between TiF_4 and WO_2 to produce a gaseous product. The second and third losses occurred at temperatures well above the sublimation temperature for TiF_4 (285.5°C)²⁹ which may help to explain, at least in part, the remaining 0.8mg loss.

$\text{TiF}_4 + \text{WO}_2$ Heated in Air to 500°C

Figure 85. TGA Plot showing the weight change during reaction between TiF_4 and WO_2 at 500°C in air.

After completing the micro-scale experiment in the TGA apparatus, gram quantities of TiF_4 and WO_2 were combined in a larger Parr[®] reaction apparatus illustrated in **Figure 52** in section 9.1.1. Results for the WFusn-19 trial were archived since the WFusn-18 experiment was terminated without preserving any FT-IR data for the gaseous reaction products made in that run.

During the WFusn-19 trial, 7.6916 grams of TiF_4/WO_2 mixture were heated slowly to 265°C over a 2.5-hour period. FT-IR spectra were collected for aliquots of gas captured in the gas cell when the reactor temperature reached 85°C, 185°C, 187°C, 190°C and 245°C. At 85°C, a stream of white vapor was again seen exiting the scrubber line. This was the point at which the first aliquot of gas was isolated in the gas cell. Approximately 32 minutes into the reaction period, the flow of air through the vessel to the scrubber stopped. Pressure in the reactor rose to ~30psi with the temperature at ~180°C. The contents of the vessel were vented through the gas cell and several aliquots were analyzed at this juncture. The last sample of reactor off-gas was taken when the reactor was at 245°C. Following that sample, the reactor was closed to flow and the experiment allowed to continue for an additional 30 minutes at a pressure of ~10psi with the temperature between 245°C-265°C. During this period, the pressure in the vessel did not change which was taken as a sign that the reaction did not produce additional gaseous products so the trial was terminated.

The FT-IR spectra collected at the aforementioned temperatures are shown in **Figure 86** along with the times during the reaction the aliquots were taken. It was clear that the samples captured at temperatures of 185°C and 187°C contained strong absorption peaks in the range between 4000-3000 cm^{-1} , 1350-1100 cm^{-1} and 950-700 cm^{-1} . At the 190°C plateau 89 minutes into the reaction, the intensity of the absorption peaks dropped off dramatically and at 245°C the absorption intensity of the sample was diminished to near-background levels.

Interpretation of the FT-IR data shown in **Figure 86** was started by comparing the spectrum for the 185°C aliquot with reference spectra for HF and WF_6 , as shown in **Figure 87**. The highly absorbing specimen collected at 185°C was subsequently pulsed several times with aliquots of ultra-high purity (UHP) grade helium gas to dilute the material and bring the strong absorption peaks within the range of the spectrometer's detector. The five narrow peaks between 4000-3700 cm^{-1} indicated the presence of HF , which was essentially present in all the aliquots of reactor off-gas examined. The strong absorption band between 3700-3100 cm^{-1} became better defined in the spectrum for the diluted sample, revealing the presence of two peaks with maxima at ~3500 cm^{-1} and 3380 cm^{-1} and a shoulder band at ~3200 cm^{-1} . As yet, these bands remain unidentified but their presence suggest the specimen contained more species than the two reference compounds shown. The broad bands in the 1350-1100 cm^{-1} region diminished in the diluted sample and also did not correspond with the reference materials. The small narrow peak located at ~1025 cm^{-1} indicated the presence of SiF_4 , which could be traced back to the fluorination of silicon-based lubricant used in the *Swagelok*[®] valves used to close the entrance and exit ports on the gas cell and exit lines from the *Parr* reaction vessel. The remaining three broad bands across the 950-700 cm^{-1} region corresponded with peak locations found in the WF_6 reference spectrum and could be the first indications that WF_6 was produced during the reaction.

After completing the trial, the reaction system was disassembled in stages to learn more about where blockages in the exit line formed which stopped flow of gas to the scrubber. The 1/8" OD tube connecting the 3-way valve to the scrubber (refer to **Figure 52**) was packed with a white solid at the connection to the 3-way valve. The sections of 1/4" OD line from the 3-way valve to the ball valve and ball valve to reactor top also contained a heavy deposit of white residue. Upon opening the *Parr* vessel, the underside of the reactor lid was totally covered

Figure 86. FT-IR spectra of gaseous samples collected at various reactor temperatures during the WFusn-19 reaction.

Figure 87. FT-IR spectra of the gas aliquot collected at 185°C, the same sample after diluting with helium and reference spectra for WF₆ and HF.

with a layer of white solid. After sitting exposed to the air for an hour the solid appeared to hydrolyze, leaving a wet surface in areas where the residue was not very thick. At this point, the reactor lid was submerged in distilled water to remove the residue. The resulting solution had a blue tint and the material sticking to the underside turned dark blue in color. The solid remaining in the lower section of the reactor was a mix of gray and white particles of loose powder that did not appear to change or adsorb moisture after standing in air for several hours. The post-reaction solid was not analyzed by x-ray diffraction due to the potential for release of HF vapors during the analysis. However, the residue collected from the underside of the reactor lid in the aqueous solution was examined further by x-ray diffraction after drying the solution to recover the solid. The x-ray diffraction pattern for the dried material is shown in **Figure 88** along with the matching reference pattern for TiOF_2 (pdf# 08-0060). Based on the presence of oxyfluoride after contact with water, the white solid deposited on the lid and accumulated downstream causing the blockages in the lines was most likely TiF_4 which separated from the reaction mixture via sublimation. The hydrolysis reaction to produce the TiOF_2 is given in equation (9.4) below,

Although the TiF_4 sublimation temperature of 285°C was not reached, the temperature of the reaction vessel was high enough to cause a significant amount of TiF_4 to volatilize and collect downstream on cooler surfaces.

Figure 88. X-ray diffraction pattern for the hydrolyzed residue recovered from the underside of the reactor lid and the reference pattern for TiOF_2 (pdf# 08-0060).

9.2.2 Selection of suitable materials of construction for producing WF_6 .

The nickel boat used to hold the uranium tetrafluoride/tungsten oxide mixtures during the many experiments to produce WOF_4 showed significant corrosion and deterioration. An investigation into the corrosion was begun in order to learn what effects the high temperature fusion chemistry would have on a reaction system constructed of nickel. To document the corrosion, several images of the boat were collected and are presented below in **Figure 89**, **Figure 90** and **Figure 91**.

Figure 89. Image of nickel boat used in the high temperature fusion reactions between UF_4 and WO_2/WO_3 mixtures.

Figure 90. Side view image of the nickel boat showing the green-brown corrosion layer covering the exterior and interior walls. The arrow shows where a piece of scale was removed from the exterior wall.

Figure 91. A close-up image of the nickel boat showing the corrosion of the interior walls.

It was clear much of the boat's exterior and interior walls were covered with a green-brown layer of flaky solid. A large piece of the corrosion layer was removed (refer to **Figure 90**) and divided into two specimens for characterization by x-ray diffraction. One piece of scale was mounted exposing the outward-facing surface of the flake to the x-ray beam while the other sample was prepared with the interfacial side (side oriented against the wall of the boat) facing the analysis beam. The x-ray diffraction patterns for the two specimens are given in **Figure 92**, showing dissimilar patterns at first glance. Both patterns were then analyzed in detail and indexed to constituent phases. As shown in **Figure 93**, the outward facing surface of the flake was matched to three phases including NiO (pdf# 47-1049), NiWO₄ (pdf# 15-0755) and NiF₂ (pdf# 24-0791). Here, the peak intensities indexed to each compound were about equal. As depicted in **Figure 94**, the interfacial side of the flake was also indexed to the same three compounds with the exception that the intensity of the NiO component was the dominant phase by a wide margin.

Using the x-ray results of the scale material, the corrosion of nickel can be described by the following sequence of reactions:

Figure 92. X-ray diffraction patterns for the outward and inward facing sides of the scale removed from the side of the nickel boat shown in Figure 90.

Figure 93. X-ray diffraction pattern for the outward facing side of the scale and reference patterns for NiO (pdf# 47-1049), NiF₂ (pdf# 24-0791) and NiWO₄ (pdf# 15-0755).

Figure 94. X-ray diffraction pattern for the inward facing side of the scale and reference patterns for NiO (pdf# 47-1049), NiWO₄ (pdf# 15-0755) and NiF₂ (pdf# 24-0791).

As shown in **Table 50** below, both reactions displayed favorable thermodynamic parameters¹⁴ (negative *Gibbs* free energy change, $-\Delta G$) over the temperature ranges used in the fusion experiments. The interfacial side of the scale was essentially nickel oxide (NiO) since that surface had little or no direct contact with WOF₄ vapor. The reaction in equation (9.6) (page 187) will likely occur on all the oxidized nickel surfaces around and downstream from the heated reaction zone, including the boat and the walls of the Ni reaction tube.

Table 50.

Thermodynamic calculations describing the two-step corrosion process occurring on the surface of nickel.

Step (1): $2\text{Ni} + \text{O}_2(\text{g}) \longrightarrow 2\text{NiO}$				
T(°C)	delta H(kcal)	delta S(cal)	delta G(kcal)	K
0.00	-114.608	-45.249	-102.248	6.555E+081
100.00	-114.383	-44.567	-97.753	1.809E+057
200.00	-113.936	-43.522	-93.344	1.316E+043
300.00	-113.234	-42.162	-89.069	9.249E+033
400.00	-113.100	-41.946	-84.864	3.587E+027
500.00	-112.859	-41.611	-80.687	6.456E+022
600.00	-112.639	-41.345	-76.539	1.443E+019
700.00	-112.436	-41.124	-72.416	1.839E+016
800.00	-112.242	-40.934	-68.313	8.192E+013
900.00	-112.051	-40.764	-64.229	9.254E+011
1000.00	-111.856	-40.605	-60.160	2.128E+010

Step (2): $3\text{NiO} + \text{WOF}_4(\text{g}) \longrightarrow \text{NiWO}_4 + \text{NiF}_2$				
T(°C)	delta H(kcal)	delta S(cal)	delta G(kcal)	K
0.00	-92.628	-42.610	-80.989	6.389E+064
100.00	-92.260	-41.410	-76.807	9.749E+044
200.00	-92.437	-41.799	-72.660	3.670E+033
300.00	-93.116	-43.122	-68.401	1.215E+026
400.00	-93.172	-43.215	-64.082	6.412E+020
500.00	-93.113	-43.134	-59.764	7.853E+016
600.00	-92.989	-42.984	-55.457	7.623E+013
700.00	-92.820	-42.801	-51.168	3.106E+011
800.00	-92.606	-42.592	-46.898	3.562E+009
900.00	-92.336	-42.352	-42.650	8.834E+007
1000.00	-91.995	-42.074	-38.429	3.956E+006

The choice of nickel as a suitable material from which to construct a reaction system appears to have significant corrosion issues that must be resolved before a production system can be built. One approach requiring further investigation and verification would be to passivate the boat and internal surfaces of the nickel reaction tube with a tightly bound layer of NiF_2 as suggested by Dr. Beitz at *Argonne National Laboratory*. His description of such a procedure is included below,

"... it struck me that you might not be aware of a property of nickel that influences its passivation with respect to good fluorinating agents.

That property is its tendency to have some oxidation (nickel oxide) on its surface. Nickel oxide does not readily convert to nickel fluoride and has the tendency to flake off when the nickel part is heated to high temperature. In consequence, bare nickel can suddenly be exposed to the fluorinating agent at high temperature which, in the case of fluorine gas, might lead to burn through.

For these reasons, it is useful to heat nickel in hydrogen gas to reduce any surface oxide to elemental nickel. Ideally, the next step is to heat in fluorine gas at sub-atmospheric pressure (without having exposed the hydrogen-reduced surface to air or oxygen) to produce an adherent nickel fluoride passivation layer. For our vacuum systems, this process is straightforward, because we can add hydrogen gas, heat the metal parts (aside from the valve bodies) with a hand torch, pump out the hydrogen gas, and then add fluorine gas and heat again."

The boundary layer of NiF_2 would nullify the first step in the sequence of corrosion reactions (equation 9.5, p.187), thereby blocking the formation of NiO and prevent subsequent interactions with WOF_4 .

9.3 Discussion - WF₆.

9.3.1 Producing the WOF₄ Intermediate.

Tungsten tetrafluoride oxide, WOF₄, was successfully produced by reacting either WO₂ or WO₃ with UF₄. At 800°C, there is little difference in the weight loss curves recorded during the TGA experiments using these constituents (refer to **Figure 67**). However, at lower temperatures around 700°C, it appears that the preferred tungsten source is WO₂. In the presence of air, the reaction scheme describing the process is given below along with the calculated (ref) *Gibbs* free energy change (ΔG).

WO₂ Reaction Scheme

	T (°C)	ΔG (kcal)
(A) $4UF_4 + 2WO_2 + 3O_2(g) \longrightarrow 2WOF_4(g) + 4UO_2F_2$	700	-33.344
	800	-31.631
(B) $12UO_2F_2 + 6WO_2 + O_2(g) \longrightarrow WOF_4(g) + 4U_3O_8$	700	+11.683
	800	-10.721
(C) $2WO_2 + O_2(g) \longrightarrow 2WO_3$	700	-85.994
	800	-82.594

It is important to note that equation (C) plays a role in how far equations (A) and (B) proceed before the reaction dynamic switches to that for a scheme involving WO₃.

WO₃ Reaction Scheme

	T (°C)	ΔG (kcal)
(D) $2UF_4 + WO_3 + O_2(g) \longrightarrow WOF_4(g) + 2UO_2F_2$	700	+9.654
	800	+9.666
(E) $6UO_2F_2 + 3WO_3 \longrightarrow 3WOF_4(g) + 2U_3O_8 + O_2(g)$	700	+134.833
	800	+118.530
(F) $2UO_2F_2 + WO_3 \longrightarrow WOF_4(g) + 2UO_2 + O_2(g)$	700	+73.106
	800	+65.557
(G) $3UO_2 + O_2(g) \longrightarrow U_3O_8$	700	-42.242
	800	-39.070

In comparing schemes for both tungsten oxides, all equations written with WO₂ show spontaneous behavior (negative ΔG values) except for equation (B) at 700°C while all equations using WO₃ have positive free energies at all temperatures. This trend bolsters the observation that UF₄/WO₂ mixtures showed greater reactivity at lower reaction temperatures. At the 800°C

temperature, conversion using either WO_2 or WO_3 appeared similar since the oxidation of WO_2 to WO_3 in an air-laden stream was rapid (see **Figure 53**) and redirects the reaction pathway to equation (D). Further consumption of UO_2F_2 to make WOF_4 and U_3O_8 or UO_2 is thermodynamically hindered (equations (E) and (F)). X-ray diffraction results of the post-reaction solids reclaimed from the TGA trials showed only minimal amounts of the U_3O_8 phase, which was more likely due to the thermal decomposition of UO_2F_2 than equation (E) above.

Bench-scale trials were successful in making WOF_4 in larger quantities. Condensation of the intermediate within the reaction system caused blockages during several early experiments, bringing them to an end prematurely. The first significant amount of WOF_4 was made in WFusn-10 where 3.17 grams was collected in a redesigned capture vessel. In the following run, WFusn-11, 2.44 grams of crystalline product was collected when WO_3 was fused with UF_4 at a reaction temperature of 790°C . From these two experiments it is apparent that significant amounts of the same material can be made using either oxide source.

Of the ten experiments performed in the tube reactor, seven trials showed larger than predicted weight loss by the reagents ranging from 15.7% to 37.4%. This excessive weight loss is reflected in the calculated 'Reaction Conversion' values given in **Tables 48** and **49** reporting conversions greater than 100%. The only reasonable explanation for the extraordinary weight loss suggests that some of the UO_2F_2 by-product is being lost from the reagent boat, possibly as fine particulate. This may be occurring as the volume of reactants undergoes a large expansion on the order of 200-300%. In particular, after the WFusn-10 trial, the contents of the reagent boat had expanded so much that some of the UO_2F_2 yellow powder spilled out of the boat before removing it from the reaction zone in the tube reactor. In several experiments (WFusn-14 and -15), the furnace temperature was ramped too aggressively, causing UF_4 to carry downstream into the condensation flask and contaminate the WOF_4 powder. Here the release of gaseous intermediate was so rapid that particles of solid became entrained in the gas stream. The fluidization of UF_4 was ultimately controlled by slowing down the furnace-heating schedule to a level where the reagent bed was left undisturbed.

9.3.2 Fluorinating WOF_4 to form WF_6 .

After studying the chemistry to form the WOF_4 compound, emphasis shifted to finding a suitable fluorinating agent for converting the oxyfluoride to tungsten hexafluoride. Candidate reactions using UF_4 and TiF_4 as fluoride sources showed that WOF_4 was resistant to conversion up to the vaporization temperature of the oxyfluoride ($\sim 187^\circ\text{C}$). Likewise, a probe reaction using SiO_2 to extract fluorine away from the tungsten compound was unsuccessful at bringing about a transformation where the thermodynamic variables were shown to be very favorable ($-\Delta G$ value). When the reaction between WO_2 and TiF_4 was performed in the TGA apparatus to evaluate the single-step synthesis route, a significant weight loss was observed and taken to be the start of the fluorination process. Potential reaction schemes describing the process are shown below including their thermodynamic assessment.

WF₆ Reaction Schemes

	T (°C)	ΔG (kcal)
(H) 3TiF ₄ + 2WO ₂ + O ₂ (g) → 2WF ₆ (g) + 3TiO ₂	200	-49.207
	500	-53.608
(I) 2TiF ₄ + 2WO ₂ + O ₂ (g) → 2WOF ₄ (g) + 2TiO ₂	200	-41.676
	500	-51.951
(J) 2WOF ₄ (g) + TiF ₄ (g) → 2WF ₆ (g) + TiO ₂	100	-16.660
	200	-5.038
	500	+6.223
(K) 4TiF ₄ + 2WO ₂ + O ₂ (g) → 2WOF ₄ (g) + 4TiOF ₂ (g)	200	+228.204
	500	+168.124

The feasibility of equations (H) and (I) are supported by spontaneous free energy changes up to the 500°C plateau temperature attained during the trial. However, there is a steady weight loss starting about 44°C shown in **Figure 85** that should not occur if equation (I) were the controlling pathway. WOF₄(g) generated by equation (I) could not vaporize until the temperature reached at least 187°C. Only then would a significant weight loss be observed. Beyond the 300°C mark, weight loss shown in the TGA result is most likely due to vaporization of unreacted TiF₄ out of the TGA cup. The TiF₄/WO₂ reaction was heated to a maximum of 500°C to prevent oxidation of WO₂ to WO₃. All reaction schemes between TiF₄ and WO₃ possessed positive *Gibbs* free energy values, thereby reducing the feasibility of making WF₆ by that alternative pathway.

