

## **Development of NF<sub>3</sub> Deposit Removal Technology for the Portsmouth Gaseous Diffusion Plant**

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### **ABSTRACT**

This paper summarizes the Battelle, Stoller, and WASTREN (BSW) team's efforts, to date, in support of the United States Department of Energy's plans to remove uranium and technetium deposits before decommissioning the Portsmouth Gaseous Diffusion Plant. The BSW team investigated nitrogen trifluoride (NF<sub>3</sub>) as a safer yet effective alternative gaseous treatment to the chlorine trifluoride (ClF<sub>3</sub>)-elemental fluorine (F<sub>2</sub>) treatment currently used to remove uranium and technetium deposits from the uranium enrichment cascade. Both ClF<sub>3</sub> and F<sub>2</sub> are highly reactive, toxic, and hazardous gases, while NF<sub>3</sub>, although toxic [1], is no more harmful than moth balls [2].

BSW's laboratory thermoanalytical and laboratory-scale prototype studies with NF<sub>3</sub> established that thermal NF<sub>3</sub> can effectively remove likely and potential uranium (UO<sub>2</sub>F<sub>2</sub> and UF<sub>4</sub>) and technetium deposits (a surrogate deposit material, TcO<sub>2</sub>, and pertechnetates) by conversion to volatile compounds. Our engineering evaluations suggest that NF<sub>3</sub>'s effectiveness could be enhanced by combining with a lesser concentration of ClF<sub>3</sub>. BSW's and other's studies indicate compatibility with Portsmouth materials of construction (aluminum, copper, and nickel).

### **INTRODUCTION**

In support of the U.S. Department of Energy's (DOE's) plans to deactivate and decommission the Portsmouth Gaseous Diffusion Plant, the Battelle, Stoller, and WASTREN (BSW) team, in a potential three-phase program, identified and investigated state-of-the-art alternatives for characterizing and removing solid uranium and technetium deposits from process equipment and piping. In Phase I, BSW identified potential alternatives. In Phase II, BSW investigated 1) NF<sub>3</sub> as an alternative reagent to ClF<sub>3</sub>/F<sub>2</sub> for removing uranium and technetium deposits arising from reaction of UF<sub>6</sub> with humid air and steel and 2) bremsstrahlung radiation as a measure of technetium content in Portsmouth deposits in ductwork and piping. If performed, Phase III will consist of testing and demonstrating the selected characterization and removal technologies on actual gaseous diffusion plant equipment at the Portsmouth site. This paper summarizes the results of our Phase II deposit removal studies and evaluations.

### **Portsmouth Gaseous Diffusion Plant Description**

The Portsmouth Gaseous Diffusion Plant is located on a 3,714-acre (1,503-hectare), DOE-owned reservation in Pike County, south-central Ohio. Plant construction began in 1952, and production of enriched uranium began in 1954. During the operating history at Portsmouth, about 1,100 metric tons of irradiated uranium with 60 to 90 kilograms (kg) of technetium were fed into the plant. As of March 1999, the technetium inventory at Portsmouth was estimated to be about 35 kg, or about 600 curies (Ci).

The process equipment at Portsmouth consists of 1) converters containing the sintered nickel gaseous diffusion barriers used to separate the uranium isotopes, 2) compressors used to provide the driving force to cause the uranium hexafluoride ( $UF_6$ ) gas molecules to diffuse through the barrier pores, 3) gas coolers, and 4) nickel-coated steel piping.

### **Nature of Uranium and Technetium Deposits**

Deposits of uranium and technetium arose from hydrolysis reactions of  $UF_6$  and possibly  $TcF_6$  with humid air and with steel equipment that had lost its protective nickel coating through erosion. Riddle [3] and the National Academy of Sciences [4] postulate that the primary uranium deposits arising from reaction of  $UF_6$  with water are  $UO_2F_2$  with secondary amounts of other uranium oxyfluorides. Uranium deposits that arose from reaction of  $UF_6$  with the exposed steel surfaces are likely uranium tetrafluoride ( $UF_4$ ), uranium pentafluoride ( $UF_5$ ) [3], diuranium ennefluoride ( $U_2F_9$ ), and tetrauranium decaheptafluoride ( $U_4F_{17}$ ) [5], with the latter two being the reported black deposits found on nickel-coated steel ducting/piping where the nickel has eroded away. Simmons and Munday [6] and Simmons [7] postulate that the technetium compounds within the cascade include the volatile species  $TcO_3F$ ,  $HTcO_4$ ,  $TcOF_4$ , and  $TcF_6$  and the condensed phases  $Tc_2O_7$ ,  $TcO_2$ ,  $HTcO_4$ , and  $TcO_2F_3$ .

### **Current Deposit Removal Technology**

Uranium and technetium deposits are currently removed from the Portsmouth cascade equipment with application of a mixture of  $ClF_3/F_2$  with a classified composition. The disadvantages of this current fluorinating/oxidizing treatment include the hazard of handling the very reactive and highly toxic  $ClF_3/F_2$ , the potential to form unstable reaction products, and the treatment's variable and largely unknown removal efficiency. While other laboratory-scale testing suggests 70 to 98% removal, two tests in the Portsmouth Gaseous Diffusion Plant have recounted lower decontamination factors of between 50 and 70%, even after repeated treatments [3, 8]. At a similar plant in the United Kingdom, the Capenhurst Gaseous Diffusion Plant, decontamination treatment with  $ClF_3/F_2$  removed approximately 80% of the deposited uranium [4].

### **BSW Deposit Characterization and Removal Project**

The full project to develop alternative technologies for deposit characterization and removal was originally planned to be conducted in three phases. Phases I and II have been completed and Phase III may be performed. Phase I [9] evaluated available alternative technologies for characterization and removal of deposits. In the Phase I evaluation, the BSW team identified  $NF_3$  as an attractive agent for converting uranium compounds to volatile  $UF_6$ . Phase II, which we just completed, consisted of:

- Laboratory-scale measurement of technetium-99 (Tc-99) in deposits using bremsstrahlung radiation
- Mock-up tests using a gamma imager to characterize deposits
- Laboratory and prototype-scale tests using nitrogen trifluoride ( $NF_3$ ) to remove uranium and technetium deposits.

If performed, Phase III will consist of testing and demonstrating the selected characterization and removal technologies on actual gaseous diffusion plant equipment or parts in the field at the Portsmouth site.

This paper summarizes the basis for selecting  $\text{NF}_3$  for further study, the results of thermoanalytical and prototype experimental  $\text{NF}_3$  decontamination studies, and engineering evaluations of potential  $\text{NF}_3$  process enhancements to develop the  $\text{NF}_3$ -based gaseous treatment process to remove uranium and technetium deposits from the Portsmouth Gaseous Diffusion Plant uranium enrichment cascade.