The reaction between TiF₄ and WO₂ was then repeated in a flow-through bench-top reactor (WFusn-19) where the gas stream was analyzed by FT-IR spectroscopy to identify volatile reaction products. An aliquot of gas collected when the reactor temperature reached 85°C showed absorption bands assigned to HF, which was most likely formed by the interaction of adsorbed moisture (bound to WO₂) with TiF₄. Weight loss observed during the micro-scale experiment in this temperature region may have been due to the same TiF₄ hydrolysis side-reaction. However, the gas samples collected at 185°C and 187°C showed new bands that presented a challenge in matching their vibrational frequencies to known reference compounds. What is more interesting is the temperature at which the new bands show up in the gas stream. The intense absorption bands appeared at the same temperature that WOF₄ converts to a gas. If this is the case, then the reaction given in equation (I) may be the preferred pathway. As the temperature climbed above 200°C the absorption intensities of the new bands disappeared. This could be caused by the loss of intimate contact between the reagents as the evolving gas pushed the reactants further apart, thereby limiting the conversion to only nearest-neighbor proximity. Above 285°C TiF₄ goes into the gaseous state and could react with WOF₄(g), as in equation (J). However, the thermodynamic feasibility shifts to a non-spontaneous situation where the gas/gas scenario is not favored.

Since the reaction between TiF₄ and WO₂ may require a temperature above 300°C to bring about conversion, a static-bed flow-through reactor configuration like the one used here is not the most efficient design to facilitate a reaction between a gas and solid. At 285°C and above, titanium tetrafluoride would separate from the reaction mixture before significant

conversion could take place. This was indeed the case in WFun-19 where a layer of white solid (TiF₄) collected on the underside of the *Parr* reactor lid during the course of the experiment.

As a result of the limited interaction observed in WFusn-19, the TiF₄/WO₂ reaction scenario may be evaluated more effectively using a fluid bed reactor. This would require setting up an apparatus to create a continuous vapor stream of TiF₄ for passing through a bed of WO₂ maintained at a temperature up to 500°C. This reaction scheme is given in equation (L) along with relevant thermodynamic calculations.

(L) $3\text{TiF}_4(\text{g}) + 2\text{WO}_2 + \text{O}_2(\text{g}) \longrightarrow 2\text{WF}_6(\text{g}) + 3\text{TiO}_2$	<table> <tr> <th>T(°C)</th><th>ΔG (kcal)</th></tr> <tr> <td>100</td><td>-68.876</td></tr> <tr> <td>200</td><td>-59.001</td></tr> <tr> <td>500</td><td>-29.969</td></tr> </table>	T(°C)	ΔG (kcal)	100	-68.876	200	-59.001	500	-29.969
T(°C)	ΔG (kcal)								
100	-68.876								
200	-59.001								
500	-29.969								

Before concluding the discussion concerning fluorinating agents, several other candidate reactions can be proposed for converting the WOF₄ intermediate to WF₆. The chemistries are tabulated as above, showing the calculated *Gibbs* free energy change at the indicated temperature.

Potential Fluorination Routes

(M) $2\text{WOF}_4 + \text{GeF}_4(\text{g}) \longrightarrow 2\text{WF}_6(\text{g}) + \text{GeO}_2$	<table> <tr> <th>T(°C)</th><th>ΔG (kcal)</th></tr> <tr> <td>100</td><td>-16.622</td></tr> <tr> <td>200</td><td>-16.999</td></tr> <tr> <td>500</td><td>-15.027</td></tr> </table>	T(°C)	ΔG (kcal)	100	-16.622	200	-16.999	500	-15.027
T(°C)	ΔG (kcal)								
100	-16.622								
200	-16.999								
500	-15.027								
(N) $5\text{WOF}_4 + 2\text{As}_2\text{F}_5 \longrightarrow 5\text{WF}_6(\text{g}) + \text{As}_2\text{O}_5$	<table> <tr> <td>100</td><td>-47.291</td></tr> <tr> <td>200</td><td>-51.189</td></tr> <tr> <td>500</td><td>-54.881</td></tr> </table>	100	-47.291	200	-51.189	500	-54.881		
100	-47.291								
200	-51.189								
500	-54.881								
(O) $\text{WOF}_4 + 2\text{F}_2(\text{g}) \longrightarrow \text{WF}_6(\text{g}) + \text{OF}_2(\text{g})$	<table> <tr> <td>100</td><td>-72.958</td></tr> <tr> <td>200</td><td>-72.471</td></tr> <tr> <td>500</td><td>-69.382</td></tr> </table>	100	-72.958	200	-72.471	500	-69.382		
100	-72.958								
200	-72.471								
500	-69.382								
(P) $3\text{WOF}_4 \longrightarrow 2\text{WF}_6(\text{g}) + \text{WO}_3$	<table> <tr> <td>100</td><td>-45.089</td></tr> <tr> <td>200</td><td>-48.695</td></tr> <tr> <td>500</td><td>-54.649</td></tr> </table>	100	-45.089	200	-48.695	500	-54.649		
100	-45.089								
200	-48.695								
500	-54.649								

Equation (M) presents an interesting pathway where germanium can be used to shuttle fluorine from UF₄ to WF₆ via GeF₄. More traditional fluorinating agents such as arsenic pentafluoride

and elemental fluorine also have the necessary thermodynamic favorability to transform WOF_4 to WF_6 , as shown in equations (N) and (O), respectively. Lastly, WF_6 has been generated electrochemically³⁰ from acetonitrile solutions containing WOF_4 . All of these alternatives would require further study in order to establish their commercial viability and economic feasibility.

Conclusions

9.4 Conclusions - GeF_4 .

A process to produce GeF_4 of exceptional purity has been developed based on *Starmet's* new fluoride extraction technology. In this process, fluorine contained in UF_4 is recovered as a high-value fluoride gas when green salt is reacted with germanium dioxide. Of the nine tasks outlined in the Phase II work plan, seven have been completed, leaving two items concerning product qualification and fabrication of a production-scale apparatus to be addressed in the future as the demand for high purity material in the electronics and semiconductor sectors rebounds from an 18 month slump in the global marketplace.

From investigations performed here, it was determined that a horizontally oriented, tube-style reaction apparatus fabricated from nickel 200 alloy outperformed a larger crucible reactor setup constructed from *Haynes* HR160[®] alloy. The best overall performance observed during the reactor design trials occurred in GeFusn-28 where a conversion of 89.4% was posted in combination with a 97.7% capture efficiency. Here the reaction temperature reached a high of 700°C. Conversions as high as 98.1% were observed when UF_4 was reacted with GeO_2 at 775°C-800°C in a helium sweep stream. However, the highest capture efficiency in the helium-only carrier was 75.8% in contrast to 97.7% when the reactor sweep stream contained 10-12 vol.% of dry air. The presence of air in the sweep stream was beneficial in reducing the formation of GeF_2 residue by maintaining an oxidizing atmosphere above the reactant bed and initiating the reaction at a lower temperature.

Reaction sequences describing the synthesis of GeF_4 in inert and air-laden streams were proposed based on the experimental results collected. Those reactions where a pure helium stream was used revealed the formation of a UGeO_4 intermediate, which appeared to be the dominant germanium containing species left in the latter stages of the reaction. In contrast, only UO_2F_2 and UF_4 could be detected in residues collected where conversion was incomplete using a helium/air sweep stream. Kinetics of the UF_4/GeO_2 reaction could not modeled using the *Avrami* equation when air was present in the sweep stream as was the case for runs made in pure helium.

Corrosion studies revealed that materials such as copper, Monel, type 304 stainless steel and *Haynes* HR160[®] alloy were significantly compromised from attack by GeF_4 , forming germanium-rich scale and intermetallic compounds. Inconel 600, *Haynes* 242 and nickel 200 alloy were considered acceptable materials of construction if first passivated in a fluorine environment.

It was shown that the UF_4/GeO_2 reaction began just above 400°C with the release of a significant amount of moisture. A 1-2 hour pre-reaction drying period at ~450°C was inserted into the reactor- heating schedule to off-load the moisture from the reactants and the system before collecting GeF_4 of high quality. When compared with a reference material possessing 99.99% purity, the *Starmet* product was shown to contain the least number of elemental impurities and fewest infrared-active species. ICP-MS analysis of a lab-synthesized sample could not detect uranium above a detection limit of 0.019ppm-wt.

The fluoride gas was also examined using two new methods under development at *Argonne National Laboratory* for determining trace levels of U. Analyses by ultraviolet optical absorption spectroscopy to detect U as UF_6 found both the unfiltered and filtered batches of gas void of uranium at detection limits of 0.75 and 0.64ppm-vol., respectively. The second method

being investigated involving laser-induced photoluminescence spectroscopy encountered several problems, which impacted the ability to measure the luminescence of uranyl ions first in a glassy GeO_2 matrix and later in treated solutions of hydrolyzed GeO_2 particulate at a sensitivity in the range of 1-40 parts-per-trillion (ppt). The "chloride volatility" approach was unsuccessful due to the inability to convert hydrolyzed GeO_2 particulate to uranyl chloride using concentrated hydrochloric acid and acid vapor reflux conditions. Fluorescence measurements performed on hydrofluoric acid solutions of dissolved GeO_2 particulate revealed intense broad band interference arising from low molecular weight polymer leached from the wall of the perfluoroalkoxy (PFA) Teflon[®] containers used in preparing the hydrolyzed GeF_4 material.

Based on information learned throughout the program, conceptual drawings of a 6-station manifold reaction system involving tube-style reactors and a gas collection station were made. The production-scale system was configured to generate and package up to 2kg of product per day when operated to capacity. Production of the gas can be started with operation of just one station and additional capacity phased-in over time as demand for GeF_4 grows.

9.5 Conclusions - WF_6 .

Development of a process to make WF_6 using the same fluoride extraction technology perfected for GeF_4 proved to be more challenging. Before carrying out trials using a bench-scale apparatus, milligram quantities of UF_4 and two different tungsten oxide compounds were reacted in the thermogravimetric analyzer (TGA). It was determined that both forms of tungsten oxide could be converted to the oxyfluoride intermediate at temperatures in the range between 700°C-800°C when reacted in air. It was also shown that WO_2 was oxidized to WO_3 beginning about 500°C, adding a degree of complexity to the reaction scheme in deriving WOF_4 . At 700°C, the UF_4/WO_2 combination appeared to react at a faster rate and went essentially to 100% completion while the UF_4/WO_3 mixture yielded only 70% of the expected weight loss and the formation of a new solid phase that could not be matched to any substance in the x-ray database. At 800°C, there was little difference in the weight loss curves using either combination of reagents.

Reactions to produce the white crystalline oxyfluoride compound were moved to a horizontally oriented, tube-style reactor constructed of nickel 200 alloy. Best results were achieved in WFusn-10 where 3.17 grams of material were collected when UF_4 was reacted with WO_2 at 790C for 2 hours. In contrast, 2.44 grams of WOF_4 were recovered when WO_3 was reacted with green salt under similar conditions in WFusn-11 . When contacted with H_2O , both residues from WFusn-10 and -11 formed similar hydrolysis products as shown by x-ray diffraction, notably $\text{WO}_3 \cdot \text{H}_2\text{O}$ and $\text{WO}_3 \cdot 2\text{H}_2\text{O}$.

After defining the chemistry to make WOF_4 , several candidate reactions were selected for completing the process to make WF_6 . Based on favorable thermodynamic assessments, UF_4 , SiO_2 and TiF_4 were employed as probes to explore the reactivity of the oxyfluoride. Uranium tetrafluoride was not able to convert WOF_4 to WF_6 below 196°C since the oxyfluoride began to separate from the reaction mixture above 187°C, the boiling point for the intermediate. Silicon dioxide was reacted with WOF_4 in a similar manner to test the stability of the W-F bond in the presence of a strong fluoride scavenger. It, too, did not react up to a temperature of 185°C. In contrast, when TiF_4 was heated in the presence of the oxyfluoride, there were indications that a gaseous product was released, signaling the need for a more detailed investigation.

Based on this result, a new pathway to WF_6 was proposed whereby WO_2 is directly fluorinated using TiF_4 . A milligram-scale experiment where a WO_2/TiF_4 mixture was heated to 500°C in air, showed significant weight loss at temperatures below 285°C (TiF_4 's sublimation temperature). The same reaction was repeated in a bench-scale apparatus where the volatile reaction products were analyzed by FT-IR spectroscopy as the temperature was raised to 265°C . Intense absorption bands appeared in the infrared spectrum of the sample collected at 185°C , which dissipated as the reactor temperature increased. Bands with maxima located at 3500cm^{-1} and 3380cm^{-1} could not be easily identified while those in the $950\text{-}700\text{cm}^{-1}$ region corresponded with absorption band frequencies observed for a reference sample of WF_6 . Further experimentation is required in order to confirm if TiF_4 is a feasible and effective fluorinating agent in converting WO_2 to WF_6 .

Finally, the corrosion layer occurring on the nickel boat and in the tube reactor during the WF_6 development program was investigated. The formation of surface scale was described by a two-step process whereby the nickel surface is first oxidized to NiO in an oxygen containing environment followed by reaction of the oxidized surface with tungsten oxyfluoride. It is anticipated that nickel will be a suitable material for constructing a production-scale reaction system once it is properly passivated with fluorine to form a tightly bound protective layer of NiF_2 .

11 LITERATURE CITED

- 1 U.S. Department of Energy, *DUF₆ Materials Use Roadmap*, M.J. Haire and A.G. Croff Editors, ORNL-6968, Oak Ridge National Laboratory (August 27, 2001).
- 2 U.S. Department of Energy, *Final Programmatic Impact Statement for Alternative Strategies for Long-Term Management and Use of Depleted Uranium Hexafluoride*, DOE/EIS-0269 (April, 1999).
- 3 "Record of Decision for Long-Term Management and Use of Depleted Uranium Hexafluoride", *Fed. Reg.* 43358, 64(153), August 10, 1999.
- 4 Quapp, W. J., "DUCRETE Shielding Applications in the Yucca Mountain Repository", Waste Management 99, Feb. 28 to March 4, 1999, Tucson, AZ.
- 5 Cogema, Allied Signal, and Siemens
- 6 D.S. Schlier and B.M. Smyser, "Production of High-Value Fluoride Gas From Uranium Tetrafluoride Using a Rotary Calciner", Waste Management '01, Feb. 25 to March 1, 2001, Tucson, AZ.
- 7 Justification of this estimated cost savings is based upon market studies and the combined production of gases such as those discussed in this proposal as well as SiF₄, TiF₄, and BF₃. The SiF₄ and BF₄ are also used in the semiconductor industry as process gases as well as evolving uses for producing special isotopic variants for advanced semiconductor applications. TiF₄, the subject of another SBIR research program, will be used to produce ultra pure TiO₂ and possibly Ti metal.
- 8 C.J. Hoffman and J.S. Gutowsky, *Inorg. Syn.*, Vol. 4, 1953, 147.
- 9 N. Barlett and K.C. Yu, *Can. J. Chem.*, Vol. 39, 1961, 80.
- 10 I. Harada, Y. Yoda, N. Iwanaga, T. Nishitsuti and A. Kikkawa, European Patent EP 89-104364, March 11, 1989.
- 11 S.P. Mallela, O.D. Gupta and J.M. Shreeve, *Inorg. Chem.*, 27(1), 1988, pp. 208-209.
- 12 R. Doetzer, German Patent DE 3841212, June 13, 1990.
- 13 International Centre for Diffraction Data, Newtown Square, PA, Powder Diffraction File Release 1997, Data Sets 1-47.
- 14 HSC Chemistry for Windows, Chemical Reaction and Equilibrium software, Version 2.03, Outokumpu Research Oy, 1994.
- 15 G.Y. Lai, High-Temperature Corrosion of Engineering Alloys, ASM International, Materials Park, OH, 1990, p. 110.
- 16 *ibid.* p. 109.
- 17 *ibid.* p. 109-110.
- 18 D.F. Shriver and M.A. Drezzdon, The Manipulation of Air-Sensitive Compounds, 2nd Edition, John Wiley & Sons, New York, 1986, p. 228.
- 19 M. Maeno et al, "Fluorine Passivation of Metal Alloy Surface with Volatile Reaction Enhanced Mechanism", *Journal of the Electrochemical Society*, Vol. 139, (7), 1992, pp. 1865-1869.
- 20 Bartlett, N. et al, *Can J. Chem.*, 1961, Vol. 39, p. 80.
- 21 Mutterties, E.L., *Inorg. Chem.*, 1962, Vol. 1, p. 342.
- 22 Kirk-Othmer Encyclopedia of Chemical Technology., 3rd Edition, Wiley, New York, 1978-1984, Vol. 10, p. 720.
- 23 "Production of High Value Fluorine Gases for the Semiconductor Industry", Phase I Final Report, DOE SBIR Grant # DE-FG02-99ER82894, 1999, p.14-16.

- 24 Avrami, *Journal of Chemical Physics*, Vol. 7, 1939, p.1103.
- 25 William D. Callister, Jr., Materials Science and Engineering: An Introduction, Third Ed., John Wiley & Sons, Inc., 1994.
- 26 "Extraction of Fluorine from Uranium Hexafluoride for the Production of Titanium Metal", DOE SBIR Grant No. DE-FG02-99ER82893 Phase I-FY1999, awarded to *Starmet Corporation*, M.D. Stephens, Principal Investigator.
- 27 "The Chemistry of Uranium, Part I, The Element, Its Binary and Related Compounds:", Joseph J. Katz and Eugene Rabinowitch, McGraw-Hill Book Co., New York, 1951, p570.
- 28 Handbook of Chemistry and Physics, 66th ed., Robert C. Weast editor, CRC Press Inc., Boca Raton, FL, 1985-1986.
- 29 "Fluorine Compounds, Inorganic", Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed., John Wiley & Sons Inc., New York, 1994, Vol. 11, pp. 456.
- 30 Thomas W. Boyle, C. David Desjardins and David W. A. Sharp, *J. Fluor. Chem.*, Vol. 11, (3-4), 1978, pp. 399-406.

General References

"Germanium Tetrafluoride", A. Misra, J.D. Hogan and R. Chorush, *Handbook of Chemicals and Gases for the Semiconductor Industry*, John Wiley & Sons, Inc. 2002.

"Tungsten Hexafluoride", A. Misra, J.D. Hogan and R. Chorush, *Handbook of Chemicals and Gases for the Semiconductor Industry*, John Wiley & Sons, Inc. 2002.

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12 APPENDIX A

Interim progress reports from *Argonne National Laboratory*

"Ultratrace Determination Of Uranium In Germanium Tetrafluoride"

March 12, 2001 Progress Report (J.V. Beitz and C.W. Williams)

October 23, 2001 Progress Report (J.V. Beitz and C.W. Williams)

May 11, 2002 Progress Report (J.V. Beitz and C.W. Williams)

March 17, 2003 Progress Report (J.V. Beitz)

ULTRATRACE DETERMINATION OF URANIUM IN GERMANIUM TETRAFLUORIDE

March 12, 2001 Progress Report

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The cover photograph of this report shows the characteristic yellow-green luminescence of uranyl ion in an ultraviolet-illuminated sample of uranium-doped glassy germanium dioxide.

Abstract

We are developing two methods for ultratrace determination of uranium in germanium tetrafluoride (GeF_4) gas. Both methods are designed primarily for determination of uranium based on its most probable volatile chemical compound, namely uranium hexafluoride (UF_6). The first method relies on detection and measurement of UF_6 via its characteristic and very strong ultraviolet optical absorption spectrum. The scientific basis for this method is well established, although it is technically challenging to implement. Most of our work to date has been carried out to establish the scientific basis for our second method which relies on laser-induced fluorescence of uranyl ions in glassy germanium dioxide (GeO_2). Hydrolysis of GeF_4 that contains UF_6 and subsequent treatment with ammonium hydroxide is expected to generate hydrated germanium dioxide (GeO_2) that contains uranyl hydroxo complexes. Thermal fusion of this material and rapid cooling should produce glassy GeO_2 that contains uranyl ions. Although this is a plausible scheme for ultratrace determination of uranium in GeF_4 , it rests on the presumption that uranyl ions are chemically stable in molten GeO_2 . We now have carried out studies on uranyl-doped glassy GeO_2 that have shown that 1) uranyl ions are stable for hours in molten GeO_2 , 2) uranyl ions in glassy GeO_2 at ambient temperature are strongly luminescent, and 3) the likely limit of detection for uranium in GeF_4 using this method is 50 ppt (parts per trillion), or better, on a weight basis. Using our present non-optimized apparatus, we have achieved signal-to-noise ratios for uranyl ion luminescence in glassy GeO_2 that are equivalent to a limit of detection of 500 ppt.

Introduction

Determination of uranium in germanium tetrafluoride (GeF_4) is challenging due to the chemically aggressive nature of GeF_4 and the strong fluorinating ability of the most probable volatile uranium impurity in GeF_4 , namely uranium hexafluoride (UF_6) gas. Conventional high sensitivity methods, such as ICP-based mass spectrometry or atomic emission spectroscopy, lose sensitivity because GeF_4 must be hydrolyzed in water (diluted) prior to analysis of the hydrolysis solution.

Objectives

We are developing two methods for ultratrace determination of uranium in GeF_4 gas. Both of these methods are primarily sensitive to uranium as uranium hexafluoride (UF_6). Our first method relies on the very strong optical absorbance of UF_6 gas in the ultraviolet [1] at wavelengths where GeF_4 should be essentially transparent [2]. This method is non-destructive (does not involve chemical alteration of GeF_4), and may be suitable for on-line monitoring of UF_6 impurity levels during GeF_4 production.

Our second method relies on laser-induced fluorescence measurement of uranium, as uranyl ion (UO_2^{2+}), in glassy GeO_2 and requires destructive analysis of GeF_4 . This method, in our present plan, starts with hydrolysis of a sample of GeF_4 gas. Any UF_6 impurity in the GeF_4 will hydrolyze to uranyl ions (UO_2^{2+}). Hydrolysis of GeF_4 is reported [3] to follow the chemical reaction

although no detailed study of this reaction has been reported nor are the properties of H_2GeF_6 well established. It is known [4] that UF_6 hydrolyzes according to the reaction

In addition, uranyl fluoride (UO_2F_2) is one of the most water-soluble uranyl salts known. With excess water, the above reactions should give an aqueous solution that contains GeO_2 , H_2GeF_6 ,

and UO_2^{2+} and its fluoride ion complexes as well as hydrofluoric acid (HF) and fluoride ion (F^-) in amounts that depend on the pH of the solution. We expect that addition of excess ammonium hydroxide to the solution, followed by heating to volatilize excess water, ammonium hydroxide, and ammonium fluoride, will give a hydrated GeO_2 gel that contains trapped within it uranyl ions, likely as hydroxo complexes. Fusion of this GeO_2 gel will produce glassy GeO_2 for subsequent analysis for uranyl content by laser-induced fluorescence. Glassy GeO_2 is preferred over crystalline GeO_2 for two reasons. The first is that GeO_2 can exist in either of two crystalline modifications and preparation of it in a single crystalline phase is difficult [3]. The second is that crystallization tends to concentrate impurities, such as uranyl ions, along defects or grain boundaries. This is undesirable because uranyl species frequently undergo luminescence self-quenching (some times referred to as concentration quenching). Such quenching would reduce the sensitivity for detecting uranyl via laser-induced fluorescence.

Our experimental work to date has largely centered on development of laser-induced fluorescence analysis for detection of uranyl in GeO_2 . This is to ensure that the fundamental basis of this method is sound and due to ordering and delivery delays in our procurement of high purity (99.99%) GeF_4 from a commercial source (Advance Research Chemicals).

Nothing has been reported in the literature concerning the photophysics of uranyl-doped glassy GeO_2 so we began our work in this area by preparing glassy GeO_2 that contains added uranium. Our objectives were to

1. Determine the chemical stability of uranyl ion in molten GeO_2 and glassy GeO_2
2. Optimize the heating cycle requirements for producing glassy GeO_2 of acceptable optical quality.
3. Generate benchmark data for the photophysics and spectroscopy of uranyl ions in glassy GeO_2 .

We prepared uranium-doped glassy GeO_2 material by adding uranyl nitrate in nitric acid to GeO_2 powder and then heating this material as detailed below.

Although uranyl luminescence has been studied in many phases, no utilization of such luminescence for uranium analysis in vitreous GeO_2 has been reported. Based on literature reports, however, vitreous GeO_2 is a very favorable matrix for such analyses. The reported optical absorption bands of vitreous GeO_2 [5] occur further into the ultraviolet than do those of the lowest lying excited electronic states of uranyl ion. Excitation of the low lying uranyl states generally provides the highest quantum yield, and therefore best sensitivity, for luminescence detection of uranyl. In addition, the reported emission bands of GeO_2 [6] occur at wavelengths that should provide little interference with quantification of uranyl luminescence.

Materials and Methods

Vitrification of GeO_2

The GeO_2 that we used was specified by its manufacturer (Alfa) to be 99.999% pure on a metals basis. Physically, this material is a white, finely divided powder. We confirmed that it is largely the hexagonal form of GeO_2 by the heat evolved as it underwent dissolution in hydrofluoric acid [3]. We detected the presence of tetragonal phase GeO_2 in that a small fraction of this material did not dissolve in 25% hydrofluoric acid solution.

A Linderg/BlueM horizontal tube furnace capable of attaining 1700 °C was fitted with a 3 inch diameter Coors high purity alumina tube that was capped at each end with a Fiberfrax insulating plug. Platinum foil (0.002 inch thick) was shaped into a 0.94 cm wide by 0.94 cm long square boat and used as the primary container for melting GeO_2 samples. Uranium-doped GeO_2 was prepared by placing a weighed amount of GeO_2 (typically 0.7 g) into a Pt boat on a hot plate. An aliquot of uranyl nitrate stock solution (5.24 μg uranium per milliliter) in 0.3 mol/liter nitric acid was added to the GeO_2 . Visible liquid was evaporated under a stream of dry nitrogen gas. The Pt boat then was placed within an open top, high purity alumina boat. In some cases, the Pt boat was covered with Pt foil; in other cases, the Pt boat was left uncovered. The boat assembly was placed within the 3 inch alumina tube in the furnace and centered on its hot zone. The furnace controller was programmed to carry out the desired heating profile. When the furnace temperature returned to ambient, the boat assembly was removed from it. The Pt foil was mechanically stripped from the glassy GeO_2 sample that had been molded by the Pt foil boat into

the form of a square plate which was thinner in the middle due to a meniscus that formed as the molten GeO_2 contracted during solidification.

The heating profile most commonly used for vitrification of GeO_2 is shown in Fig 1. It consists of a constant rate ramp to 1400°C , a four hour soak at 1400°C , natural cool down of the furnace (no power to the heating elements) to 500°C (which is the glass transition temperature of GeO_2 [7]), and then cooling at 2°C per minute to ambient temperature. The heating cycle shown in Fig 1 produces strain-free glassy GeO_2 at the level of 0.7 g GeO_2 in a 0.94 cm long x 0.94 cm wide platinum foil boat as judged by viewing the produced glass between crossed polarizing filters.

Fig 1. Heating profile typically used to produce glassy GeO_2 .

Fig 2 shows in more detail the portion of the observed furnace temperature during the cool down period. Cooling from 1000°C to 800°C requires approximately 15 minutes.

Fig 2. Enlarged detail of the rapid cool down portion of the heating profile typically used to produce glassy GeO_2 . The measured furnace temperatures are shown as symbols (•) and are connected by a straight line segment to aid the eye in following trends.

The heating cycle selected (Fig 1) is based in part on consideration of literature studies on the viscosity of GeO_2 [7] in which GeO_2 commonly was reported to have been heated to 1400 °C for at least several hours to as much as 24 hours prior to the melt being cooled and viscosity measurements made. It also is based on our observation that application of the heating cycle shown in Fig 1 results in approximately 10% loss of GeO_2 from the Pt boat in which it is heated if that boat is open (has no cover).

Photomicrography

A Nikon CoolPix 990 digital camera was used to record digital images of some of the produced glassy GeO_2 samples. This camera has a 3.3 megapixel, uncooled CCD photosensor and is equipped with a zoom lens that in macro mode focuses down to object-to-lens distances of just under one inch. This produces a slightly larger than life size image of the object on the photosensor. The ultraviolet lamp used as the illumination source for some images was a UVP Products model Pen-Ray® type 11SC-1 which is a low pressure mercury arc lamp. The lamp was fitted with a UVP Products model "G-275, LW" long wavelength pass filter that restricted the

emitted wavelengths primarily to the 330 nm to 390 nm wavelength range. A Schott Glass low fluorescence long pass filter, model KV500, was used to eliminate yellow and shorter wavelengths from images recorded using ultraviolet illumination.

Laser-induced fluorescence studies

A Continuum model Surelite I-10 Q-switched Nd:YAG laser system provided 5 ns (nominal) duration 355 nm excitation pulses at a repetition rate of 10 pulses per second and a pulse energy typically of 0.1 millijoule. Emission spectra were recorded on an Acton 275 spectrograph (27.5 cm focal length) that was equipped with a 150 groove/millimeter ruled grating and a Princeton Instrument model RE/IRY-700 optical multichannel spectral analyzer (OSMA) that was fitted with a CFC-100 photocathode cooler run with -15 °C coolant and a model PG-10 pulse generator. The OSMA provides an on:off gating ratio of $10^7:1$ with gate width and gate delay each of which is variable from ~50 ns to 10 ms. This spectrograph system was used to record time- and wavelength-resolved emission spectra of glassy GeO_2 samples from 400 nm to 800 nm without changing the spectrograph wavelength setting. OSMA data typically were recorded for 300 laser pulses (30 seconds) and were averaged together to obtain an emission spectrum. The 355 nm laser beam was focused at a point in space a few centimeters in front of the sample so that the beam was diverging as it passed through the sample.

Light emitted from the sample was collected perpendicular to the laser beam path using a f/1.5 UV-grade fused silica lens. The collimated luminescence light then was focused onto the slits of the spectrograph using a f/4.0 UV-grade fused silica lens. A Schott Glass low fluorescence, long pass optical filter (model KV418) passed wavelengths longer than 418 nm to the spectrograph. The luminescence decay of a sample following 355 nm excitation was recorded using a cooled RCA model 31034A photomultiplier (GaAs photocathode) as the photodetector. Luminescence from the sample passed through a series of Schott Glass low fluorescence filters before it entered the photomultiplier housing. This and the properties of the photomultiplier restricted the detected luminescence to wavelengths from approximately 500 nm to 900 nm. The current from the anode of the 31034A passed through a coaxial cable to a variable value load resistor that was located at the input of Tektronix TDS 640A digital oscilloscope. Oscilloscope sweeps were triggered by a synchronization pulse from the laser power supply. Typically, the data from 128

sweeps were averaged together by the TDS 640A. The averaged luminescence decay data were transferred to a personal computer and analyzed using nonlinear least squares fitting to model equations. This fitting was carried out using PSI-PLOT software (Poly Software International, Pearl River, NY).

Experimental Observations

Visual observations

The photomicrograph at the left in Fig 3 was recorded using visible light. It shows an edge on view of a uranyl-doped glassy GeO_2 sample tipped at an angle of approximately 45 degrees within a 1 cm x 1 cm square cross section spectrometer cuvette. The meniscus resulting from contraction during cooling of the molten GeO_2 is clearly visible. The glassy GeO_2 sample contained 11 ppm uranium by weight. The photomicrograph at the right in Fig 3 shows the characteristic yellow-green luminescence of uranyl ion from the same sample when the illumination was switched from visible light to ultraviolet light.

Fig 3. Photomicrographs of a uranium-doped glassy GeO_2 sample that contained 11 ppm uranium. The 1 cm x 1 cm sample cell was illuminated by visible light (left photo above) and ultraviolet light (right photo above). The characteristic yellow-green luminescence of uranyl ion is easily seen under ultraviolet illumination.

Luminescence spectrum of uranyl ion in glassy GeO₂

The observed emission spectrum of uranyl-doped glassy GeO₂ is shown in Fig 4. These data also are shown plotted with a logarithmic intensity axis in Fig 5. The observed emission spectrum peaks at 536 nm, has a full width at half maximum of 65 nm, and is typical of uranyl ions that are distributed over several types of sites. The sample contained 11 ppm uranium on a weight basis. This characteristic uranyl emission spectrum was not observed in the absence of uranyl doping of glassy GeO₂.

Fig 4. Luminescence emission spectrum of uranyl-doped glassy GeO₂ recorded at 22 °C after pulsed excitation at 355 nm following a 1.2 μs gate start delay (red curve), a 320 μs gate start delay (green curve), and a 750 μs gate start delay (blue curve). A constant gate width (320 μs) was used.

Fig. 5 The data of Fig 4 are re-plotted here using a logarithmic intensity axis. The observed spectrum changes little with time following pulsed excitation.

Estimated limit of detection

Luminescence emission data such as that shown in Fig 4 can be used to estimate the limit of detection for uranyl ions in glassy GeO_2 using our apparatus as configured for these studies. The uncertainty in the zero luminescence light intensity level in the recorded data can be assessed by statistical analysis of the observed data from 420 nm to 460 nm where there is little if any sample luminescence. The resulting standard deviation (σ) is 7.6 ADC counts per photosensitive element of the OSMA system. Summing together the observed ADC counts for photosensors that recorded a light intensity level of 5% or larger of the peak intensity level (i.e., integrating the spectrum from 489 nm to 630 nm) gives the signal + dark level with little contribution from dark level uncertainty. Subtracting the dark level over these same photosensors gives the net signal intensity. Dividing this value by the expected uncertainty in the dark level for these photosensors gives a signal-to-dark noise level ratio of 69206. Assuming that the term "limit of detection" (LOD) is defined as an observed signal level whose value is 3σ where σ is the standard deviation in the measured value in the absence of the analyte, then we have achieved a

sensitivity for detecting uranyl ion in glassy GeO_2 that is equivalent to an LOD of 0.5 parts per billion (ppb) of uranium in GeO_2 if the only luminescence recorded is that from uranyl.

Photophysics of uranyl ion in glass GeO_2

Luminescence decay rate data were recorded, following pulsed 355 nm excitation, using a cooled photomultiplier, long pass optical filters, and a signal averaging digital oscilloscope. These data are shown in Fig 6. The observed decay is complex and not single exponential. Such complex decays typically arise for one of two reasons. The first is energy transfer from an initially electronically excited UO_2^{2+} ion to a neighboring ground state UO_2^{2+} species having a different local environment and therefore a somewhat different emission spectrum. When such energy transfer occurs, the observed emission spectrum changes as a function of time following pulsed excitation because the fraction of the total emission due to each type of UO_2^{2+} ion changes with time. The other physical situation that gives rise to complex decays is initial excitation of a distribution of UO_2^{2+} species each of which then undergoes radiative and nonradiative decay processes that are first order in time. The net result is that the observed decay is the sum of multiple independent first order decays, each arising from UO_2^{2+} ions of differing local environments. Given the low uranium concentration (11 ppm uranium by weight, which is equivalent to 1.49×10^{-4} mol/liter UO_2^{2+} in glassy GeO_2), energy transfer among uranyl ions is unlikely to cause the observed complex decays. In addition, the observed emission spectra are not significantly time-dependent. For these reasons, the observed luminescence decay was fit to a phenomenological model consisting of a sum exponential decays in which the number of decays included was increased until a plot of the residuals (the difference between the observed and calculated intensity at a particular time) showed no systematic deviations. In the least square error sense, the model equation

$$I(t) = 1997\exp(-64530t) + 6158\exp(-10625t) + 2969\exp(-3529t) \quad (3)$$

where $I(t)$ is the calculated intensity at time t in seconds, provides the best fit to the observed data. The three fit decay rates (64530 s^{-1} , 10625 s^{-1} , and 3529 s^{-1}) are typical of uranyl ions in local environments that induce nonradiative decay to degrees that vary from moderate to weak to none, respectively. It should be emphasized that Eqn 3 represents a phenomenological model

and should not be taken to imply that there are only three local environments for UO_2^{2+} in glassy GeO_2 .

Fig 6. The observed luminescence decay of uranyl-doped GeO_2 following pulsed 355 nm excitation is shown as symbols ($\bullet$). The solid red line is the result of fitting a "sum of three exponential decays" model to the observed data (see text).

Crystallization of GeO_2 can occur with our present apparatus

The heating profile that we have used is not optimal in terms of ensuring formation of bubble-free glassy GeO_2 . Fig 7 shows an example of a partially successful attempt to produce a glassy GeO_2 sample for laser-induced fluorescence analysis. The photomicrograph shows a GeO_2 sample, tipped on edge, within a 1 cm x 1 cm square spectrometer cuvette. Small gas bubbles that nucleated at the surface of the platinum boat failed to rise to the surface of the molten GeO_2 before the end of the 1400 °C soak period.