### BASIS FOR SELECTING $\text{NF}_3$

The BSW evaluation in Phase I [9] identified  $\text{NF}_3$  as a promising candidate for removing uranium and possibly technetium deposits. This selection was based on promising reaction thermodynamics, the experimental work of others using process enhancements such as radiofrequency (RF) activation of  $\text{NF}_3$  to fluorinate uranium compounds, and  $\text{NF}_3$ 's low hazard.

The calculated free energies ( $\Delta\text{G}$ ) using data from Wagman et al. [10] were encouraging. Table I provides calculated free energies of fluorination reactions of  $\text{NF}_3$  with potential uranium deposit materials as well as postulated reactions for reaction of  $\text{NF}_3$  with suspect technetium compounds. Unfortunately, we were unable to find thermodynamic data for similar calculations for technetium compounds.

Table I. Reaction Free Energies and Enthalpies of Postulated Reactions of  $\text{NF}_3$  with Potential Uranium and Technetium Deposits

Postulated Reaction	$\Delta\text{H}$ , kJ/mole U	$\Delta\text{G}$ , kJ/mole U
$\text{UO}_2\text{F}_{2(s)} + 4/3 \text{NF}_{3(g)} \rightleftharpoons \text{UF}_{6(g)} + 2/3 \text{N}_2 + \text{O}_2$	-333	-401
$\text{UF}_{4(s)} + 2/3 \text{NF}_{3(g)} \rightleftharpoons \text{UF}_{6(g)} + 1/3 \text{N}_2$	-150	-185
$\text{UF}_{5(s)} + 1/3 \text{NF}_{3(g)} \rightleftharpoons \text{UF}_{6(g)} + 1/6 \text{N}_2$	-30.5	-67.5
$\text{TcO}_{2(s)} + 2 \text{NF}_{3(g)} \rightleftharpoons \text{TcF}_{6(g)} + \text{N}_2 + \text{O}_2$	Not available	Not available
$\text{Tc}_2\text{O}_{7(s)} + 4 \text{NF}_{3(g)} \rightleftharpoons 2 \text{TcF}_{6(g)} + 2 \text{N}_2 + 7/2 \text{O}_2$	Not available	Not available
$\text{HTcO}_{4(s)} + 2 \text{NF}_{3(g)} \rightleftharpoons \text{TcF}_{6(g)} + \text{N}_2 + 7/4 \text{O}_2 + 1/2 \text{H}_2\text{O}$	Not available	Not available
$\text{TcO}_3\text{F}_{(s)} + 5/3 \text{NF}_{3(g)} \rightleftharpoons \text{TcF}_{6(g)} + 5/6 \text{N}_2 + 3/2 \text{O}_2$	Not available	Not available
$\text{TcOF}_{4(s)} + 2/3 \text{NF}_{3(g)} \rightleftharpoons \text{TcF}_{6(g)} + 1/3 \text{N}_2 + 1/2 \text{O}_2$	Not available	Not available
$\text{TcO}_2\text{F}_{3(s)} + \text{NF}_{3(g)} \rightleftharpoons \text{TcF}_{6(g)} + 1/2 \text{N}_2 + \text{O}_2$	Not available	Not available

Although  $\text{NF}_3$  had not been demonstrated to directly fluorinate/oxidize the materials in the Portsmouth Gaseous Diffusion Plant deposits, El-Genk and Saber [11] and Veilleux et al. [12] successfully fluorinated/oxidized  $\text{UO}_2$  to  $\text{UF}_6$  by creating atomic F from  $\text{NF}_3$  using an RF plasma. These results, in combination with statements by Golja et al. [13] that, at elevated temperatures,  $\text{NF}_3$ 's reactivity approaches that of fluorine, suggested that under the proper conditions,  $\text{NF}_3$  could convert the already oxidized and partially fluorinated  $\text{UO}_2\text{F}_2$  to the volatile  $\text{UF}_6$ . The favorable  $\text{NF}_3$ -uranium reaction thermodynamics raised our hopes that  $\text{NF}_3$  would also be effective for technetium deposits.

In addition,  $\text{NF}_3$  was attractive as a fluorinating reagent because of its ready commercial availability and its low reactivity and toxicity hazard.  $\text{NF}_3$  is used industrially for large-scale surface etching [13]. It has low reactivity at ambient temperature and thus does not react with water at ambient temperature or with most metals at temperatures up to  $250^\circ\text{C}$ , and will not violently react with hydrocarbons up to  $350^\circ\text{C}$ . As mentioned earlier, although it is toxic [1], Tremblay [2] reported that  $\text{NF}_3$  has the same relative hazard as mothballs. The monograph on  $\text{NF}_3$  by Anderson et al. [14] provides an extensive discussion of  $\text{NF}_3$ 's properties and chemistry.

The work and reviews by Woytek et al. [1], Golja et al. [13], Barkanic et al. [15], El-Genk and Saber [11], and Veilleux et al. [12] about  $\text{NF}_3$  chemistry and with RF-generated  $\text{NF}_3$ -plasmas show that  $\text{NF}_3$  can be activated to enhance its reactivity. Woytek et al. [1] report that  $\text{NF}_3$  has reactivity similar to elemental fluorine because of thermal dissociation, 1 ppm  $\text{NF}_2/\text{F}$  at  $400^\circ\text{C}$  based on equilibrium calculations. In their review of  $\text{NF}_3$  chemistry, Golja et al. [13] simply report that the reactivity of  $\text{NF}_3$  increases with increasing temperature and does not react with most metals below  $250^\circ\text{C}$ . Adiabatic compression of the gas, thermal activation, or RF activation are potential methods to produce fluorine radical from  $\text{NF}_3$ .

The following represent significant advantages for the use of  $\text{NF}_3$  over  $\text{ClF}_3$ :

- Transportation and long-term storage of quantities of  $\text{NF}_3$  are safer than  $\text{ClF}_3$  because  $\text{NF}_3$  is less corrosive to storage materials at ambient temperatures [13, 1].
- $\text{NF}_3$  is much less reactive with water or water vapor at room temperature than  $\text{ClF}_3$  and, in general, does not react with organics except at elevated temperatures [13, 1].  $\text{ClF}_3$  violently reacts with water and hydrocarbons. Reaction of water with  $\text{ClF}_3$  produces the corrosive halogen acids to which Portsmouth equipment materials are vulnerable Ullmanns 2005 [16].
- If the reaction proceeds as postulated in Table I, the products of the  $\text{NF}_3$  decontamination treatment should be  $\text{UF}_6$ , a volatile technetium compound, oxygen ( $\text{O}_2$ ), and nitrogen ( $\text{N}_2$ ). The heavy gases can be separated using existing technologies at the Portsmouth Gaseous Diffusion Plant and these permanent gases can be permissibly released to the environment.  $\text{NF}_3$  has the potential to release more environmentally benign products than  $\text{ClF}_3$ , and  $\text{NF}_3$ , itself, is more environmentally benign than  $\text{ClF}_3$ .

Based on the favorable thermodynamics, the availability of various approaches to enhance  $\text{NF}_3$ 's reactivity to levels approaching that of elemental fluorine and its environmentally benign by-products, the BSW team identified  $\text{NF}_3$  as a potentially attractive reagent to convert uranium and technetium deposits to volatile compounds that could be recovered using existing Portsmouth processes.

## EXPERIMENTAL MATERIALS, METHODS, AND APPARATUS

This section describes the thermoanalytical methods, the laboratory-scale prototype used, and the preparation of synthetic surrogate uranium and technetium deposit materials used for the  $\text{NF}_3$  deposit removal testing; actual Portsmouth uranium and technetium deposit materials were not available for our studies.

### Preparation of Surrogate Uranium Deposit Material

The suspected primary uranium deposit is uranyl fluoride in various states of hydration, although at the dryness in the cascade the  $\text{UO}_2\text{F}_2$  may be anhydrous. Using the approach employed by Portsmouth staff to prepare characteristic uranium deposit material, the BSW team prepared uranium fluoride dihydrate by hydrolyzing condensed  $\text{UF}_6$  with an excess of deionized water in a Teflon<sup>®</sup> flask. The light-yellow solids were air-dried at room temperature for three hours and then dried at  $40^\circ\text{C}$  over night.

The chemical analyses, the Raman and infrared spectrometric analyses, the X-ray diffraction (XRD) spectroscopic analysis, and the thermogravimetric analysis (TGA) found that the prepared uranyl fluoride hydrate 1) had an F:U molar ratio of 2:1, 2) contained 1.82  $\text{H}_2\text{O}$  ( $\text{UO}_2\text{F}_2 \cdot 1.82 \text{H}_2\text{O}$ ) rather than the expected 2 waters of hydration, 3) lost water when heated to  $200^\circ\text{C}$ , and 4) was poorly crystalline; however, the XRD pattern matched the known XRD pattern for uranyl fluoride hydrates. The Raman spectrum was fairly uninformative, having a single band at  $872 \text{ cm}^{-1}$  that is characteristic of the trans oxo stretching in the uranyl cation. These characterization results were consistent with a hydrated uranyl fluoride; it is likely that in the nominally anhydrous conditions within the enrichment cascade, the deposit will be anhydrous.

### **Preparation of Surrogate Technetium Deposit Material**

In the absence of any literature method to prepare a surrogate technetium deposit(s), the team used thermoanalytical methods to identify a path to prepare a volatile fluorinated technetium species from ammonium pertechnetate or technetium dioxide using  $\text{NF}_3$ . We used a three-step path to prepare a surrogate technetium deposit material by 1) drying  $\text{TcO}_2$  at  $120^\circ\text{C}$  through multiple purgings with argon of the Monel pressure vessel, 2) introducing at 30 psi  $\text{NF}_3$ , 3) slowly heating to  $400^\circ\text{C}$ , and 4) reacting the volatile technetium compound with water. The last step assumed that the technetium deposit would arise from a similar path as uranium does with its volatile form(s) reacting with water.

The immediate hydrolysis product was a red-purple. Over several days, brown-black and green solids formed with room-temperature emission of red-brown and green gases. We did not observe any colored gases above the red-purple solid, but the technetium migrated in a persistent room-temperature flow of argon. No additional chemical or physical characterizations were performed.

### **Description of Thermoanalytical Methods**

We used simultaneous TGA and differential thermal analysis (DTA) thermoanalytical methods. Because the platinum sample holders were severely attacked after initial testing, we replaced these holders with nickel and added a nickel  $\text{NF}_3$  delivery tube that could be heated to  $500^\circ\text{C}$  to test thermal activation of  $\text{NF}_3$ .

TGA measures mass change of a mg-sized sample at operator-controlled thermal conditions. The sample can either be heated or cooled at a known and controlled rate or can be controlled isothermally. Thermogravimetric results often are also presented as the mass change rate or the differential of the mass change.

By monitoring mass changes in the TGA, we were able to determine whether and how effectively  $\text{NF}_3$  converts the uranium and technetium test deposit materials to volatile species, such as  $\text{UF}_6$  for uranium or  $\text{TcF}_6$  for technetium; other volatile technetium compounds exist and may also form from the technetium deposit material. Returning the uranium and technetium to volatile forms permits these volatiles to be managed as normal process gases in the gaseous diffusion plant. TGA heat/cool ramp and isothermal results can also be used to determine Arrhenius kinetic parameters.

DTA measures heat flow as a mg-sized sample is heated or cooled at a known and constant rate or controlled isothermally; DTA reports the difference between the sample and the reference thermocouples. Alumina typically is used as the reference material. DTA is used to determine whether a reaction is exothermic (heat-producing) or endothermic (requires heat to proceed).

One can use DTA to quantify reaction enthalpies ( $\Delta H$ ). Unfortunately, DTA and its cousin, differential scanning calorimetry (DSC), which is designed to directly provide  $\Delta H$ , are not effective methods for measuring  $\Delta H$  for exothermic gas-producing reactions because the DTA and DSC will not see the latent reaction heat removed by the gaseous product as it leaves. As with TGA, DTA and DSC can be used in their heat/cool ramp and isothermal modes to determine kinetic parameters.

### **Laboratory-Scale Prototype**

The laboratory-scale prototype provided a representative test bed for treating synthetic Portsmouth deposits arising from the hydrolysis of  $\text{UF}_6$  and mobile technetium species. The prototype (Fig. 1) was a simple device where deposit material or Portsmouth materials of construction could be exposed to  $\text{NF}_3$  or  $\text{ClF}_3/\text{F}_2$  over extended periods of time with either fresh or recycled gas, and the gas could be preheated before introduction into the furnace-heated treatment chamber. The furnace tube and all connective lines were Monel, a fluorine-resistant copper-nickel alloy.  $\text{NF}_3$  does not require the use of Monel for storage.

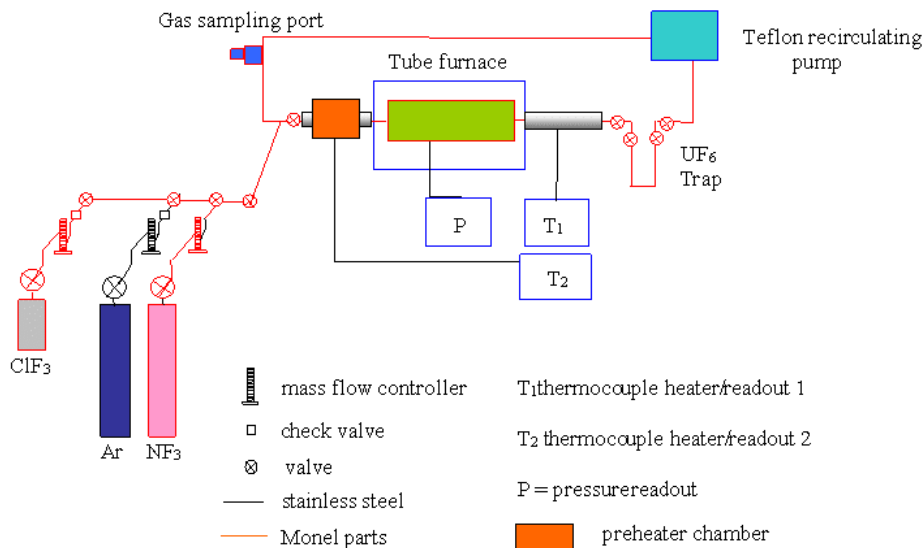


Fig. 1. Schematic of laboratory prototype apparatus

We designed the prototype to operate in both a once-through pass mode and a gas-recycle mode. To test the integrity of the prototype, we charged the apparatus with less than one atmosphere of argon, heated it to 400°C, and monitored the system's pressure and determined it to be leak-free over several hours.