Fig. 7. Photomicrograph of a glassy GeO_2 sample in the bottom of a 1 cm x 1 cm spectrometer cuvette showing incomplete removal of trapped gas bubbles and partial crystallization (white area at upper left) during vitrification of the GeO_2 .

The upper left portion of the above photograph is shown enlarged in Fig 8. The cool down time from 1400 °C to 500 °C evidently was insufficiently rapid to prevent some crystallization of the GeO_2 because a mass of crystallites formed (see upper left corner of the enlarged photo).

Fig 8. The upper left portion of Fig 7 is shown above enlarged to emphasize the presence of microcrystallites that evidently began forming in a corner of the Pt fusion boat and propagated toward the bulk of the GeO_2 before crystallite growth was terminated by the increasing viscosity of the glassy GeO_2 as it cooled.

Using the heating cycle shown in Fig 1 with GeO_2 dried at 110°C in a laboratory oven produced glassy GeO_2 that had such a high concentration of small gas bubbles that the resulting material was translucent milky white rather than being clear, colorless, and transparent. This observation is evidence that the initial water content of GeO_2 is an important parameter in determining the viscosity of molten GeO_2 at 1400°C . A similar phenomena occurs in the case of glassy silica (often referred to as fused quartz). The presence of water (often denoted as "OH" in the fused quartz literature) reduces the viscosity of vitreous silica. For example, a grade of fused silica that contains 1000 ppm OH is reported to have a strain point temperature that is 117°C lower than that of a grade of nominally "water-free" fused silica [8].

Discussion

We have found that platinum foil boats are acceptable for making glassy GeO_2 samples. Our visual observations have shown that near ultraviolet illumination in a dark room is sufficient to detect the presence of uranyl, at the ppm level, in glassy GeO_2 . This provides evidence that uranyl ions are appreciably luminescent in glassy GeO_2 . Blaase and Grabmaier's monograph provides a good introduction to luminescing materials in general and provides some insight into uranyl luminescence [9]. A classic reference concerning uranyl luminescence is the work of Rabinowitch and Belford [10] although it contains little information about uranyl in glass phases. Denning's review article provides the most definitive information about the photophysics and spectroscopy of uranyl ions [11] although it too deals primarily with uranyl in crystalline phases. Near ultraviolet excitation of uranyl populates a charge transfer state whose emission to the ground state is a formally "forbidden" transition. Emission becomes partially allowed due to coupling of that excited electronic state to a vibrational motion of the linear dioxo (O-U-O) uranyl cation. This results in highly structured luminescence spectra that exhibit a long progression of "vibronic" transitions. The purely radiative lifetime of uranyl ion typically is on the order of 1 ms. Nonradiative decay processes frequently result in shorter observed uranyl luminescence lifetimes.

Because our heating cycle involves holding molten GeO_2 at 1400 °C for four hours and the only uranium species that we have detected in the glassy GeO_2 that we have made is uranyl ion, it is clear that uranyl ions are chemically stable for hours in molten GeO_2 . Our laser-induced fluorescence studies have shown that luminescence from uranyl ion in glassy GeO_2 peaks at 536 nm in a broad band that contains a number of shoulders. The near-invariance of the observed emission spectrum with time following pulsed 355 nm excitation and the complex observed luminescence decays are consistent with the presence of uranyl ions having differing local environments. This likely arises because uranyl ions are positively charged species for which negatively charged compensating species, such as OH^- , necessarily must be present although the framework of a GeO_2 glass contains no charged species. Uranyl ions, in consequence, likely reside on a variety of sites that differ in terms of the position and nature of neighboring atoms

and the location of charge compensating species. The vibronic progressions usually clearly evident in uranyl ion emission spectra are less obvious in the present case (Fig 4). This is attributed to the observed emission being the sum of the slightly differing vibronic progressions from uranyl ions whose local environments differ.

Issues for future work

The precision and accuracy that we ultimately will achieve using our laser-induced fluorescence method are likely to depend on the degree to which we achieve dimensionally uniform glassy GeO_2 samples that are free of bubbles, strain, and embedded microcrystallites of GeO_2 . Our present heating cycle produces strain-free glass. Finding optimal methods for eliminating bubbles and microcrystallites is challenging.

Ensuring bubble-free glassy GeO_2

Three issues concerning preparation of high optical quality glassy GeO_2 are interrelated. These are the volatility of liquid GeO_2 , the viscosity of liquid GeO_2 , and removal of trapped gas bubbles from molten GeO_2 . Normally, removal of trapped bubbles from a glass is achieved by increasing temperature or applying mechanical agitation. In our case, significant temperature increase is likely to result in unacceptable volatilization of GeO_2 . In addition, heating to a higher temperature in a closed or sealed metallic container is more likely to favor chemical reduction of uranyl which has not been a problem using our present heating cycle. Fortunately, our preliminary evidence suggests that increased water content lowers the viscosity of molten GeO_2 . Hydrolysis of GeF_4 and subsequent treatment with ammonium hydroxide is likely to increase the water (more accurately, OH) content of GeO_2 that is produced during analysis of GeF_4 , relative to that in the samples that we have prepared to date. For this reason, it may be that our present heating cycle will prove adequate for all GeF_4 analysis purposes although it may not guarantee bubble-free glassy GeO_2 when starting from dry GeO_2 . The impact of OH content on uranyl luminescence in GeO_2 is unknown at present.

Suppressing crystallization

The key to suppressing crystallization of GeO_2 is the rapidity with which molten GeO_2 is cooled to below its glass transition temperature ($\sim 500^\circ\text{C}$ [7]) and, based on literature reports [7], more particularly, the rate at which it is cooled from 1000°C to 800°C . Using our present heating cycle, we can not guarantee achieving samples that are 100% free of microcrystallites. We are exploring relatively simple modifications to our furnace system that may enable removal of a molten GeO_2 sample to a relatively cold zone in a matter of a few seconds. We expect that this would suppress crystallization in all samples of interest.

Analytical limits

The upper (highest concentration) limit for determination of uranyl in GeO_2 is likely to be set by the solubility limit of uranyl in glassy GeO_2 which has not been reported in the literature. Due to the necessity of charge compensation, it seems unlikely the solubility of uranium as uranyl in glassy GeO_2 will be high. Precipitation of uranate or germanate phases is likely to set the practical upper limit. The limit of detection (lowest concentration detectable) for this method is likely to be set by impurities other than UF_6 in the GeF_4 , if such impurities result in interfering luminescence.

The temperature dependence of the observed complex uranyl luminescence decays should be determined to establish the degree of temperature control that must be maintained to obtain reproducible measurements of the uranium content of glassy GeO_2 .

Ultraviolet Absorption Analysis for UF_6 in GeF_4

We expect delivery of 100 grams of 99.99% pure GeF_4 before the end of this week. When this material arrives, we will begin hydrolysis studies as well as record the ultraviolet absorption spectrum of GeF_4 with and without added UF_6 . These latter studies will establish the basis for ultraviolet absorption analysis of UF_6 in GeF_4 gas and will provide a measure of the UF_6 detection sensitivity that we can achieve with our conventional dual beam optical spectrometer in conjunction with our present nickel-bodied gas cell that is equipped with single crystal aluminum oxide windows. The basis of this method is the very strong and characteristic ultraviolet

absorption spectrum of UF_6 [1] and an expected lack of interfering absorbance in the ultraviolet from GeF_4 [2].

Conclusions

The conclusions that we have reached to date in our research on the luminescence of uranyl ions in glassy GeO_2 are:

1. Uranyl ion is chemically stable at least for several hours at 1400 °C in molten GeO_2 in contact with air.
2. Platinum crucibles are acceptable containers for preparation of glassy GeO_2 as to ease of removal of the produced glassy GeO_2 and lack of significant addition of luminescing impurities to the produced glassy GeO_2 .
3. GeO_2 heated to 1400 °C and then cooled to below its glass transition temperature over a span of 60 minutes can form water clear, colorless, glassy GeO_2 although more rapid cooling is to be preferred.
4. Uranyl ions in glassy GeO_2 are highly luminescent at ambient temperature when excited in the near ultraviolet spectral range, emit a characteristic luminescence spectrum, and exhibit long-lived, but complex luminescence decay as is typically found for luminescing metal ions dispersed in glassy phases.
5. Based on the observed signal-to-dark noise level ratio for luminescence from uranyl-doped GeO_2 , a limit of detection (LOD) of 0.5 ppb (or 500 parts per trillion) uranium (on a weight basis) in GeF_4 is expected using our present apparatus configuration which was optimized to determine the spectroscopy and photophysics of uranyl ions in glassy GeO_2 . Re-configuring our apparatus to maximize detection sensitivity is likely to result in a further LOD improvement of at least a factor of ten, i.e. 50 parts per trillion or better sensitivity for detection of uranium in GeF_4 when the chemical form of the uranium is UF_6 . This presumes the absence of significant interference from other luminescing impurities in glassy GeO_2 .

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Literature Cited

- 1) "The absorption spectrum of UF_6 from 2000 Å to 4000 Å", G. L. DePoorter and C. K. Rofer-DePoorter, *Spectroscopy Letters*, **8** (1975) 521 - 524.
- 2) "Absorption spectra of Si_2Cl_6 , SiF_3CH_3 , and GeF_4 in the VUV region", T. Ibuki, N. Washida, U. Itoh, Y. Toyoshima, and H. Onuki, *Chem. Phys. Let.* **136** (1987) 447 - 450.
- 3) "The Chemistry of Germanium", F. Glocking, Academic Press, London, 1969.
- 4) "Uranium Hexafluoride: A Manual of Good Handling Practices", U. S. DOE Field Office, Oak Ridge, TN, Report Number ORO-651 (Rev. 6), dated October, 1991.
- 5) "Localized states in germanate glasses. Ultraviolet absorption tail of crystalline and glassy germanium dioxide and alkali germanate", A. N. Trukhin and P. Kulis, *J. Non-crystalline Solids*, **188** (1995) 125-129.
- 6) "Optical transitions in germanium dioxide", X.-L. Xu, L.-X. Zhu, T. P. Chen, S. Fung. and S.-M. Li, *Thin Solid Films*, **283** (1996) 230 -234.
- 7) "Handbook of Glass Data, Part B - Single Component and Binary Non-silicate Oxide Glasses", O. V. Mazurin, M. V. Streltsina, and T. P. Shvaiko-Shvaikovskaya, Elsevier, Amsterdam, 1985, pgs. 353-384. This is volume 15 of Elsevier's Physical Sciences Data Series.
- 8) "Silica (Vitreous)" in "Kirk-Othmer Encyclopedia of Chemical Technology", 3rd Edition, Vol. 20 (John Wiley and Sons, New York, 1982), pgs 787-788.
- 9) "Luminescent Materials", G. Blasse and B. C. Grabmaier, Springer-Verlag, Berlin, 1994.
- 10) "Spectroscopy and Photochemistry of Uranyl Compounds", E. Rabinowitch and R. L. Belford, Pergamon Press, New York, 1964.
- 11) "Electronic Structure and Bonding in Actinyl Ions", R. G. Denning, *Structure and Bonding*, **79** (1992) 215-276.

ULTRATRACE DETERMINATION OF URANIUM IN GERMANIUM TETRAFLUORIDE

October 23, 2001 Progress Report

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Abstract

One approach that we are investigating to improve analytical methods for quantifying uranium hexafluoride (UF_6) in germanium tetrafluoride (GeF_4) is hydrolysis of impure GeF_4 gas to generate GeO_2 and uranyl fluoride. Subsequent heating produces uranyl ions embedded in glassy GeO_2 . In our earlier work, we showed that laser-induced fluorescence analysis for uranyl ion had the potential to detect less than 0.5 parts per billion of uranium in glassy GeO_2 . We also noted difficulty in reproducibly creating visually clear, bubble-free glassy GeO_2 on the one gram scale. Bubble-free GeO_2 is required to achieve reproducible measurement of luminescence intensity. Such reproducibility is essential for quantitative measurement of uranium impurity content in analyzed samples via the standard addition method.

Based on a parametric study, we now have identified a simple means of producing visually clear, bubble-free glassy GeO_2 on the gram scale. However, this method creates an impurity that, following excitation at 355 nm, luminesces such that its emission spectrum and luminescence decay overlap those of uranyl ion in glassy GeO_2 . The impurity species likely is the result of thermal reduction of some tetravalent Ge in GeO_2 to divalent Ge. The impurity species grows in with increased sample residence time in the high temperature zone of the furnace. This impurity interference is present to varying degrees in all other methods that we investigated to minimize the presence of small bubbles in GeO_2 glass produced by melt processing in air. Given difficulties in producing glassy GeO_2 of acceptable quality for quantitative uranyl luminescence analysis, we began a search for alternate, but related methods of achieving our goal of improved ultratrace analysis for UF_6 in GeF_4 gas. We have identified a promising method that does not require high temperature processing and so is likely to be more easily and economically implemented in a quality assurance laboratory.

Our new approach retains the same initial step, namely, hydrolysis of GeF_4 gas in water to generate GeO_2 , H_2GeF_6 , and HF , and the same second processing step, namely sub-boiling point distillation of volatile species. Our new approach then dissolves the resulting non-volatile

residue (GeO_2 and uranyl fluoride, if any UF_6 was present in the GeF_4) in concentrated hydrochloric acid. This converts GeO_2 to volatile GeCl_4 that is removed, along with excess hydrochloric acid, by a second sub-boiling point distillation. The residue (uranyl chloride and trace amounts of GeO_2) is taken up in dilute phosphoric acid solution. The uranium content of the resulting solution is quantified by laser-induced fluorescence and the standard addition method. This new approach will permit use of 266 nm excitation which has the advantage of being more strongly absorbed by uranyl in dilute phosphoric acid than is light at 337 nm (nitrogen laser) or 355 nm (tripled Nd:YAG laser). In consequence, limits of detection for uranyl comparable to the best reported in the literature (1 to 40 ppt) are expected. The primary interference that we anticipate in our germanium chloride volatilization process is luminescence from trace level organic contaminants leached from the perfluoropolymer distillation vessel. We expect to eliminate such interference by 185 nm photolysis that should photochemically destroy such contaminants. In our initial studies of this new approach, we have hydrolyzed GeF_4 gas and verified volatilization of the resulting GeO_2 from concentrated hydrochloric acid.

Using a 9.3 cm path length nickel-bodied, elastomer-free cell equipped with single crystal aluminum oxide windows, we have recorded the ultraviolet absorption spectrum of Starmet-produced GeF_4 gas. Based on those spectra and literature values for the molar absorptivity of uranium hexafluoride gas, Starmet-produced GeF_4 contains less than 0.75 parts per million (by volume) of UF_6 . Based on an observed small decreases in pressure upon contact of Starmet-produced GeF_4 gas with a clean, passivated vacuum system and subsequent FT-IR analysis of that GeF_4 gas using our nickel-bodied cell, we have concluded that the sample of Starmet-produced GeF_4 that we analyzed contains approximately 0.8% hydrogen fluoride (HF) gas by volume.

Introduction

Determination of uranium in germanium tetrafluoride (GeF_4) is challenging due to the chemically aggressive nature of GeF_4 and the strong fluorinating ability of the most probable volatile uranium impurity in GeF_4 , namely uranium hexafluoride (UF_6) gas. Conventional high sensitivity methods, such as inductively coupled plasma mass spectrometry (ICP-MS) or atomic emission spectroscopy, lose sensitivity because GeF_4 must be hydrolyzed in water (diluted) prior to analysis of the hydrolysis solution and due to interference from hydrolysis products of GeF_4 . Such interference often is termed a "matrix" effect.

We are developing methods for ultratrace determination of uranium in germanium tetrafluoride (GeF_4) gas as part of a Small Business Innovative Research Phase II project of Starmet Corporation. This progress report covers work carried out since March 19, 2001. Our methods are designed primarily for determination of uranium based on its most probable volatile chemical compound, namely uranium hexafluoride (UF_6). Our first method relies on detection and measurement of UF_6 via its characteristic and very strong ultraviolet optical absorption spectrum. The scientific basis for this method is well established, although it is technically challenging to implement. The second method that we are developing seeks to establish the scientific basis for ultratrace determination of UF_6 via one of its hydrolysis products, namely the uranyl ion, as detected by laser-induced fluorescence. Most of our studies to date have focussed on use glassy germanium dioxide (GeO_2) as the matrix in which such uranyl ions are embedded by heating GeO_2 that is produced when a GeF_4 sample is hydrolyzed in water. In effect, the sample to be analyzed generates the matrix in which uranyl is analyzed. Our past work showed uranyl ions are stable for hours in molten GeO_2 that is in contact with air and that uranyl ions in glassy GeO_2 at ambient temperature are strongly luminescent. It also showed that

Objectives

We are developing two methods for ultratrace determination of uranium in GeF_4 gas. Both of these methods are primarily sensitive to uranium as uranium hexafluoride (UF_6). Our first method relies on the very strong optical absorbance of UF_6 gas in the ultraviolet [1] at wavelengths where GeF_4 should be essentially transparent [2]. This method is non-destructive

(does not involve chemical alteration of GeF_4), and may be suitable for on-line monitoring of UF_6 impurity levels during GeF_4 production.

Our second method relies on destructive analysis of GeF_4 and is based on laser-induced fluorescence (LIF) measurement of uranyl ion (UO_2^{2+}) that is formed when UF_6 reacts with water. Most of our effort has been directed towards use of a GeF_4 hydrolysis product, GeO_2 , as the matrix in which uranyl ions are embedded prior to LIF analysis. This method starts with hydrolysis of a sample of GeF_4 gas. Any UF_6 impurity in the GeF_4 will hydrolyze to uranyl ions (UO_2^{2+}). Hydrolysis of GeF_4 is reported [3] to follow the chemical reaction

although no detailed study of this reaction has been reported nor are the properties of H_2GeF_6 well established. It is known [4] that UF_6 hydrolyzes according to the reaction

In addition, uranyl fluoride (UO_2F_2) is one of the most water-soluble uranyl salts known. With excess water, the above reactions should give an aqueous solution that contains GeO_2 , H_2GeF_6 , UO_2^{2+} and its fluoride ion complexes, and hydrofluoric acid (HF) and fluoride ion (F^-) in amounts that depend on the pH of the solution. Sub-boiling point distillation of the hydrolysis solution results in hydrated GeO_2 and uranyl fluoride. Fusion of this GeO_2 will produce glassy GeO_2 for subsequent analysis for uranyl content by laser-induced fluorescence. Glassy GeO_2 is preferred over crystalline GeO_2 for two reasons. The first is that GeO_2 can exist in either of two crystalline modifications and preparation of it in a single crystalline phase is difficult [3]. The second is that crystallization tends to concentrate impurities, such as uranyl ions, along defects or grain boundaries. This is undesirable because uranyl species frequently undergo luminescence self-quenching (sometimes referred to as concentration quenching). Such quenching would reduce the sensitivity for detecting uranyl via laser-induced fluorescence.