In the once-through mode, the furnace tube was controlled at the target temperature between 100°C and 400°C, and controlled at 600 torr NF<sub>3</sub> by restricting gas flow from the furnace tube. Gases were exhausted to the hood plenum. In the gas recycle mode of operation, a Teflon<sup>®</sup> pump recirculated the gases through the apparatus. A cooled (0°C) U-tube trapped the heavy gases (UF<sub>6</sub>) produced during the NF<sub>3</sub> treatment.

Gases for infrared (IR) analysis were acquired through the gas sampling port. The BSW team quantified the progress of the reaction gravimetrically by measuring mass at the beginning and end of each experiment.

To date in the prototype, we have investigated the interaction of NF<sub>3</sub> with UO<sub>2</sub>F<sub>2</sub>, turbine oil, and metals characteristic of Portsmouth materials of construction used at the plant. For actual sample runs, about 0.5 gram UO<sub>2</sub>F<sub>2</sub> was put in the furnace tube. The prototype was filled to 300 torr argon and the system heated to 150°C. At this temperature, the sample mass was nearly constant after loss of physisorbed water and waters of hydration. In latter runs, we reweighed the sample at this point and put it back into the apparatus.

The apparatus was reconditioned with argon at 150°C. The U-tube trap was held at 0°C with an active chiller, and the argon was circulated through the system or purged at constant argon pressure directly to the hood plenum. NF<sub>3</sub> was used to purge the argon from the system, then the NF<sub>3</sub> pressure was added to 300 to 500 torr. The furnace tube temperature was adjustable, and provision was made to heat the inlet side of the tube furnace.

## NF<sub>3</sub> DEPOSIT REMOVAL STUDIES RESULTS AND DISCUSSION

To understand the effectiveness of NF<sub>3</sub> as a deposit removal agent, the BSW team studied NF<sub>3</sub> for surrogate uranium and technetium deposits and thermal preactivation of NF<sub>3</sub> for uranium deposit removal. In addition to the experimental studies, the BSW team

- performed engineering analyses to consider RF-activation and ClF<sub>3</sub> activation
- conducted uranium testing using TGA/DTA for both uranium and technetium and the laboratory prototype
- studied thermal NF<sub>3</sub> conversion of UO<sub>2</sub>F<sub>2</sub>, the postulated primary deposit material, using heating ramp and isothermal TGA/DTA and the laboratory prototype
- studied NF<sub>3</sub>'s reaction(s) with UF<sub>4</sub> using TGA/DTA
- studied the thermal preactivation of NF<sub>3</sub> by preheating the NF<sub>3</sub> to its decomposition temperature and then exposing a lower-temperature uranium surrogate deposit material.

### Uranium Deposit Removal Studies: Thermoanalytical Studies

Treating surrogate uranium deposit material UO<sub>2</sub>F<sub>2</sub> with 25% NF<sub>3</sub>/argon effectively converted UO<sub>2</sub>F<sub>2</sub> to a volatile uranium compound, as shown in Fig. 2. At 5°C/min, the uranyl fluoride lost 10 mass% (likely water) endothermically between the start of heating and 140°C. Near 320°C, the dehydrated sample gained 2 mass% endothermically. The uranium began to volatilize near 340°C, accelerating to a very rapid volatilization rate at 525°C, completing within 5 min. Inspection of Fig. 2 shows that the reaction's heat production rate was sufficiently fast to heat the sample faster than the instrument heat rate of 5°C/min.

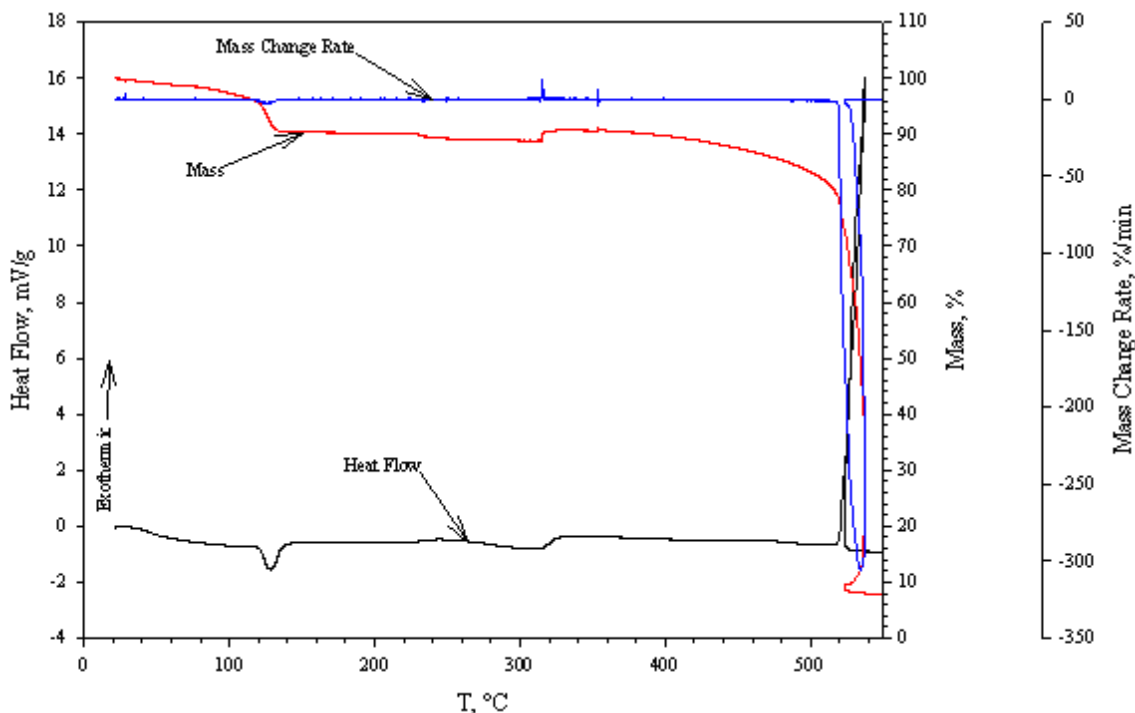


Fig. 2. Volatilization of UO<sub>2</sub>F<sub>2</sub> (UF<sub>6</sub> hydrolysis product) by 25% NF<sub>3</sub>/Ar as measured by TGA/DTA at 5°C/min

The product gas was  $\text{UF}_6$ , based on the light-yellow color of the gas and Veilleux et al.'s [12] reported vapor pressures of  $\text{UF}_6$  and other uranium/fluorine compounds. We were unable to observe  $\text{UF}_6$  in the product gases by IR because the high relative concentration of  $\text{NF}_3$  masked the  $\text{UF}_6$ 's expected low-intensity IR absorption;  $\text{UF}_6$  compounds should have a low-intensity IR absorption because of their high symmetry.