Ultraviolet Absorption Analysis for UF_6 in GeF_4

The basis of this method is the very strong and characteristic ultraviolet absorption spectrum of UF_6 [1] and an expected lack of interfering absorbance in the ultraviolet from GeF_4 [2]. The vacuum system that we have used for handling GeF_4 is shown schematically in Fig 1.

Schematic Diagram of GeF_4 Gas Handling System

Figure 1. Schematic diagram of GeF_4 gas handling system.

As noted in Fig. 1, our GeF₄ gas handling system consists of

- A rough vacuum ($\sim 10^{-3}$ torr) manifold constructed from nickel, monel, and copper fittings and tubing
- A main manifold constructed out of Autoclave Engineers high pressure fittings
- A high vacuum ($\sim 10^{-6}$ torr) glass and metal vacuum manifold
- A sub-manifold constructed from Autoclave Engineers high pressure tubing and fittings and that contains a high accuracy capacitance manometer

The rough, main, and high vacuum manifolds were originally constructed for studies involving WF₆ and WF₆ that contained trace level UF₆. It subsequently has been heated with both hydrogen and fluorine gases to remove tungsten and uranium fluorides from its surfaces and re-passivate its nickel and monel surfaces. The sub-manifold was constructed specifically for use with GeF₄. Its 1000 torr full scale MKS Baratron capacitance manometer is a model 629B13TACJ2B. It is an absolute pressure sensor and has a dynamic range of $\sim 10^5$ and accuracy of 0.12%. Gases contact only Inconel, its internal volume is 6.3 cubic centimeters, and its sensor is thermostated at 45 C. The voltage output of the manometer was displayed on a Keithley model 197 5-1/2 digit digital voltmeter. The Autoclave Engineers (AE) tubing ("nipples") used in constructing the main and sub-manifolds was 3/8 inch od and 1/8 inch id nickel or monel. The AE fittings use metal-metal contact seals that employ a cone and taper principle. The nickel or monel AE valves are 30VM series and are all metal-construction aside from PTFE packing on their non-rotating stems. The relatively small diameter of the fittings minimizes the internal volume of manifold sections. The fluorine gas used for passivation of the main and sub-manifolds had been purified by fractional distillation at cryogenic temperature. The commercial GeF₄ that we used was purchased from Advance Research Chemicals, Inc, (Catoosa, OK) and was specified to be 99.99% pure by its manufacturer.

During commissioning of a new nickel or monel-based manifold section, it is first He leaked tested, then filled with hydrogen gas and heated to reduce any surface metal oxides. It is pumped out and filled with a few torr of fluorine gas. It is then heated to fluorine-passivate the metal surfaces and pumped out. This fluorine-passivation procedure is repeated with increasing fluorine pressures to ensure formation an adherent passivation layer. Metal surfaces in the sub-

manifold that contact GeF_4 were passivated by exposure to commercial high purity GeF_4 . Sub-manifold sections exposed to the atmosphere (such as those between manifold and cylinders valves, when a cylinder is removed), after being thoroughly evacuated following such exposure, are then re-passivated by exposure to commercial GeF_4 gas and then thoroughly evacuated.

Nickel Gas Cell Assembly

The nickel gas cell assembly that we have used for our ultraviolet and near-infrared spectral studies is shown in Figs 2, 3, and 4. These are several views of the cell assembly from different angles. The numbered divisions of the ruler in Figs 3 and 4 are spaced by 1 cm. The cell assembly is constructed of nickel and monel tubing and fittings and is equipped with single crystal aluminum oxide (sapphire) windows. The rim of each window was metalized and then brazed onto a thin metal transition flange that in turn was welded to the main cell body. The cell assembly originally was used in a flow loop so it was equipped with an inlet tube near one end window and an outlet tube near the other end window. For use as a static gas cell, a plug was welded onto the end of one of these tubes and the other was machined down to 3/8 inch outer diameter (od). A 3/8 inch Swagelok "tee" connector was added to which was attached a Hoke 413A all-metal packless diaphragm valve and a 3/8 inch od tube bent into an "L" shape and into whose opposite end was welded a plug. An Autoclave Engineers 3/8 inch od "nipple" fitting was welded to the Hoke valve to facilitate connection of the gas cell assembly to the vacuum systems such as our GeF_4 vacuum system. The "L"-shaped tube is used as a side arm that can be immersed in a cryogenic fluid, such as liquid nitrogen, to freeze out the gas in the cell and so remove it from the optical path length of the cell. The oblique view in Fig 2 shows the cell resting on a right angle aluminum support. The "L" -shaped tube is to the left and the Hoke valve is above the cell body. The Autoclave Engineers fitting is above the Hoke valve and is capped with a PTFE cap to prevent dust from entering the interior of the fitting. The only materials that gas contacts in the nickel gas cell assembly are nickel, monel, and single crystal aluminum oxide.

Fig. 2. Oblique view of nickel gas cell assembly.

Fig. 3. End on view through single crystal aluminum oxide window on nickel gas cell.

Fig. 4. Side view of nickel gas cell assembly.

Ultraviolet Absorption Spectrum of Starmet-Produced GeF₄

The 200 nm to 400 nm absorption spectrum of the nickel gas cell that contained 713 torr (at 298 K) of Starmet-produced GeF₄ was recorded digitally three times on a Olis-converted Cary 17 dual beam optical spectrometer with the side arm of the cell at ambient temperature. Without moving the cell, the side arm of the cell was immersed in liquid nitrogen and the absorption spectrum of the cell was recorded three times again. Immersing the side arm of the cell in liquid nitrogen freezes out GeF₄ and removes it from the optical path length of the cell. The arithmetic mean of each of these two sets of spectra was calculated. The resulting mean spectrum of the cell with liquid nitrogen on its side arm was subtracted from the mean spectrum of the cell with Starmet-produced GeF₄ in its optical path. The resulting "differential" absorption spectrum shown is Fig. 5. This is the absorption spectrum of the Starmet-produced GeF₄ plus residual noise and any systematic baseline deviations. Based on the literature [1b] one expects UF₆ to absorb most strongly at 214 nm in a band whose width is approximately 30 nm (see Fig 6 and note that the wavelength scales for Figs 5 and 6 differ). There is no evidence of such a peak in Fig 5 and in consequence we conclude that observable amounts of UF₆ were not present in the Starmet-produced GeF₄ sample that we investigated. We can provide an upper bound for the amount of UF₆ based on the reported molar absorptivity of UF₆ gas at 273 K [1b], which is 3200 (mole/liter)⁻¹ cm⁻¹, the noise level in the differential absorption spectrum, and the concentration of GeF₄ in the gas cell. The overall pattern of the differential absorption spectrum (decrease from a positive deviation at 200 nm to a negative deviation maximum near 230 nm followed by a positive deviation and then a gradually decreasing deviation into negative values at 400 nm) was present when any of the three as-recorded spectra of the cell with its side arm in liquid nitrogen was subtracted from any of the as-recorded spectra with the cell side arm at ambient temperature.

Fig. 5. Absorption spectrum of 713 torr of Starmet-produced GeF_4 shows no evidence of UF_6 or other gases that absorb significantly in the ultraviolet.

Fig. 6. Strongest ultraviolet absorbing band of UF_6 gas at 273 K as reported by R. McDiarmid [1b].

This suggests that the slight change in index of refraction due to the presence or absence of GeF_4 gas at approximately one atmosphere pressure in the cell is the cause of such systematic baseline deviations. For this reason, the standard deviation for our absorption measurement was calculated using the data from 250 nm to 350 nm in Fig 5 and is 2.84×10^{-4} absorbance units. The concentration of GeF_4 in the cell was 0.0383 M. If one uses three times the observed standard deviation of the measurement as the "limit of detection" criterion, then the largest concentration of UF_6 that might have been present without our detecting it would have been

$$(2.84 \times 10^{-4} \times 3) / (3200 \text{ M}^{-1} \text{ cm}^{-1} \times 9.3 \text{ cm}) = 2.86 \times 10^{-8} \text{ M UF}_6$$

where 9.3 cm is that gas path length of our nickel gas cell. The concentration of GeF_4 in the gas cell was 3.83×10^{-2} M. This means that the Starmet-produced GeF_4 gas contained less than

$$(2.86 \times 10^{-8} \text{ M} / 3.83 \times 10^{-2} \text{ M})(1 \times 10^6) = 0.75 \text{ ppm UF}_6$$

on a volume basis relative to GeF_4 .

Investigation of Initial Pressure Loss

Observation of a Small Initial Pressure Loss

We observed a small loss of gas pressure when Starmet-produced GeF_4 gas was introduced into the sub-manifold + capacitance manometer section of our gas line. That gas was pumped out briefly and additional Starmet-produced GeF_4 was introduced into the sub-manifold. Very little pressure loss was observed (less than 0.1 torr in 3 minutes) so the sub-manifold was again briefly pumped on, the valve to the evacuated nickel gas cell was opened, and a nearly atmospheric pressure amount of Starmet-produced GeF_4 was introduced into the sub-manifold + capacitance manometer + nickel gas cell. The pressure values reported by the capacitance manometer were recorded periodically and are shown in Fig 7. It is evident that there was a small but very rapid initial pressure drop followed by a period during which a smaller pressure drop occurred and the loss of pressure decreased at a nearly exponential rate that was $0.137 \text{ minute}^{-1}$. After

Fig. 7. Pressure drop observed upon introduction of Starmet-produced GeF_4 into the sub-manifold + capacitance manometer + nickel gas cell volumes which had been passivated by previous exposure to commercial high purity GeF_4 and then evacuated. The upper panel shows the observed pressure (symbols) and a fit (solid line) to a part of that data using a single exponential decay model:

$$P_{\text{obs}} = 713.06 + 1.7096\exp(-0.1366t)$$

where P_{obs} is the observed pressure in torr and t is time in minutes. The lower panel shows the same observed data plotted as percent pressure change from the time that the gas was introduced into the cell.

26 minutes residence time, the gas pressure was nearly independent of time and $\sim 0.8\%$ of the initial gas pressure had been lost. The nickel gas cell was valved off and the sub-manifold pumped out. The nickel gas cell was transferred to the sample compartment of a UV-VIS dual beam optical spectrometer where the ultraviolet absorption spectra discussed above were recorded and then to an FT-IR spectrometer where near-infrared absorption spectra were recorded because it seemed likely that the observed pressure drop was due to the presence of hydrogen fluoride (HF) gas. If this is the case, then the observed behavior suggests that HF in the GeF_4 was sorbed onto the metal fluoride passivation layer on interior of the nickel gas cell. The sorbed HF presumably generated a metal fluoride-HF adduct layer that retarded further sorption of HF and thereby resulted in diffusion-limited sorption of additional HF until an equilibrium between gas and surface-bound HF was reached.

Near-Infrared Absorption Spectrum of Starmet-Produced GeF_4

Near-infrared absorption spectra of the nickel gas cell that contained 713 torr of GeF_4 were recorded on a Nicole Magna 860 Fourier transform infrared (FT-IR) spectrometer which is a nitrogen gas purged, single beam instrument that was operated at 1 cm^{-1} spectral resolution (0.5 cm^{-1} data point spacing). The spectrometer was equipped with a calcium fluoride beamsplitter and a KBr-windowed DTGS pyroelectric detector. The spectral range 1700 cm^{-1} to 5000 cm^{-1} was scanned and 128 sweeps of that range were averaged. Because our nickel gas cell assembly, when mounted in the sample compartment, did not allow closing the sample compartment cover, we used a "tent" made of plastic sheeting over the open sample compartment to improve nitrogen gas purging of the sample compartment. This reduced, but did not eliminate, interference from atmospheric water vapor and carbon dioxide. The only infrared absorbing gas observed within the nickel gas cell was hydrogen fluoride (HF). The P-branch transitions from its ground vibrational state to its first excited vibrational state were overlapped by residual atmospheric water vapor lines. Its R-branch lines, however, were free of such interference. The portion of spectra recorded over the R-branch region are shown in Fig 8. Fig 8a shows the spectrum observed with 713 torr of Starmet-produced GeF_4 in the nickel gas cell. The nickel gas cell then was put back on the GeF_4 vacuum line and evacuated to less than 0.1 torr through the rough vacuum manifold and pumped on with the high vacuum manifold system for a few minutes. The gas cell was put back in the FT-IR spectrometer, the sample compartment was purged with nitrogen gas, and spectra were recorded. An example of those spectra is shown in Fig 8b. The

Fig 8. Portion of the observed FT-IR absorption spectrum of a) 713 torr of Starmet-produced GeF_4 in the nickel gas cell shown in Figs 2, 3 and 4, b) the nickel gas cell after pumping out the Starmet-produced GeF_4 for a few minutes, and c) the nickel gas cell after 15 hours of evacuation. To facilitate comparison, a constant has been subtracted from each of the above spectra to bring the trace start or end to zero absorbance. The 6 equally spaced absorbance peaks in panel a are R-branch vibration-rotation bands of hydrogen fluoride (HF) gas as are the narrow peaks at the same wavenumber values in panel b.

nickel gas cell was returned to the vacuum line and pumped on with the high vacuum manifold system for 15 hours. It was then put back in the FT-IR spectrometer, the sample compartment was purged with nitrogen gas, and spectra were recorded. An example of one of those spectra is shown in Fig 8c. It is clear from the spectra shown in Fig 8 that

- Hydrogen fluoride (HF) gas was present in the nickel gas cell filled with Starmet-produced GeF_4
- Prolonged pumping on that gas cell was necessary to remove observable HF from the cell.

Unfortunately, the recorded FT-IR spectra do not provide a quantitative measure of the amount of HF in the nickel gas cell. At low pressure and 298 K, the true width of an R-branch HF vibration-rotation line is 0.011 cm^{-1} based on the usual expression for the Doppler width of a transition of a gas phase absorber [5]. At higher pressure (a few torr total pressure) pressure broadening increases the true width of these transitions and what was a nearly Gaussian line shape tends toward Lorentzian. At atmospheric pressure, the line width is dominated by pressure broadening effects and the line shape is nearly Lorentzian.

Because the spectral resolution of our FT-IR is poor compared to the true line width of R-branch HF lines at any of the gas pressures used in our work, the observed absorbances will not follow Beers law. For example, the observed absorbance of a given HF R-branch line in Fig 8b is smaller than that for the same line in Fig 8a. However, the HF partial pressure in the gas cell may have been larger in the case of Fig 8b than it was in the case of Fig 8a. At low pressure and with spectral resolution that is less than the true line width, very little of the analysis light will be absorbed near an HF R-branch line because the line shape for those lines will be Gaussian. At atmospheric pressure, the line shape becomes nearly Lorentzian. A Lorentzian line shape decreases more slowly as one moves away from line center than is the case for a Gaussian line shape. For this reason, two gas samples with equal HF partial pressures, but differing total pressures, will exhibit differing observed absorbance values for HF R-branch lines under our

experimental conditions such that the largest absorbance will occur for the sample whose total pressure is highest.

The traditional method for making quantitative measurement of absorbing gas concentration under these experimental conditions is preparation of a series of gas samples in which the partial pressure of the absorbing gas and an inert broadening gas are systematically varied. The absorption spectra of these gas samples are recorded at a fixed spectral resolution. Plotting either the observed peak or integrated line intensities as a function of absorbing and total gas pressures generates calibration curves that can be used with samples to be analyzed. Unfortunately, HF self-associates with increasing HF partial pressure and it adsorbs on most surfaces. For these reasons, preparation of a series of gas samples of known HF partial pressure and total gas pressure is extremely difficult and we have not attempted it.

Preparation and Characterization of Glassy GeO₂

Our experimental work in this area has focussed on determining the conditions under which visually clear, colorless, bubble-free glassy GeO₂ can be produced that is suitable for quantitative uranyl analysis via LIF and the standard addition method. Our past work [6] largely centered on development of laser-induced fluorescence analysis for detection of uranyl in GeO₂. It identified two problems. These were difficulty in preparing glassy GeO₂ at the level of 1 gram of GeO₂ that was free from crystalline inclusions and that contained no trapped air bubbles. The GeO₂ that we used was specified by its manufacturer (Alfa) to be 99.999% pure on a metals basis. Physically, this material is a white, finely divided powder. We confirmed that it is largely the hexagonal form of GeO₂ by the heat evolved as it underwent dissolution in hydrofluoric acid [3]. We detected the presence of tetragonal phase GeO₂ in that a small fraction of this material did not dissolve in 25% hydrofluoric acid solution.

We varied a number of factors in our preparations of glassy GeO₂. These factors included:

- The pH and composition of the aqueous phase in contact with powdered GeO₂ immediately prior to heating. Specifically, commercial GeO₂ (Alfa, 99.999% pure metals basis) was contacted with nitric acid, high purity water, and concentrated ammonium hydroxide.

- The melting temperature used and the time at the melt temperature
- The crucible material (platinum, polycrystalline alumina, and single crystal aluminum oxide) and whether or not the crucible was covered during heating.
- The presence or absence of added uranyl nitrate.

Visually clear, colorless, bubble-free glassy GeO_2 was produced from GeO_2 that had been immersed in concentrated ammonium hydroxide solution, dried under a stream of dry nitrogen gas, and then loaded into a shallow square crucible formed from 0.002 inch thick platinum foil. This crucible was placed in an alumina boat and that assembly was placed within a horizontal tube furnace and heated to 1400 °C. After being held at 1400 °C for the desired time, the sample was quickly withdrawn from the hot zone of the furnace by pulling on a platinum wire attached to the alumina boat. Contacting GeO_2 powder with concentrated ammonium hydroxide likely produced a gel layer on the surface of the GeO_2 particles and thereby promoted reduced viscosity and increased gas permeability. As detailed below, however, it gave rise to other, luminescence-related problems

Rapid withdrawal of the sample from the hot zone prevented the formation of crystalline inclusions that we sometimes had observed when samples were cooled within the furnace at its natural rate following cut off of electrical current to its heating elements. The key to suppressing crystallization of GeO_2 is the rapidity with which molten GeO_2 is cooled to below its glass transition temperature (~500 °C [7]) and, based on literature reports [7], more particularly, the rate at which it is cooled from 1000 °C to 800 °C. Using a platinum wire attached to an alumina boat, we rapidly pulled the GeO_2 fusion crucibles in the alumina boat out of the hot zone of the furnace. Our horizontal tube furnace is equipped with a round Coors high purity alumina process tube. The platinum wire was threaded through a small hole bored through an insulating plug that is inserted into the alumina process tube. The small GeO_2 fusion crucibles in the alumina boat could be withdrawn in a few seconds from the heated zone of the furnace into a relatively cool, unheated zone of the alumina process tube. We have found that this suppressed crystallization in all of the GeO_2 samples that were prepared using this cooling method.

Laser-induced Fluorescence Characterization

The glassy GeO_2 that we produced was characterized as to its luminescence properties using the laser-induced fluorescence techniques and apparatus described in our March 19, 2001 progress report. Briefly, we used 355 nm pulses from a frequency tripled, Q-switched Nd:YAG laser as the excitation light source and recorded luminescence emission spectra and lifetimes at ambient temperature.

Fig 9 compares some of the observed emission spectra for GeO_2 samples heated to 1400 °C for 4 hours. The red curve shows emission due to the uranyl ion that peaks at 536 nm in glassy GeO_2 . Treatment of GeO_2 powder with nitric acid followed by drying in a 110 °C oven generates nearly the same emission spectrum peaking at 620 nm as seen upon heating untreated GeO_2 powder except that the observed intensity is much more larger. This emission band is so intense that in a similarly nitric acid-treated sample that contained 0.1 ppm uranium, no uranyl emission was observable. As noted above, treatment of GeO_2 powder with concentrated ammonium hydroxide gives a visually clear, colorless, and bubble-free glass when heated to 1400 °C. Unfortunately, it also generates a broad, intense emission band peaking near 650 nm (Fig 9, blue curve).

The broad intense red emission bands likely arise from thermal reduction of tetravalent Ge to divalent Ge. These impurity luminescence bands spectrally overlap luminescence from uranyl in glass GeO_2 as is evident in Fig 9. Fig 10 compares the luminescence decays observed from glassy GeO_2 that contained 11 ppm uranium and from a clear, colorless, bubble-free sample of glassy GeO_2 made from GeO_2 powder that been treated with concentrated ammonium hydroxide. As is evident in Fig 11, there is not a sufficiently large difference in lifetime between uranyl ions and the impurity species to enable effective discrimination against the strong luminescence from impurity species that form when GeO_2 treated with nitric acid or concentrated ammonium hydroxide is heated to 1400 °C for prolonged periods.

Fig. 9. Comparison of the observed emission spectra, recorded at 295 K following pulsed 355 nm excitation, from glassy GeO_2 that had been heated to 1400 °C and contained 11 ppm uranium (red curve) or contained no uranium (green curve). The black curve is that for GeO_2 treated with nitric acid and then heated to 1400 °C. The blue curve is that for GeO_2 treated with concentrated ammonium hydroxide and then heated to 1400 °C. The spectra have been scaled to equal peak intensity to facilitate comparison.

Fig. 10. Comparison of the observed luminescence decays at 295 K following pulsed 355 nm excitation of glassy GeO_2 that contained 11 ppm uranium and had been heated to 1400 °C (curve a, red symbols) and glassy GeO_2 prepared by heating GeO_2 that had been treated with concentrated ammonium hydroxide prior to being heated to 1400 °C (curve b, black symbols).

Melting GeO_2 in alumina or single crystal aluminum oxide did not significantly alter the ingrowth of the impurity specie or species that gives rise to the red luminescence that strongly interferes with ultratrace determination of uranyl in glassy GeO_2 . Holding a given GeO_2 sample at 1400 °C for increasingly longer times in any of the crucibles investigated increased the intensity of impurity species luminescence following 355 nm excitation.

Ultratrace Uranium Analysis Using a Chloride Volatility Approach

Given difficulties in producing glassy GeO_2 of acceptable quality for quantitative uranyl luminescence analysis, we began a search for alternate, but related methods of achieving our goal of improved ultratrace analysis for UF_6 in GeF_4 gas. We have identified a promising method that does not require high temperature processing and so is likely to be more easily and economically implemented in a quality assurance laboratory.

Our new approach retains the same initial step, namely, hydrolysis of GeF_4 gas in water to generate GeO_2 , H_2GeF_6 , and HF, and the same second processing step, namely sub-boiling point distillation of volatile species. Our new approach then dissolves the resulting non-volatile residue (GeO_2 and uranyl fluoride, if any UF_6 was present in the GeF_4) in concentrated hydrochloric acid. This converts GeO_2 to volatile GeCl_4 that is removed, along with excess hydrochloric acid, by a second sub-boiling point distillation step. The residue (uranyl chloride and trace amounts of GeO_2) is taken up in dilute phosphoric acid solution. The uranium content of the resulting solution is quantified by laser-induced fluorescence and the standard addition method. This new approach will permit use of 266 nm excitation which has the advantage of being more strongly absorbed by uranyl in dilute phosphoric acid than is light at 337 nm (nitrogen laser) or 355 nm (tripled Nd:YAG laser) [8].

Our new approach removes most of the fluoride content of GeF_4 in the first sub-boiling point distillation. To remove any remaining fluoride and all but traces of germanium, GeO_2 from hydrolysis of GeF_4 is reacted with excess concentrated hydrochloric acid solution. This generates GeCl_4 and converts any fluoride into HF. Pure GeCl_4 is a rather volatile liquid whose boiling point is 83.1 °C [3]. Due to its significant vapor pressure [9], volatilization of GeCl_4 from concentrated hydrochloric acid has been used as a means of purifying germanium. We expect that any UF_6 initially present in the GeF_4 that is undergoing analysis will be converted through

our process into uranyl chloride (UO_2Cl_2). Uranyl chloride is not volatile nor is it significantly luminescent at ambient temperature. To enhance uranyl luminescence, the residue (containing the uranyl chloride) from the second sub-boiling point distillation step will be taken up in dilute phosphoric acid solution. This is a uranyl luminescence enhancing medium that is the basis for literature reports of detection of uranyl at concentrations as low as 1 ppt [10] to 40 ppt [11]. It is significant for our new approach that chloride ion quenching of uranyl luminescence is suppressed to a considerable degree by dilute phosphoric acid. By removing fluoride and HF, our approach enables use of high purity, ultraviolet grade fused silica fluorescence cells that exhibit very low luminescence following ultraviolet excitation. Our tests of single crystal aluminum oxide (sapphire) from several sources, following ultraviolet excitation, showed significant luminescence in the spectral region where uranyl emits. Sapphire is, however, highly resistant to HF.

The primary interference that we anticipate in our germanium chloride volatilization process is luminescence from trace level organic contaminants leached from the perfluoropolymer distillation vessel or the Kel-F hydrolysis can. We expect to eliminate such interference, it is significant, by 185 nm photolysis which is a sufficiently short wavelength that it should photochemically destroy such contaminants. Several alternative oxidation methods exist, if other impurities in the solution absorb 185 nm to an extent that renders 185 nm photodestruction of organics ineffective. These alternative oxidation methods include addition of hydrogen peroxide followed by 254 nm photolysis (this produces highly reactive hydroxyl radicals) and addition of nitric acid as well as concentrated hydrochloric acid following the first sub-boiling point distillation step (this mixture of acids is a form of aqua regia and generates chlorine atoms and reactive nitrogen oxides).

In our initial studies of key steps this new approach, we have verified volatilization of germanium from GeO_2 dissolved in concentrated hydrochloric acid. We did observe a very thin film deposit on the upper portion of the PFA Teflon® distillation pot after volatile species were distilled away. It seems likely that the thin film is GeO_2 deposited as the equilibrium

becomes displaced toward the left as the partial pressure of HCl decreases at the distillation end point.

It should be noted that our chloride volatility approach should generate solutions suitable for analysis by other ultratrace methods such as inductively coupled plasma mass spectrometry (ICP-MS). Attempting ICP-MS directly on hydrolyzed GeF_4 results in a significant "matrix" interference due to the high concentration of germanium species in such a solution. By removing nearly all of the germanium from the hydrolysis solution, "matrix" interference should be eliminated. This should allow analysis of selected samples that have been processed using our chloride volatility approach by both laser-induced fluorescence and higher cost ICP-MS methods for quality assurance and technique development purposes.

Hydrolysis Procedure for GeF_4

The volume of the nickel can on the sub-manifold of our GeF_4 gas handling system is 323 cm^3 and that of the Kel-F can is 596 cm^3 (see Fig 1). The amount of GeF_4 gas hydrolyzed is determined based on the assumption of ideal gas behavior

$$PV = nRT$$

where P is the gas pressure, V is volume of the gas, T is its temperature, R is the gas constant, and n is the number of moles of gas. The volume V is that of the nickel can, P is measured with a high accuracy (0.12%) thermostated capacitance manometer, and T is measured adjacent to the metal fitting. The Kel-F can has a demountable cap and a polytetrafluoroethylene (PTFE) sealing gasket. Kel-F is a chlorofluoropolymer that is stiffer and more readily machined to a precise shape than is PTFE. The Kel-F can assembly is a design originally used for studies on liquid anhydrous HF. A measured amount of water from a Barnstead E-Pure water purification system is added to the Kel-F can, its cap and gasket fitted, and that seal is He leak checked with the bottom section of the can assembly in liquid nitrogen (to freeze out water and its vapor). Freeze-thaw pumping is used to vacuum degas the water. The Kel-F can assembly is put on the sub-manifold of the GeF_4 vacuum system, its connection to the sub-manifold is thoroughly evacuated, and its bottom section is immersed in liquid nitrogen. The sub-manifold down to the Kel-F can valve is then exposed to commercial GeF_4 to ensure passivation and then it is

thoroughly evacuated. The nickel can valve is opened, the sub-manifold is isolated, and Starmet GeF_4 is added to the desired pressure as recorded by the capacitance manometer. The nickel can valve is closed and the sub-manifold is pumped out. The sub-manifold is isolated, the nickel can valve is opened, and then the Kel-F can valve is opened. This cryopumps the GeF_4 into the Kel-F can. After a few minutes, the Kel-F can valve is closed and the capacitance manometer reading is recorded (normally, this is less 0.1 torr). The sub-manifold and nickel can are thoroughly evacuated and the bottom of the Kel-F can is allowed to warm to ambient temperature. Reaction of GeF_4 with the water (ice) in the Kel-F can occurs as the GeF_4 warms and begins to assert its vapor pressure.

Sub-boiling Point Distillation Apparatus

This apparatus shown schematically in Fig. 11 has been used for removal of the volatile species created during hydrolysis of GeF_4 . In use, a thermocouple was immersed in the oil-filled beaker and its output connected to a temperature controller that regulated the electrical power supplied to a heating tape that was wrapped around the beaker. The solids and liquid resulting from hydrolysis of GeF_4 in water were removed from the Kel-F can (Fig 1) and transferred into the distillation pot (vessel "a" in Fig. 11) using a syringe constructed from Teflon tubing and fittings with suction supplied by a conventional glass syringe. The walls and bottom of the can were rinsed with aliquots of water that were added to the distillation pot. A slow stream of dry nitrogen gas swept vapors from the distillation pot through the traps.

Vessels a, b, c, and d are molded PFA Teflon® 60 ml "impingers", supplied by Savillex. Vessel "a" contains the solution undergoing sub-boiling point distillation. Vessels "c" and "d" are immersed in a dry ice slurry contained in a glass Dewar flask.

Figure 11. Schematic diagram of sub-boiling point distillation apparatus.

Issues for Future Work

1. Given the finite time and financial resources available for development of methods for ultratrace determination of UF_6 in GeF_4 , a decision likely will have to be made as to whether those resources primarily should be directed toward development and publication in a peer-reviewed journal of our chloride volatility approach or toward development and demonstration of long path ultraviolet absorption spectroscopy to measure UF_6 impurity in GeF_4 gas. Our chloride volatility approach which requires hydrolysis of GeF_4 and wet chemistry processes. It should achieve 40 parts per trillion or better sensitivity for uranium in GeF_4 . Long path length ultraviolet absorption spectroscopy is a potential on-line, near real time process monitor for UF_6 impurity in GeF_4 gas. It should achieve a sensitivity of 15 parts per billion (by volume) or better for UF_6 impurity in GeF_4 gas using a 1 meter path length.
2. In our new chloride volatility approach, traces of GeO_2 may remain in the distillation pot. We need to determine if trace level GeO_2 is soluble in dilute phosphoric acid and whether it enhances, diminishes, or otherwise interferes with ultratrace determination of uranyl via laser-induced fluorescence and the standard addition method. We also need to determine the degree to which the uranium content of a known amount of UF_6 in GeF_4 gas is recovered and converted into luminescing uranyl ions in phosphoric acid in our new approach.
3. The temperature dependence of the intensity of uranyl luminescence in dilute phosphoric acid has not been reported. We should determine the degree of sample temperature control that is required to eliminate temperature variation as a significant factor in applying the standard addition method in our chloride volatility-based approach to ultratrace determination of UF_6 in GeF_4 .

Conclusions

1. Formation of crystalline inclusions in glassy GeO_2 was eliminated by rapid withdrawal of molten GeO_2 samples from the hot zone of the alumina process tube of our horizontal tube furnace into a relatively cool end zone of that process tube.
2. Treatment of GeO_2 with concentrated ammonium hydroxide followed by heating to 1400°C for four hours resulted in visually clear, colorless, bubble-free glassy GeO_2 . Unfortunately, it also produced impurities whose strong luminescence following ultraviolet excitation precluded use of this method for generating glassy GeO_2 that was suitable for ultratrace determination of uranyl via the standard addition method.
3. Although we varied a number factors, we found no processing conditions that produced glassy GeO_2 of a quality suitable for quantitative determination of uranyl at the ultratrace level via the standard addition method.
4. Using the same initial processing steps as required for production of glassy GeO_2 , we have identified a promising chloride volatility-based approach for ultratrace determination of the uranyl ions that result from hydrolysis of UF_6 in impure GeF_4 gas. We have verified a key step in this new approach, namely the volatility of GeCl_4 resulting from reaction of GeO_2 with concentrated hydrochloric acid. This method promises a limit of detection of 40 parts per trillion or better for uranium (as UF_6 gas) in GeF_4 .
5. Using ultraviolet absorption spectroscopy, we examined a sample of Starmet-produced GeF_4 and determined that it contained less than 0.75 parts per million (ppm) of UF_6 on a volume basis. No other ultraviolet absorbing gas species were observed.
6. Based on an observed small decrease in pressure when a sample of the Starmet-produced GeF_4 gas was brought into contact with clean, passivated metal surfaces and observation of vibration-rotation bands of hydrogen fluoride (HF) gas in the near-

infrared absorption spectrum of the gas, we concluded that the sample of Starmet-produced GeF_4 that we analyzed contained approximately 0.8% HF gas by volume.

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Literature Cited

- 1a) "The absorption spectrum of UF_6 from 2000 Å to 4000 Å", G. L. DePoorter and C. K. Rofer-DePoorter, *Spectroscopy Letters*, **8**, 521 - 524 (1975).
- b) "Assignments in the electronic spectrum of UF_6 ", R. McDiarmid, *J. Chem. Phys.*, **65**, 169-173 (1976).
- 2) "Absorption spectra of Si_2Cl_6 , SiF_3CH_3 , and GeF_4 in the VUV region", T. Ibuki, N. Washida, U. Itoh, Y. Toyoshima, and H. Onuki, *Chem. Phys. Let.* **136** (1987) 447 - 450.
- 3) "*The Chemistry of Germanium*", F. Gloeking, Academic Press, London, 1969.
- 4) "*Uranium Hexafluoride: A Manual of Good Handling Practices*", U. S. DOE Field Office, Oak Ridge, TN, Report Number ORO-651 (Rev. 6), dated October, 1991.
- 5) "*Resonance Radiation and Excited Atoms*", A. C. G. Mitchell and M. W. Zemansky (Cambridge Univ. Press, London, 1971), Eqn 33, page 99.
- 6) "*Ultratrace Determination of Uranium in Germanium Tetrafluoride, March 19, 2001 Progress Report*", J. V. Beitz and C. W. Williams, Chemistry Division, Argonne National Laboratory, unpublished, 2001.
- 7) "*Handbook of Glass Data, Part B - Single Component and Binary Non-silicate Oxide Glasses*", O. V. Mazurin, M. V. Streltsina, and T. P. Shvaiko-Shvaikovskaya, Elsevier, Amsterdam, 1985, pgs. 353-384. This is volume 15 of Elsevier's Physical Sciences Data Series.

8. "Uranyl phosphorescence at the parts-per-trillion level", R. Kaminski, F. J. Purcell, and E. Russavage, *Anal. Chem.* **53**, 1093-1096 (1981).
9. "Vapor pressure of germanium tetrachloride over its aqueous hydrochloride solutions", M. I. Boluntsova and M. Ya. Shpirt, *Zh. Fiz. Khim.*, **45**, 2106-2107 (1971).
10. "Kinetic analysis of laser-induced phosphorescence in uranyl phosphate for improved analytical measurements", B. A. Bushaw, *Anal. Chem. Symp. Ser.* **19** (*Anal. Spectrosc.*), 57-62 (1984).
- "Direct detection of trace levels of uranium by laser-induced kinetic phosphorimetry", R. Brina, and A. G. Miller, *Anal. Chem.* **64**, 1413-1418 (1992).
11. "Fluorescence determination of trace amounts of uranium(VI) in various materials by a repetitive laser technique", G. I. Romanovskaya, V. I. Pogonin, and A. K. Chibisov, *Talanta*, **34**, 207-210 (1987).

ULTRATRACE DETERMINATION OF URANIUM IN GERMANIUM TETRAFLUORIDE

May 11, 2002 Progress Report

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Introduction

As noted in our October 23, 2001 Progress Report, our initial approach to ultratrace determination of uranium (as uranium hexafluoride, UF_6) in GeF_4 relied on hydrolysis of GeF_4 (and any UF_6 present) followed by removal of fluoride and fusion of the resulting GeO_2 . This process would convert UF_6 to uranyl ion which we showed luminesced strongly in GeO_2 glass. However, we also found that fusion of GeO_2 at the gram scale in air at sufficiently high temperature to minimize bubbles and crystallization also results in formation of a ultraviolet-absorbing, visible light emitting species whose presence severely interfered with ultratrace determination of uranyl ion via luminescence detection. For this reason, we have begun work on an alternate approach to determination of uranium (as uranium hexafluoride) in GeF_4 that we term chloride volatility.