The TGA potentially provides insights into the reaction mechanism for  $\text{NF}_3$  volatilization of uranyl fluoride. The following series of reactions could explain the TGA-observed mass changes provided in Fig. 2. Relative to a starting material of  $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$ , dehydration would cause a 10.5% loss, and conversion to  $\text{UF}_4$  would cause a 1.7 mass% gain. If the starting material were  $\text{UO}_2\text{F}_2 \cdot 1.8\text{H}_2\text{O}$ , the relative TGA-observed mass changes would be 7.8 and 1.8 mass%, respectively. Because the 320°C mass gain did not occur when uranyl fluoride was heated in argon, the mass gain is due to reaction of  $\text{UO}_2\text{F}_2$  with  $\text{NF}_3$ . This mass gain occurred at other heating rates. Supposition based on the TGA results provides a reasonable path regarding the product of the 320°C reaction, but confirmation requires characterization by XRD or other chemical analyses. The TGA results suggest that the reaction path for converting uranyl fluoride to  $\text{UF}_6$  passes through  $\text{UF}_4$ , which is consistent with some of our prototype results where we saw  $\text{UF}_4$  in the product.

The DTA-observed endothermic nature of the 320°C reaction is not consistent with the thermodynamics of the  $\text{UF}_4$  and  $\text{NF}_3$  reaction path postulated in Table I, where the  $\Delta H$  for converting  $\text{UF}_4$  to  $\text{UF}_6$  is an exothermic -150 kJ/mole U. This difference suggests that the reaction path differs from that provided in Table I.

Our TGA/DTA investigation of  $\text{NF}_3$  volatilization of another potential cascade deposit material,  $\text{UF}_4$ , found that when heated at 5°C/min in 25%  $\text{NF}_3/\text{Ar}$ ,  $\text{UF}_4$  begins to react endothermically near 350°C, consistent with the onset temperature of the uranium volatilization provided in Fig. 2, but not consistent with the DTA-observed exothermic heat flow shown in Fig. 2. There is no clear explanation other than a different mechanism than that provided in Table I for why the  $\text{UF}_4$ - $\text{NF}_3$  reaction was reproducibly endothermic, while the thermodynamics provided in Table I suggest the reaction should be exothermic. The  $\text{NF}_3$  effectively converted the  $\text{UF}_4$  to  $\text{UF}_6$ . The mass and mass change rate curves suggest that the reaction is a single step, and the TGA/DTA analyses performed at 10°C/min and 20°C/min are consistent with a single-step process.

When we used the preheater installed in the TGA/DTA to investigate thermal pretreatment, the reaction was not enhanced at lower temperatures.

With the encouraging results from our heat ramp studies, the BSW team performed several longer-term isothermal studies using 25%  $\text{NF}_3/\text{Ar}$  at 180°C, 270°C, 320°C, 370°C, and 390°C. The effect of temperature on volatilization of surrogate uranium deposit material at constant temperatures is presented in Fig. 3. At 390°C and 25%  $\text{NF}_3/\text{Ar}$ , six hours were required to convert 98% of the  $\text{UO}_2\text{F}_2$  to  $\text{UF}_6$ . At 320°C, six hours were required to volatilize 44% of the  $\text{UO}_2\text{F}_2$ . At 180°C, no detectable mass change occurred in 24 hours.



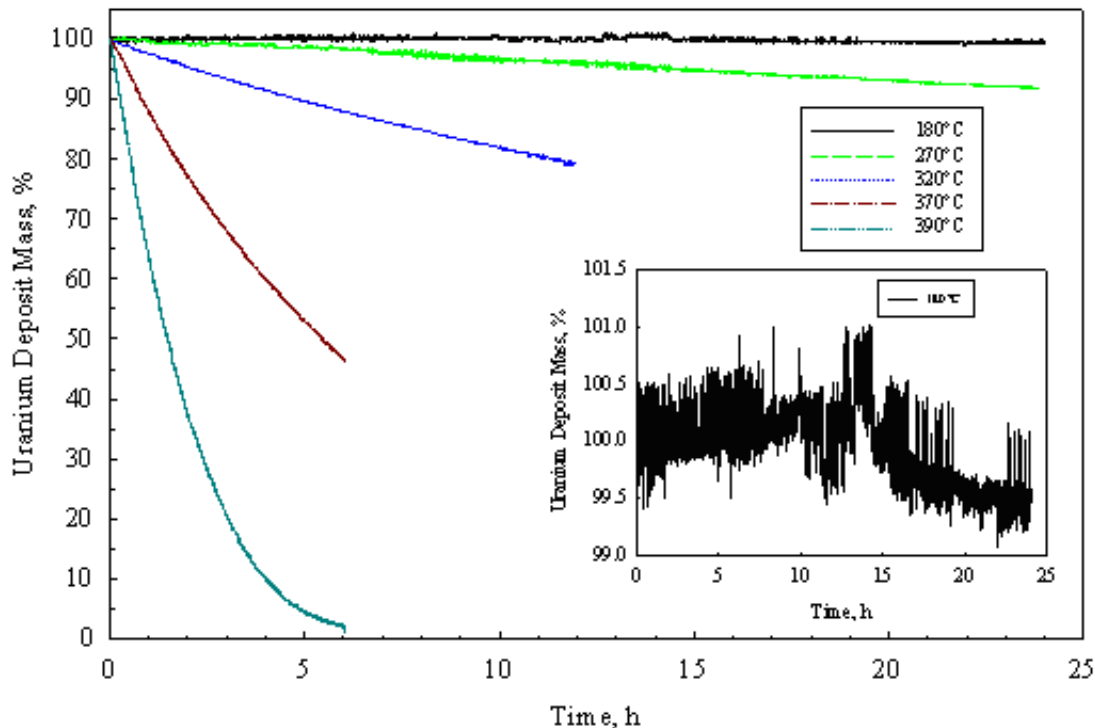


Fig. 3. Isothermal volatilization of  $\text{UO}_2\text{F}_2$  by 25%  $\text{NF}_3/\text{Ar}$  as measured by TGA at 180°C, 270°C, 320°C, 370°C, and 390°C

### Uranium Deposit Removal Studies: Kinetics

Using the isothermal TGA results provided in Fig. 3 and assuming pseudo-first order kinetics at a constant excess  $\text{NF}_3$  concentration, we determined an Arrhenius activation energy  $E_a$  of 106 kJ/mol and an Arrhenius pre-exponential  $A$  of  $1.6 \times 10^7$  for the Arrhenius equation

$$k_{obs} = A \exp\left(\frac{-E_a}{RT}\right) \quad (\text{Eq. 1})$$

where  $k_{obs}$  is the rate constant for the first order rate equation,  $T$  is temperature in K, and  $R$  is the gas constant.