Chloride Volatility

As with our previous approach, the first step of our chloride volatility method is hydrolysis of GeF_4 in water which is reported [1] to occur via the overall reaction:

Assuming that the H_2GeF_6 can be further hydrolyzed to produce GeO_2

addition of concentrated aqueous hydrochloric acid would then dissolve GeO_2 with formation of GeCl_4 via

Simple distillation should be sufficient to remove most of the germanium as GeCl_4 and leave behind nonvolatile uranyl chloride formed via hydrolysis

and mass displacement:

Because GeCl_4 (boiling point: 83.1°C [1]) is relatively volatile in comparison with uranyl chloride which exhibits no volatility until temperatures approaching 800°C , simple distillation should suffice to remove most germanium as GeCl_4 while retaining

nonvolatile uranyl chloride for subsequent analysis via laser-induced luminescence in dilute phosphoric acid used as a uranyl luminescence enhancing medium [2-5].

Testing Process Simplification

The above sequence of reactions suggested that process simplification might be achieved by hydrolyzing the analyte GeF_4 gas in water, taking the resulting solution to dryness via sub-boiling point distillation, adding concentrated HCl , and again removing volatiles, expected to be GeCl_4 and the excess HCl [6], via sub-boiling point distillation.

To test this hypothesis, 1 gram of GeF_4 gas was hydrolyzed in 10 ml of water using the procedure described in October 23, 2001 Progress Report. The contents of the Kel-F hydrolysis reactor were rinsed into a Savillex 60 ml PFA Teflon "impinger" with an additional 10 ml of water. The impinger was used as the distillation pot of the PFA Teflon apparatus shown in Figure 11 of our October 23, 2001 Progress Report. Sub-boiling point distillation was carried out at 95 °C under a slow flow of high purity nitrogen gas. After cooling to ambient temperature, approximately 15 ml of 9 mole/liter hydrochloric acid was added to the distillation point and sub-boiling point distillation again carried out. Upon cooling to ambient temperature, solid residue remained in the distillation pot so approximately 15 ml of concentrated (~12 mole/liter) hydrochloric acid was added and sub-boiling distillation resumed. After cooling to ambient temperature, solid residue remained in the distillation pot. The solid was recovered and placed in a capped borosilicate vial. After several days, some fogging of the interior of the vial was observed to have occurred. This suggested that the solid contained fluoride ions that were capable of undergoing hydrolysis to produce hydrofluoric acid (HF).

Infrared Analysis of Hydrolysis Solids

Infrared analysis of the white solid residue was carried out by grinding a few milligrams of it with white powdered FT-IR grade cesium iodide (CsI) in an agate mortar and pestle in a nitrogen gas-purged plastic gloved bag. During grinding the powdered mixture turned yellow. The yellow powder was pressed into a 10 mm diameter pellet using a press ("Econo-Press", Aldrich catalog number Z28,188-3). Infrared absorption spectra of

pellets were recorded on a Nicole Magna 860 Fourier transform infrared (FT-IR) spectrometer which is a nitrogen gas purged, single beam instrument that was operated at 1 cm^{-1} spectral resolution (0.5 cm^{-1} data point spacing). The spectrometer was equipped with a silicon beamsplitter and a CsI-windowed DTGS pyroelectric detector. The spectral range 1200 cm^{-1} to 200 cm^{-1} typically was scanned and 128 sweeps of that range were averaged.

Fig 1. FT-IR absorption spectrum of a CsI pellet that contained the solid remaining after twice hydrochlorinating hydrolyzed GeF_4 gas.

In Fig 1, two peaks, those centered at 600 cm^{-1} and 350 cm^{-1} , were so intense that the spectrometer could not accurately record their peak absorbance.

For comparison purposes, a few mg of 99.999% pure GeO_2 from Alfa were ground with CsI to produce a white powder that was pressed into a pellet whose FT-IR spectrum was recorded (see Fig 2). Based on observed incomplete dissolution of the Alfa GeO_2 in hydrofluoric acid, this GeO_2 contains a mixture of hexagonal and tetragonal GeO_2 (tetragonal GeO_2 is nearly insoluble in hydrofluoric acid [1]).

Fig 2. FT-IR absorption spectrum of a CsI pellet that contained commercial 99.999% pure GeO_2 .

As is evident in comparing Figs 1 and 2, GeO_2 is present in the “twice hydrochlorinated hydrolyzed GeF_4 ” sample. A search of literature IR absorption spectra of germanium containing species was carried out to identify the species that gave rise to the two most intense bands (600 cm^{-1} and 350 cm^{-1}) in Fig 1. A literature study of vibrational spectra of the hexafluorogermanate ion, GeF_6^{2-} , concluded that GeF_6^{2-} in cubic Cs_2GeF_6 has 6 fundamental vibrational frequencies, four of which are Raman active, two of which are infrared active, and one of which is inactive[7]. These workers report that the IR active bands of Cs_2GeF_6 are symmetric and centered at 600 cm^{-1} and 350 cm^{-1} . We presume that the source of Cs_2GeF_6 in our pellet was reaction of CsI with H_2GeF_6 during grinding:

and that the yellow color of pellet was the result of formation of triiodide ion (I_3^-) which would imply some dissociation of HI to H_2 and I_2 due to the heat generated during grinding. Taking into account the presence of GeO_2 and Cs_2GeF_6 in Fig 1, there remain weak bands in the 690 to 740 cm^{-1} region and the sharp weak band at 479 cm^{-1} that are

not attributable to either GeO_2 or Cs_2GeF_6 . Plausibly, they are due to an oxyfluoride of germanium, such as GeOF_2 .

The remaining white pot residue was transferred back into the PFA distillation apparatus along with approximately 15 ml of water. Sub-boiling point distillation was carried out again in an effort to achieve further hydrolysis of the solid. A few milligrams of the resulting white solid were ground together with CsI which produced a lighter yellow powder that was pressed into a pellet. The IR absorption spectrum of that pellet is shown in Fig 3. Note that none of the spectra presented in this Report have been "baseline corrected" to produce an artificially flat baseline. In the case of Fig. 3, the pellet contained a significant concentration of light scattering centers (most likely due to incomplete coagulation of particles during the pressing step) that resulted in light scattering being a significant contribution to the overall change in light transmission as a function of wavenumber.

Fig 3. FT-IR absorption spectrum of a CsI pellet that contained some of the solid that remained after the first hydrolysis of the material whose absorption spectrum is shown in Fig 1.

As is evident in comparing Figs 1 and 3, heating the sample material in water greatly reduced the intensity of the 600 and 350 cm^{-1} bands of Cs_2GeF_6 relative to the bands of GeO_2 and almost completely removed the 690 to 740 cm^{-1} and 470 cm^{-1} bands.

A second hydrolysis in liquid water was carried out and another CsI pellet made from an aliquot of the resulting white solid. Grinding CsI and the white solid again gave a light yellow powder. The IR absorption spectrum of the resulting pellet (not shown) differed little from the spectrum shown in Fig. 3. We presume that heating in liquid water resulted in partially hydrolysis of H_2GeF_6 which generated some HF. Because dilute HF solutions become more concentrated in HF upon evaporation, our sub-boiling point distillation process (in which the solid undergoing hydrolysis remains in contact with the liquid is being distilled) may be less effective than would a steam hydrolysis process.

Steam Hydrolysis Apparatus

We devised a simple steam hydrolysis apparatus made primarily from Savillex PFA Teflon components (see Fig 4.). In this apparatus, the solid undergoing hydrolysis is contained in a 5 ml vial that is suspended in steam that, upon further rising within the apparatus, condenses and returns to the liquid at the bottom of the 240 ml PFA vessel. An air condenser (as shown in Fig. 4) was used when total reflux was desired. An "J" shaped FEP tube (inverted) was used in place of the 18 inch long straight air-condenser tubing when partial reflux was desired. Holding the oil bath at 128 °C with partial reflux typically resulted in a 1 ml/hour condensate collection rate.

Further Infrared Analyses

A portion of the white solid residue from the sub-boiling point apparatus was transferred to the steam hydrolysis apparatus shown in Fig 4. Following steam hydrolysis, a few mg of the white solid in the 5 ml PFA vial was ground with CsI to produced a light yellow powder that was pressed into a pellet. The IR absorption spectrum of that pellet is shown in Fig. 5.

NOTE: Sheet PTFE support for drip shield and 5 ml PFA vial is not shown.

Fig. 4. Schematic cross-section view of steam hydrolysis apparatus.

Fig 5. FT-IR absorption spectrum of a CsI pellet that contained some of the solid remaining after the steam hydrolysis of the material whose absorption spectrum is shown in Fig 3.

Comparing Figs 1, 2, 3, and 5, it is most evident in comparing the intensity of the 600 cm^{-1} peak (due to Cs_2GeF_6 formed during grinding) to the intensity of the 876 cm^{-1} peak of GeO_2 , that steam hydrolysis resulted in further conversion of H_2GeF_6 to GeO_2 .

A second steam hydrolysis was carried. A few mg of the white solid was ground with CsI to a nearly white powder that was pressed into a pellet. The absorption spectrum of the pellet is shown in Fig 6.

Fig 6. FT-IR absorption spectrum of a CsI pellet that contained some of the solid remaining after steam hydrolysis of the material whose absorption spectrum is shown in Fig 5.

Comparing Fig 2 (99.999% GeO_2) and Fig 6 (multiply hydrolyzed and hydrochlorinated GeF_4), the primary visual difference is the width of the 876 cm^{-1} band. Table 1 compares the peaks reported by the Nicolet FT-IR peak find algorithm for these two sample pellets. We conclude that the FT-IR absorption spectrum shown is that of GeO_2 with no other species observable.

Table 1. Comparison of observed peaks in the infrared absorption spectrum of multiply hydrolyzed and hydrochlorinated GeF_4 and commercial 99.999% pure GeO_2 .

Hydrolyzed and hydro-chlorinated GeF_4 (cm^{-1})	Commercial 99.999% GeO_2 (cm^{-1})
960.6	960.2
875.4	876.4
585.0	585.6
549.5	552.6
516.4	518.6
334.8	334.9
251.9	250.9
211.5	212.3

Steam Hydrolysis

From the above results, steam hydrolysis to convert H_2GeF_6 to GeO_2 seemed preferable to hydrolysis in liquid water. To test this conclusion, we hydrolyzed one gram of GeF_4 gas in 10 ml of water in our Kel-F hydrolysis vessel. Using 10 ml of rinse water, the contents of the Kel-F vessel were transferred into the sub-boiling point distillation apparatus. Volatiles were removed by sub-boiling distillation. The resulting white solid was transferred to a 5 ml PFA vial that was inserted into the steam hydrolysis apparatus shown in Fig 4.

Steam hydrolysis was carried out typically for 3 to 5 hours at which time the 240 ml PFA bottle was raised out of the oil bath and allowed to cool. The liquid at the bottom of the PFA bottle was suctioned out using a "tandem syringe" (see Fig 7). The liquid contact part of the syringe was made from PFA tubing and fittings. A conventional glass syringe (with a greased piston) was used to apply suction to lift the liquid from the PFA bottle.

The pH of the solution removed from the PFA bottle was checked with pH paper and typically was 1.8 to 2. The steam hydrolysis apparatus was charged with 20 ml of water for each run. Twenty runs were required to achieve a significant drop in pH. The observed pH on the 21st run was 6 and was taken to correspond to complete hydrolysis. This means that a total of 400 ml of water and approximately 80 hours of contact with

steam at slightly above 100 °C was needed to completely hydrolyze the mixture of GeO_2 and H_2GeF_6 solids that resulted from reacting 1 g of GeF_4 with 10 ml of water. It is possible that one reason for this slow observed reaction rate is the accumulation of HF in the liquid and vapor within the steam hydrolysis apparatus. This might result in an equilibrium forming between hydrolysis of H_2GeF_6 and re-formation of H_2GeF_6 due to reaction of GeO_2 with very dilute HF vapor. The relative constancy of the observed pH values until nearly at complete hydrolysis supports this possibility.

Fig. 7. Tandem syringe used with dilute hydrofluoric acid solutions

Preliminary Vapor Phase Hydrochlorination Results

We modified our steam hydrolysis apparatus (Fig. 4) to enable vapor phase hydrochlorination of GeO_2 that had been produced by our steam hydrolysis method. We added three traps in series on the outlet of the air condenser of our steam hydrolysis apparatus. Each trap consisted of a Savillex 60 ml PFA Teflon impinger. The trap nearest the condenser was left empty, the middle trap was also left empty but was immersed in a water ice bath (0 °C), and the last trap was filled with soda-lime pellets. Soda-lime was used to ensure sorption of acidic vapors. The traps were connected with 1/4 inch outer diameter FEP Teflon tubing. The outlet of the final trap was a tube that was immersed below the surface of a dilute NaOH solution to enable observation of the gas flow rate through the apparatus. The solid plug on the lid of the 240 ml PFA bottle was

replaced with an FEP Teflon tube through which was flowed a slow stream of high purity nitrogen gas. The 240 ml PFA bottle was charged with 20 ml of ultrapure 34% hydrochloric acid (Baker Ultrex II grade); GeO_2 from steam hydrolysis was placed within the 5 ml PFA vial and the rest of the apparatus assembled. The oil bath was heated to 115 °C to achieve a slow condensate collection rate (~1/3 ml per hour). Under these conditions, the mixture of water and HCl vapors rising from the liquid hydrochloric acid is enriched in HCl compared to the liquid. The rising vapor comes in contact with GeO_2 in the 5 ml vial and then is condensed on the upper walls and lid of the 240 ml PFA bottle and flows back down into the liquid at the bottom of the 240 ml PFA bottle. The expected reaction is:

with the gaseous GeCl_4 and H_2O , along with excess HCl vapor, expected to be swept by the slow flow of nitrogen gas out of the 240 ml PFA bottle into the series of traps.

After 3 hours of refluxing, the clear, colorless liquid condensate in the first (initially empty) trap was removed. As expected, this liquid was strongly acidic and, after addition of an equal volume of water, the acidity of the solution was neutralized by addition of solid sodium bicarbonate to reach pH 6 by pH test paper. The resulting solution was colorless and no precipitate or gel was observed to form which is evidence that little, if any, GeCl_4 was present in the condensate. Hydrochlorination using a mixture of HCl and water vapors at 115 °C evidently is not a rapid means of converting solid GeO_2 to volatile GeCl_4 .

Conclusions

1. FT-IR analysis of CsI pellets that contain partially hydrolyzed GeF_4 provides a rapid method for assessing the relative amounts of GeO_2 and H_2GeF_6 present, based on absorption bands of GeO_2 and Cs_2GeF_6 respectively.

2. Hydrolysis of GeF_4 is incomplete when GeF_4 gas reacts at ambient temperature with excess water.
3. Heating the solids resulting from incompletely hydrolyzed GeF_4 in liquid water or steam slowly completes the hydrolysis reaction and resulted in production of GeO_2 .
4. Under our process conditions, heating the solids that resulted from incompletely hydrolyze GeF_4 in aqueous hydrochloric acid solution, then in liquid water, and finally in steam more rapidly completed hydrolysis and resulted in production of GeO_2 .
5. Heating GeO_2 (produced by steam hydrolysis at slightly above $100\text{ }^\circ\text{C}$) in a mixture of water and HCl vapors at $115\text{ }^\circ\text{C}$ is ineffective at rapidly generating volatile GeCl_4 for removal of germanium from any uranium initially present in GeF_4 as uranium hexafluoride.

Future Work

Our immediate emphasis will be on achieving more rapid hydrolysis of GeF_4 to GeO_2 and rapid conversion of GeO_2 to volatile GeCl_4 . This likely will require contact of the solids generated with a significant excess of aqueous hydrochloric acid. This raises the possibility that our limit of detection for uranyl that results from hydrolysis of uranium hexafluoride in GeF_4 gas will be limited by the uranium impurity level in commercial ultrapure hydrochloric acid.

Acknowledgements

Teflon is a registered trademark of the E.I. du Pont de Nemours and Company. Helpful discussions with J. B. Bulko (Starmet Corporation) concerning the properties of GeF_4 are gratefully acknowledged. This research was carried out as a subcontract to a DOE Phase II SBIR grant to Starmet Corporation (Concord, MA).

Literature References

- [1] F. Gloeking, **The Chemistry of Germanium**, Academic Press, New York, 1969.
- [2] "Kinetic analysis of laser-induced phosphorescence in uranyl phosphate for improved analytical measurements", B. A. Bushaw, *Anal. Chem. Symp. Ser.* **19** (Anal. Spectrosc.), 57-62 (1984).
- [3] "Direct detection of trace levels of uranium by laser-induced kinetic phosphorimetry", R. Brina, and A. G. Miller, *Anal. Chem.* **64**, 1413-1418 (1992).
- [4] "Fluorescence determination of trace amounts of uranium(VI) in various materials by a repetitive laser technique", G. I. Romanovskaya, V. I. Pogonin, A. K. Chibisov, *Talanta*, **34**, 207-210 (1987).
- [5] "Uranyl phosphorescence at the parts-per-trillion level", R. Kaminski, F. J. Purcell, and E. Russavage, *Anal. Chem.* **53**, 1093-1096 (1981).
- [6] "Vapor pressure of germanium tetrachloride over its aqueous hydrochloride solutions", M. I. Boluntsova, M. Ya. Shpirt, *Zh. Fiz. Khim.*, **45**, 2106-2107 (1971).
- [7] "Vibrational Spectrum of the Hexafluorogermanate Ion", J. W. Griffiths and D. E. Irish, , *Inorg. Chem.* **3**, 1134-1137 (1964).

**ULTRATRACE
DETERMINATION OF
URANIUM
IN GERMANIUM TETRAFLUORIDE**

March 17, 2003 Progress Report

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Abstract

We report ultraviolet absorbance analyses of Starmet-produced germanium tetrafluoride (GeF_4) gas and near- to mid-infrared absorbance analysis of the same sample material. An upper limit for the amount of uranium hexafluoride gas is reported based on analysis of the observed ultraviolet absorption spectra. Hydrogen fluoride and carbon dioxide gases were detected based on the recorded infrared absorption spectra. Efforts to develop a germanium tetrachloride volatility-based approach for analysis of uranium in hydrolyzed GeF_4 gas are reported. The starting point for this work was hexagonal germanium dioxide from steam hydrolysis of hydrolyzed GeF_4 gas. No experimental conditions were found that resulted in significant conversion of steam hydrolysis-produced hexagonal germanium dioxide to germanium tetrachloride. Our steam hydrolysis-produced hexagonal germanium dioxide was found to be soluble in hydrofluoric acid although the resulting solution was not suitable for high sensitivity luminescence analysis for the presence of uranyl ion due to interfering luminescing impurities that are attributed to leaching of low molecular weight polymers from the Kel-F and Teflon containers used for chemical manipulations. Recommendations for possible future studies are made. This is the final progress report concerning our studies on ultratrace determination of uranium in germanium tetrafluoride.

Absorbance Analyses of Germanium Tetrafluoride Gas

An aliquot of germanium tetrafluoride (GeF_4) gas from Starmet Sample Reference Number "GeFusn-40" (Starmet preparation date 1/11/02) underwent analysis by ultraviolet absorption spectroscopy for the presence of uranium hexafluoride gas (UF_6). This analysis and an infrared analysis were carried out using the methods, equipment, and procedures noted in our October 23, 2001 progress report to Starmet with one exception. That exception was the averaging together of ten spectral scans which resulted in slightly improved sensitivity. No absorbance attributable to UF_6 gas was observed. As filled, the gas cell contained 641 torr of gas at 27 °C. If one uses three times the observed standard deviation of the measurement as the "limit of detection" criterion, then the sample of Starmet-produced GeF_4 gas contained less than 0.64 parts per million of UF_6 gas on a volume basis relative to GeF_4 .

The sample also underwent infrared absorbance analysis in the 2000 to 5000 wave number (cm^{-1}) spectral region in the same sample cell used for ultraviolet absorption analysis. A Nicolet Magna 860 FT-IR equipped with a calcium fluoride beamsplitter coated for mid- to near-infrared use and a potassium bromide-windowed DTGS pyroelectric detector were used to acquire 128 scans of the 2000 cm^{-1} to 5000 cm^{-1} spectral range at 1 cm^{-1} spectral resolution (0.5 cm^{-1} data point spacing). The Magna 860 is a single beam instrument. Using Nicolet's OMNIC software, the observed transmission spectrum of the GeF_4 gas sample cell was converted into an absorbance spectrum by dividing it, point-by-point, with a "background" transmission spectrum acquired without the GeF_4 sample cell in the sample compartment. Due to the valve assembly on the GeF_4 gas cell and the dimensions of the sample compartment of the Magna 860, it was not possible to use liquid nitrogen to cryopump the GeF_4 into the side arm of the cell assembly to remove the gas from the optical path and thereby obtain a spectrum of the empty gas cell without physically removing the cell from the optical path. Moving the cell resulted in baseline shifts due to the high index of refraction of the single crystal aluminum oxide windows on the gas cell and difficulty in exactly reproducing its position in the optical path. Figure 1 shows the observed absorbance spectrum of the gas cell.

Fig. 1. Absorbance spectrum of an aluminum oxide-windowed gas cell that contained 641 torr of Starmet-produced GeF_4 (Starmet Sample Reference Number "GeFusn-40"). Vibration-rotation bands of hydrofluoride (HF) gas are denoted by a symbol (•).

The very narrow characteristic fundamental vibration-rotation bands of hydrogen fluoride gas (HF) were observed in the 3700 to 4200 cm^{-1} spectral range and are denoted by a dot (•) symbol. These bands had nearly the same observed absorbance (optical density) as was the case for our previous FT-IR analysis of an aliquot of GeF_4 from Starmet Sample Reference Number "GeFusn-36" (Starmet preparation date 8/06/0). The sloping background is due primarily to the single crystal aluminum oxide (sapphire) windows of the gas cell. The numerous sharp bands in the 3550 to 3900 cm^{-1} spectral range whose peaks occur as decreased absorbance (compared to the sloping background) are due to vibration-rotation bands of water vapor. Although the Magna 860 was well purged by dry nitrogen gas, some water vapor was always present in its optical path. When the GeF_4 gas cell was inserted into the optical path of the 860, the infrared analysis light path through the nitrogen gas purged interior of the instrument was reduced by about 9.3 cm in comparison with the path length when the "background" transmission spectrum was recorded. The "negative" absorbance water peaks result from that change in path length when the transmission spectrum recorded with the GeF_4 gas cell in the path was divided by the "background" transmission spectrum.

In addition, weak absorption bands (peak absorbance: 0.002 absorbance units) of the ν_3 fundamental absorption bands of carbon dioxide gas (CO_2) were observed in the 2310 to 2375 cm^{-1} spectral range and are shown in Figure 2. These peaks are on a strongly sloping background that is due to the increasing absorbance of the aluminum oxide windows of the gas cell with decreasing wave number. Because the peaks occur as increased absorbance they are indicative of the presence of CO_2 as an impurity in the GeF_4 gas in the sample cell.

Because the spectral resolution that we achieved is much broader than the true line widths of the HF or CO_2 absorption peaks, the spectra shown in Figures 1 and 2 are qualitative in nature as to the peak absorption of a given vibration-rotation transition. Put another way, the spectra identify the presence of impurity HF and CO_2 gases in the Starmet-produced GeF_4 gas sample but are insufficient to quantify the amount (concentration) of such impurities.

Fig. 2. Absorbance spectrum of an aluminum oxide-windowed gas cell that contained 641 torr of Starmet-produced GeF_4 (Starmet Sample Reference Number "GeFusn-40"). The numerous sharp peaks in the 2310 to 2375 wave number range are due to the vibration-rotation bands of carbon dioxide gas.

Development of a Chloride Volatility-Based Analysis for Uranium in Hydrolyzed Germanium Tetrafluoride

Our primary focus was evaluation of our proposed "chloride volatility" process for analysis of the uranium content of hydrolyzed GeF_4 gas. The basis of this process is detailed in our May 11, 2002 progress report. The process requires conversion of "particulate GeO_2 " into volatile germanium tetrachloride (GeCl_4). The "particulate GeO_2 " of interest is that which arises from repeated steam hydrolysis of the solids that result from reaction (hydrolysis) of GeF_4 with water. As noted in our May 11, 2002 report, the particulate GeO_2 that we produce via steam hydrolysis is of the hexagonal structure type based on its infrared absorption spectrum. Standard reviews of germanium chemistry [1] state that hexagonal GeO_2 reacts with concentrated hydrochloric acid to form GeCl_4 . We were surprised, therefore, when our particulate GeO_2 failed to react with concentrated hydrochloric acid (American Chemical Society analytical reagent grade) solution at ambient temperature over periods of time that eventually extended to several months contact. For this reason, we carried out both a literature search as to conditions

that favor reaction of GeO_2 with hydrochloric acid (HCl) and our own extensive experimental tests of the reactivity of our particulate GeO_2 with hydrochloric acid solutions.

Selection of Experimental Routes Based on Literature Search Results

The primary tool that we used was SciFinder which is a product of the American Chemical Society and provides access to the ~22 million literature and report abstracts of the Chemical Abstract Services that are on-line and typically date back as far as the 1950's and in some cases even further. Most of the literature references related to conversion of GeO_2 to GeCl_4 were published more than twenty years ago in Russian language journals. Difficulty in converting hexagonal GeO_2 to GeCl_4 arises from at least two effects. One is the higher thermodynamic stability of hexagonal GeO_2 in comparison with that of glassy GeO_2 . For example, a ~100-fold slower rate was reported for the dissolution in water of hexagonal GeO_2 , in comparison with glassy GeO_2 . [2] The other effect is the influence of particle size with higher reaction rates expected for smaller particles. There is general agreement that, in comparison with hexagonal GeO_2 , glassy GeO_2 dissolves more readily in water and is, therefore, more readily converted to GeCl_4 because dissolution of GeO_2 is believed to be the rate-limiting step in conversion to GeCl_4 . In addition, high HCl concentration is desired. Aqueous reagent grade "concentrated" HCl (nominally, 37% weight percent HCl) is the lowest recommended HCl concentration [3], at least at the start of conversion of solid GeO_2 to GeCl_4 (recall that reaction of GeO_2 to produce GeCl_4 produces H_2O which reduces the concentration of HCl over the course of the reaction). Recommended temperatures for reaction of GeO_2 with HCl from ambient to above the boiling point of GeCl_4 when separation of GeCl_4 by distillation was the goal. Dissolution of "aged" hexagonal GeO_2 has been recognized as a significant problem in the analytical chemistry of germanium. The common approach to this problem has been to heat the GeO_2 to above its melting point followed by rapid thermal quenching to achieve conversion to glassy GeO_2 . Only one study of chemical methods to achieve the same end, namely dissolution of "aged" hexagonal GeO_2 was found. It recommended use of 2.5 mole/liter sodium hydroxide at elevated temperature in preference to acidic oxidative or reductive routes. [4]

Because heating the particulate GeO_2 that we produce to convert it to a glassy state fuses the powder to a mass, grinding of the resulting fused mass of glass would be needed to produce small particles and achieve a significant rate of reaction with HCl . All means of grinding available to us would result in significant chemical contamination of the GeO_2 . Conversion to glass was rejected for that reason. Use of sodium hydroxide solution at elevated temperature likely would dissolve our particulate GeO_2 to produce a sodium germanate solution. However, laser-induced fluorescence analysis for uranyl requires acidic to near-neutral pH depending on the luminescence enhancer used. Neutralization or acidification as an aqueous solution of sodium germanate would result in formation of a gel of hydroxo or hydrated GeO_2 that would be both highly light scattering and capable of sequestering uranyl ion from an added luminescence enhancing agent such as pyrophosphate. For these reasons, solubilization of our particulate GeO_2 by dissolution in sodium hydroxide solution at elevated temperature was rejected. Based on these considerations, we carried out a concerted experimental effort to achieve an acceptable rate of chemical reaction of our particulate GeO_2 with aqueous HCl solutions to generate volatile GeCl_4 .

Our Experimental Tests

We established that reaction of our particulate GeO_2 with concentrated HCl (ACS reagent grade) did not occur over a period of weeks at ambient temperature and was not observably enhanced by elevated temperature over periods of time extending up to two days and at temperatures that included the boiling point of concentrated HCl . These tests culminated in a series of experiments in which particulate GeO_2 was held in the refluxing vapor above constant boiling point hydrochloric acid and in the refluxing vapor above concentrated hydrochloric acid. In none of these tests was any observable conversion of our particulate GeO_2 to GeCl_4 found. These tests used the PFA Teflon apparatus that we created for steam hydrolysis of hydrolyzed GeF_4 . Instead of charging the apparatus with water, it was charged with an HCl solution. Reflux was achieved using an 18 inch length of 0.25 inch outer diameter FEP Teflon tubing that extended above the PFA vessel and served as an air-cooled condenser. Portions of the refluxing vapor were collected for analysis and no evidence of GeCl_4 was found. In a separate test series, to maximize the

solution acidity, a stream of dry hydrogen chloride gas was passed through a stirred slurry of particulate GeO_2 in concentrated aqueous HCl at ambient temperature in a fused silica tube the bottom end of which had been flame-sealed to the shape of a cone. High purity Matheson HCl gas was passed through a two-stage pressure regulator and a Matheson particulate filter prior to the gas stream coming in contact with the aqueous HCl solution in the fused silica tube. No formation of liquid GeCl_4 was observed in the fused silica tube. No reduction in the amount of particulate GeO_2 in the aqueous HCl solution was evident visually after 26 hours. The vapor exiting the reaction vessel was passed through a trap held at 273 K. Analysis of the trap contents did not reveal any GeCl_4 . We conclude that our particulate GeO_2 , although of the hexagonal structure type based on its infrared absorption spectrum, exhibited a negligible reaction rate with hydrochloric acid under our experimental test conditions. For this reason, our proposed "chloride volatility" process is not suitable for high sensitivity analysis for the presence of uranium in hydrolyzed GeF_4 gas. Reaction of particulate GeO_2 with dry HCl gas at moderately high temperature (e.g., 400 °C) was not attempted due to concern about chemical reduction (due to the presence of small amounts of hydrogen gas in HCl). Such reduction of trace levels of uranyl would result in lower valent uranium chlorides whose volatility likely would compromise analytical accuracy.

Laser-induced Fluorescence on GeO_2 Dissolved in Hydrofluoric Acid Solution

In a final effort to quantify uranium in hydrolyzed GeF_4 gas, we contacted an aliquot of particulate GeO_2 with 22% hydrofluoric acid solution and found that the particulate GeO_2 readily dissolved to give a clear, colorless solution. This solution was transferred to a single crystal aluminum oxide cell that consisted of a single crystal aluminum oxide rod into which a hole that had been drilled coaxial with the cylinder axis of the rod to create a flat-bottomed "test tube" shape. A polished disk of single crystal aluminum oxide capped the cavity in the rod and prevented escape of significant amounts of HF vapor from the contained solution. Laser-induced fluorescence analysis of the solution in this cell was carried out using 355 nm excitation with the apparatus described in our March 12, 2001 progress report. Luminescence from the solution was observed

throughout the visible spectral range and exhibited complex, non-exponential decay. The luminescence initially peaked in the blue. With increasing time following a laser excitation pulse, the peak luminescence intensity wavelength shifted to longer wavelength. An aliquot of a solution of uranyl ion in dilute nitric acid was added to the solution in the cell in an amount sufficient to give approximately 6 parts per million of uranyl on a weight basis. The characteristic luminescence emission bands of uranyl ion could not be discerned in the recorded emission spectra due to the much more intense broadband, complex luminescence of the solution. This interfering luminescence likely arises from low molecular weight polymers that had leached from the Kel-F and perfluoroalkoxy (PFA) Teflon containers that we used to generate the particulate GeO_2 . Such luminescence was not observed from our HF stock solution nor was it present in solutions of commercial GeO_2 dissolved in our HF stock solution. We conclude that the sensitivity of luminescence analysis for uranyl in hydrofluoric acid solutions of particulate GeO_2 was significantly hindered by the presence of interfering luminescing species that likely are low molecular weight polymers that leached from the walls of Kel-F and Teflon containers.

Recommendations for Possible Future Studies

The most promising analysis method that we investigated for ultratrace analysis of uranium in GeF_4 gas consisted of four major steps:

- 1) Hydrolysis of GeF_4 gas to a slurry of GeO_2 and H_2GeF_6
- 2) Steam hydrolysis of the mixture of $\text{GeO}_2 + \text{H}_2\text{GeF}_6$ to produce hexagonal GeO_2
- 3) Fusion of hexagonal GeO_2 to produce glassy GeO_2
- 4) Laser-induced fluorescence analysis for uranyl ion luminescence in the produced glassy GeO_2 .

This method failed at the third step because a luminescing impurity (or impurities) grew in at the temperatures needed to produce glassy GeO_2 that was free of bubbles and crystalline inclusions. Based on a literature report[5], it seems likely that the luminescing impurity was an oxygen atom deficient site in GeO_2 . Prolonged heating of the glassy

GeO₂ in a oxygen gas atmosphere is reported to eliminate the 245 nm optical absorption band that has been attributed to an oxygen atom deficient site in glassy GeO₂. [6] Unfortunately, our high temperature furnaces were not designed for heating samples in a pure oxygen atmosphere. In consequence, we could not confirm the reported influence of an oxygen gas atmosphere on suppression of the 245 nm defect absorption band and, presumably, suppression of interfering luminescence. If the literature reports concerning oxygen atom defects in glassy GeO₂ are correct, then the above method, modified in step 3 to include fusion in a pure oxygen gas atmosphere, likely would meet a prime objective of our project, namely a limit of detection of a few parts per trillion of uranium in GeF₄ gas.

Due to the growth of a luminescing impurity at step 3 of the above process, we turned to conversion of GeO₂ to volatile GeCl₄ as a method of removing the light scattering interference of particulate GeO₂ and the potential sequestering of uranyl ions by GeO₂ prior to use of laser-induced fluorescence to quantify uranium as uranyl ion. As detailed in this progress report, our efforts to convert GeO₂ to GeCl₄ failed due to the extremely slow rate of reaction of aqueous HCl with hexagonal GeO₂ produced by steam hydrolysis (step 2 of the above process). During the writing of this report, we found an abstract for a literature report on a method for recovery of germanium from solid wastes. That methods is suggestive that a superior alternative to the use of pure HCl solutions may exist for conversion of GeO₂ to GeCl₄. Based on the abstract for that literature report, germanium from waste waters co-precipitated with basic iron carbonate and hydroxide, when treated with 6 mole/liter HCl in the presence of phosphoric acid, is converted to GeCl₄ that can be separated by distillation at 108 °C.[7] It seems likely that the co-precipitated germanium is either GeO₂ or a hydrate of GeO₂. The additional acidity due to added phosphoric acid might enhance dissolution and reaction of our hexagonal GeO₂. Because 10 weight% phosphoric acid is a good uranyl ion luminescence enhancing medium, the presence of residual phosphoric acid after volatilization of the resulting GeCl₄ would be beneficial. In addition, phosphoric acid strongly complexes uranyl ion which would ensure retention of it in the distillation vessel. However, due to the added chemical complexity and attendant possibilities for

interference from ultratrace impurities in the reagents used, the limit of detection for uranium in GeF_4 , if volatilizing GeO_2 via conversion of it to GeCl_4 , seems likely to be inferior to that of the four step process outlined in the above paragraph.

Acknowledgements

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Literature References

1. **The Chemistry of Germanium**, F. Glocking, Academic Press, London, 1969.
2. **Kinetics of dissolution of germanium oxide at 25°** I. A. Kakovskii, E. A. Knyazev, S. V. Ponomareva, Ural. Nauchno-Issled. Proektn. Inst. Mednoi Prom-sti. (1966). This is Chemical Abstract number 67:6081.
3. **Determination of traces of impurities in pure germanium tetrachloride and germanium dioxide.** E. Wunderlich, E. Goehring, Z. Erzbergbau Metallhuettenw. **18**, 121-124 (1965).
4. **Reaction chemistry of crystalline allotropes of germania.** L. Seibles, J. W. Mitchell, L. D. Blitzer, J. Am. Ceram. Soc. **72**, 1430-1433 (1989).
5. **Prospects of using germanium dioxide-based glasses for optics.** A. Margaryan and W. M. Liu. Optical Engineering **32**, 1995-1996 (1993)
6. **Photoluminescence of intrinsic defects in glassy germanium dioxide. Twofold coordinated germanium and nonbridging oxygen.** L. Skuja, Physica Status Solidi A: Applied Research **114**, 731-737 (1989).
7. **Recovery of germanium from solid wastes and neutralizing liquors from production of blanks for quartz optical fibers.** V. G. Amelin, Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i Khimicheskaya Tekhnologiya, **36**, 99-102 (1993).