Using the kinetic model based on these Arrhenius parameters at 300°C, it will require about one day to remove 90% of a uranyl fluoride deposit. At 240°C, the same conversion will require 30 days. At 125°C, 90% will be removed in about one year.  $\text{NF}_3$  can effectively remove uranyl fluoride deposits; however, temperatures above 240°C are recommended for application of  $\text{NF}_3$  to assure removal of the deposit within two to three months.

### Uranium Deposit Removal Studies: Laboratory-Prototype Studies

To investigate scale-up, gas recycle, thermal pretreatment of the  $\text{NF}_3$ , and longer exposure times, we used the laboratory-scale Portsmouth prototype. In our decontamination studies using the laboratory prototype, we treated our surrogate primary deposit material, uranyl fluoride, with  $\text{NF}_3$  at various temperatures and pressures and at various pretreatment temperatures.

Table II provides the operational conditions and experimental mass change results of our prototype experiments. We treated nominal 0.5-gram samples of  $\text{UO}_2\text{F}_2$  samples at 150 to 460°C furnace

temperature (FT) with 300 to 500 torr  $\text{NF}_3$  passed through an antechamber heated to 125 to 300°C inlet temperature (IT). The experiments ranged from 2.5 to 13 days. The mass change has been adjusted to remove any contribution from waters of hydration.

The gas-recirculating strategy was the expected mode of operation for the  $\text{NF}_3$  decontamination at Portsmouth. This recirculating strategy would provide efficient use of the treatment gases and therefore was BSW's primary focus. The first five prototype experiments tested the recirculating strategy. In the first three experiments, we used as-prepared  $\text{UO}_2\text{F}_2$  with its nominal 10% water content. In the other experiments, we dried the  $\text{UO}_2\text{F}_2$  by initially pretreating it at greater than 200°C in flowing argon in the prototype and exhausting the water-bearing gases from the prototype. We reweighed the dehydrated samples before exposing them to  $\text{NF}_3$ .

Table II. Experimental Conditions and Results for Laboratory Prototype Testing of  $\text{NF}_3$  Deposit Removal

Run Number	Duration, days	Operational mode	T, °C IT/FT	Initial $\text{NF}_3$ Pressure, torr	Initial Sample wt, g	Final Sample wt, g	% mass change
1	4	Recirculating	125/300	300	0.4774	0.4411	-7.6
2	3	Recirculating	125/300	500	0.5179	0.4838	-6.6
3	2	Recirculating	400/250	500	0.4910	0.4861	-1
4	13	Recirculating	460/250	450	0.5974	0.5812	-3
5	5	Recirculating	350/300	500	0.5362	0.5288	-1.4
6	2.5	once through	460/150	500	0.5258	0.4789	-8.9

In the first two recirculating gas experiments, the mass loss is slightly less than what our isothermal 270°C and 320°C TGA/DTA studies suggest, but significantly less than our kinetic model predicts. A possible explanation for this behavior is that the waters of hydration were trapped inefficiently by our water trapping system, remaining free to react immediately with the  $\text{NF}_3$ -generated  $\text{UF}_6$  to reproduce  $\text{UO}_2\text{F}_2$ , thus preventing uranium from escaping from the deposit. Any water in the system also would prevent efficient conversion of the  $\text{UO}_2\text{F}_2$  to  $\text{UF}_6$ .

Assuming that the active species in an RF plasma is the fluorine radical, as reported by Veilleux et al. [12], thermal activation was attempted in the next three experiments. We expected that thermal pretreatment of  $\text{NF}_3$  at temperatures found very effective by TGA/DTA would significantly improve the conversion to  $\text{UF}_6$ . However, such was not the case when applied to recirculating gas. In contrast, the single once-through experiment with thermally pretreated  $\text{NF}_3$  indicated thermal pretreatment can enhance the efficiency of the process (i.e., reduce reaction temperature) possibly by removing parasitic species from the system.

#### **Application of RF Activation of $\text{NF}_3$**

The BSW team also conducted an engineering evaluation to determine the feasibility of RF-activation as a pretreatment. We evaluated whether commercially available RF-activation units used in the silicon chip etching industry could be applied on the scale required for Portsmouth.

The evaluation indicated that RF-activation pretreatment using commercially available equipment was not feasible because of size and operating pressure constraints.

#### **Application of Chemical Activation**

Another enhanced approach that we considered was using a low  $\text{ClF}_3$  concentration in combination with  $\text{NF}_3$  to chemically heat the deposit to temperatures where the  $\text{NF}_3$  fluorination reaction will occur at substantial rates sufficient to continue and remove deposits in an acceptable time period. As mentioned earlier,  $\text{NF}_3$  is a much less toxic gas with products that are more environmentally friendly than  $\text{ClF}_3/\text{F}_2$ .

To evaluate the potential of supplemental chemical activation, BSW conducted a second engineering evaluation to determine if  $\text{ClF}_3$ , used at a suspected lower concentration than now used in the plant could be used to chemically heat a uranyl fluoride deposit to a temperature where  $\text{NF}_3$ 's reaction rate would be more useful. We considered 5%  $\text{ClF}_3$  and found that when reasonable parameter values are used, the time to heat up the deposit was short enough to expect additional heat-producing reactions with  $\text{NF}_3$ , a much safer reactant, to complete the treatment of the uranyl fluoride deposit.

The actual effectiveness of the treatment will depend on the nature of the deposit and its location. In areas where the deposits are small or are in recesses, the recovery might take longer because there will be insufficient heating to initiate the  $\text{NF}_3$  reaction. In such cases, deposit removal efficiency will depend solely on the reaction with  $\text{ClF}_3$ . The question then becomes: How long of a treatment time will be required to remove a large fraction of the uranium and technetium currently present as deposits in the cascade? Whether nearly complete recovery of the deposits can be realized in practice requires more extensive engineering evaluations combined with further experimental studies with the two gases. This analysis of  $\text{ClF}_3$  showed that heating of the deposit using 5%  $\text{ClF}_3$  is a potentially promising strategy meriting further evaluation.

### **Uranium Deposit Removal Studies: Summary**

Our uranium deposit removal studies indicate that thermal  $\text{NF}_3$  is an effective thermal agent for converting uranium fluorides or oxyfluorides to volatile  $\text{UF}_6$ . As such, it offers promise as an effective method to remove uranium deposits thus providing a decontamination method for uranium enrichment cascades. Achieving decontamination at lower temperatures compatible with cascade operations and equipment would require thermal pretreatment or combined treatment with a more kinetically reactive gas such as  $\text{ClF}_3$ .

### **Technetium Deposit Removal Studies**

Using TGA/DTA, we investigated the use of  $\text{NF}_3$  to remove surrogate technetium deposits of the Portsmouth Gaseous Diffusion Plant cascade equipment. For this study, we used, as our surrogate deposit, a synthetic, yellow-brown technetium material produced by air hydrolysis of the  $\text{NF}_3$  fluorination product of  $\text{TcO}_2$ . Supplementing this study was the treatment of ammonium pertechnetate, sodium pertechnetate, and  $\text{TcO}_2$  with  $\text{NF}_3$ ;  $\text{TcO}_2$  could be in the cascade and the pertechnetate salts could be representative of pertechnetic acid which is suspected to be in the cascade.

The reaction of our synthetic technetium deposit material with  $\text{NF}_3$  is shown in Fig. 4. The endothermic loss of what is likely physically and chemically sorbed water was followed by the endothermic conversion to  $\text{TcO}_2$  through reaction with  $\text{NF}_3$ . This reaction was followed with the exothermic loss of a volatile technetium-containing species. The weight loss was complete below 300°C with a nominal 60% loss.

Treatment of pertechnetate salts and  $\text{TcO}_2$  with  $\text{NF}_3$  in a TGA/DTA found complete volatilization of technetium based on mass loss. The reaction of  $\text{NF}_3$  with  $\text{TcO}_2$  was a single-step reaction, while the reaction with ammonium pertechnetate was two steps, with the second step appearing similar to that of  $\text{TcO}_2$ . This suggests that ammonium pertechnetate is converted to  $\text{TcO}_2$  as it is converted to a volatile fluorinated technetium species. Given the complexity of technetium chemistry and the variety of compounds that could exist in the enrichment cascade, these results indicate that  $\text{NF}_3$  has the potential to volatilize many of the Portsmouth technetium deposits.

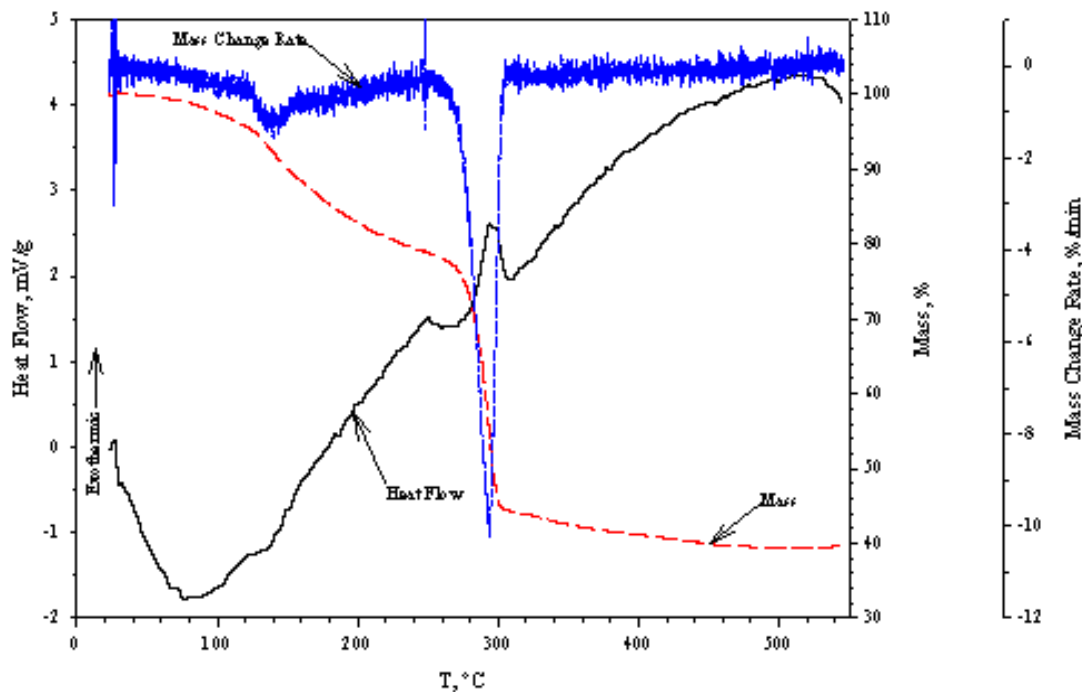


Fig. 4. Thermal reaction between 25%  $\text{NF}_3$  and model technetium deposit material. Material was prepared by  $\text{NF}_3$  fluorination of  $\text{TcO}_2$  and measured by TGA/DTA at  $5^\circ\text{C}/\text{minute}$

The reaction of  $\text{NF}_3$  with material prepared by the air hydrolysis of the  $\text{NF}_3/\text{TcO}_2$  reaction product formed volatile materials when heated to  $300^\circ\text{C}$  in 25%  $\text{NF}_3$ . A TGA/DTA study showed characteristics similar to those observed in the reaction of ammonium pertechnetate with  $\text{NF}_3$ . The limited studies performed to date indicate that the chemistry of  $\text{NF}_3$  with technetium oxides is complex and the reaction products appear sensitive to water and/or oxygen. A detailed understanding of the  $\text{NF}_3$ -technetium system is still lacking, and the apparent complexity of the chemistry indicates that significant additional study is required to understand these process details.  $\text{NF}_3$  fluorination or decontamination of the mixture of technetium oxides and oxyfluorides appears viable, but only after a thorough drying. This should be true for  $\text{ClF}_3$  treatments as well.

### Compatibility of $\text{NF}_3$ with Cascade Equipment and Materials

For the  $\text{NF}_3$  decontamination approach to be successfully implemented at Portsmouth, the construction materials used in the cascade must be resistant to attack by  $\text{NF}_3$ , at least for the time required to decontaminate the cascade equipment. Of course, the cascade has been exposed to the three powerful fluorinating agents— $\text{UF}_6$ ,  $\text{F}_2$ , and  $\text{ClF}_3$ —for years and it is likely that the less-powerful  $\text{NF}_3$  will not attack the cascade's passivated (fluoride-protected) and conditioned components.

The enrichment cascade equipment are constructed of nickel, nickel-coated steel, high-nickel alloys, copper, and aluminum [17]. The materials of construction in the Portsmouth enrichment cascade were selected based on their good resistance to attack by the fluorinating agents  $\text{UF}_6$ ,  $\text{F}_2$ , and  $\text{ClF}_3$ . The corrosion rate for pure nickel and certain high-nickel alloys was reduced by a protective coating of nickel fluoride. Initial preparation of the stage converters for cascade use included a stabilization treatment with fluorine. The stabilization process removed foreign material (e.g., water) that might later react to consume  $\text{UF}_6$  and coated metal surfaces with a protective fluoride film that reduces the rate of further reaction [17].

In addition to the materials of construction, one must be somewhat concerned about the potential interaction between  $\text{NF}_3$  and the turbine oil used in the pumps. Because  $\text{NF}_3$  is an oxidizer, it could react with such organics [1, 13, 14]. However, this concern should be minimal because this oil typically would only interact with  $\text{NF}_3$  under specific conditions; i.e., an oil leak occurring during decontamination operations. Our own attempts to study  $\text{NF}_3$  turbine oil compatibility using TGA/DTA yielded no results because the characteristic Portsmouth turbine oil evaporates below  $40^\circ\text{C}$ .

A monograph on  $\text{NF}_3$  by Anderson et al. [14] provides an extensive set of information on the reactions of  $\text{NF}_3$  with elements including metals, inorganic materials, and organics. Anderson et al. [16] provides additional information about the compatibility of  $\text{NF}_3$  with Portsmouth materials of construction.

To investigate the effects of  $\text{NF}_3$  on the various materials of construction, i.e., aluminum, copper, iron (surrogate for steel where the nickel has eroded away), and nickel, we again used TGA/DTA and performed a single qualitative experiment in our prototype where we exposed unpassivated and protected materials to  $\text{NF}_3$  at  $360$  to  $390^\circ\text{C}$ .

The qualitative experiment in the prototype found that each of the metals reacted slightly with  $\text{NF}_3$ , forming a surface layer of what we suspect is the respective fluoride with the exception of the iron filings. The iron filings powdered and were moved downstream.

Our DTA/TGA study of aluminum's behavior when exposed to  $\text{NF}_3$  found that  $\text{NF}_3$  began to react with aluminum near  $150^\circ\text{C}$ . This initial reaction reached a maximum rate of  $0.01\%/min$  at  $240^\circ\text{C}$ . A second reaction began near  $320^\circ\text{C}$  and accelerated up to  $500^\circ\text{C}$ , where the rate stabilized for the aluminum granules at  $0.05\%/min$  up to  $550^\circ\text{C}$ . Whether this reaction peaks shortly after is unknown because the experiment was stopped at  $550^\circ\text{C}$ . The mass change rate indicates that the reaction rate is not fast.

In our tests, we found that copper powder is relatively stable when exposed to  $\text{NF}_3$  while being heated at  $5^\circ\text{C}/min$ . The mass change indicated a small  $0.2\%$  mass loss after heating to  $550^\circ\text{C}$  in two steps: an initial gain of  $0.15\%$  as the analysis began, followed by a mass loss of  $0.2\%$  at completion, with the mass beginning to rise again. The mass change rate ranged from  $-0.01\%/min$  to  $+0.005\%/min$ . It was difficult to determine from the heat flow rate that any reactions were occurring. Overall, our TGA/DTA studies indicated that copper powder is relatively stable when exposed to  $\text{NF}_3$  up to  $550^\circ\text{C}$ .

As discussed in Lockheed [17], steels are not resistant to  $\text{UF}_6$ ,  $\text{ClF}_3$ , and  $\text{F}_2$  and are not used in the cascade. Our TGA/DTA testing of the interaction between  $\text{NF}_3$  and iron showed iron's susceptibility to attack by  $\text{NF}_3$ , experiencing a significant exothermic attack beginning near  $200^\circ\text{C}$ . The nominal  $30\%$  mass gain plateau observed to  $490^\circ\text{C}$  is near that corresponding to the formation of  $\text{FeF}$ . At  $500^\circ\text{C}$ , another exothermic reaction began, adding another  $18\%$  mass by the time the experiment was completed. It is likely that this second reaction would produce  $\text{FeF}_2$ .

As with the other compatibility studies, we investigated the compatibility of nickel with  $\text{NF}_3$  using TGA/DTA. The results of our  $5^\circ\text{C}/min$  TGA/DTA testing of nickel powder show significant resistance to an  $\text{NF}_3$  attack up to  $300^\circ\text{C}$ . After  $300^\circ\text{C}$ , the nickel began to react, gaining  $6\%$  mass by  $550^\circ\text{C}$ ; the reaction appeared to continue beyond  $550^\circ\text{C}$ . If the nickel completely reacted to  $\text{NiF}_2$ , the expected mass gain would be  $32\%$ . The small mass gain for this high-surface-area material indicates significant resistance of nickel to  $\text{NF}_3$ . Its resistance appears to be less than that of aluminum and copper, based on our TGA/DTA studies.

Summarizing our chemical compatibility studies, our TGA/DTA testing of aluminum granules, copper powder, iron powder, and nickel powder found that aluminum and copper are highly resistant to attack by  $\text{NF}_3$ ; nickel is resistant to  $300^\circ\text{C}$ , whereupon it is slightly attacked by  $\text{NF}_3$ , while iron is significantly attacked by  $\text{NF}_3$ . The observed behavior is consistent with the selection criteria used by Portsmouth [17] for its materials of construction. In general,  $\text{NF}_3$  appears to be compatible with the materials of construction with the exception of iron, which is generally protected by nickel (except in unexpected circumstances).

## CONCLUSION

The BSW team's Phase II laboratory and prototype-scale work with  $\text{NF}_3$  established that  $\text{NF}_3$  can effectively remove both  $\text{UO}_2\text{F}_2$ , a known component of uranium deposits in Portsmouth equipment, and  $\text{UF}_4$ , a suspected component of such deposits.

Thermoanalytical and prototype-scale work showed that  $\text{NF}_3$  can be kinetically competitive with  $\text{ClF}_3$  at temperatures greater than  $300^\circ\text{C}$ ; with thermal pretreatment and single-pass treatment or using an improved water removal approach, the temperature required for  $\text{NF}_3$  treatment would be reduced. Volatilization of suspect technetium deposit materials was effective at lower temperatures than those required for uranium compounds; with  $\text{NF}_3$  treatment removing 60% of the hydrolyzed fluorinated technetium species. Given these data, the BSW team believes that technetium deposit removal should be achieved in a reasonably acceptable timeframe at feasible temperatures. The work also shows that the Portsmouth materials of construction exposed to the fluorinated process gases are compatible with  $\text{NF}_3$ .

During Phase II, treatment gas mixtures could not be *truly* explored and optimized because the experiments were conducted on surrogate samples characteristic of Portsmouth plant deposit materials, and not on samples of actual Portsmouth deposits. The BSW team believes that the  $\text{NF}_3$  process could be optimized using  $\text{ClF}_3$  in low quantities as either a catalyst or thermal initiator. This would capture the best of both treatment processes, resulting in a process with an acceptable removal rate and safer operating conditions while minimizing cost considerations and environmental issues. The bounding concentrations of  $\text{ClF}_3$  are expected to be on the order of a few percent, combined with 20 to 30%  $\text{NF}_3$ , with the remainder  $\text{N}_2$  serving as an inert carrier gas.

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