Application of Nitrogen Trifluoride as the Fluorinating Agent in Fluoride Volatility-Based Recycle – Early Studies

Randy Scheele, Bruce McNamara, Andy Casella, Anne Kozelisky, and Doinita Neiner

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Exploiting the volatility of U and Pu fluorides has long been recognized as an attractive small-footprint, pyrochemical approach for recovering valuable nuclear materials. *Fluoride Volatility Recycle* has recently been receiving renewed attention. Table 1 provides the list of spent nuclear fuel constituents that have volatile fluorides.

Table 1. Spent Fuel Constituents with Volatile Fluorides

Highly Volatile			Moderately Volatile		
Substance	T_{melt} °C	T_{boil} °C	Fluoride	T_{melt} °C	T_{boil} or Tsubl, °C
Kr	-157.2	-153.4	IF_7	5	4
CF_4	-184	-129	MoF_6	17.6	33.9
Xe	-111.8	-108.1	RuF_6	32.1	45.9
TeF_6		-38.6	NpF_6	54.8	55.2
SeF_6		-34.5	TcF_6	37.9	55.2
			UF_6	64	56.5
			PuF_6	51.9	62.2
			IF_5	9.4	98
			SbF_5	6	142.7
			NbF_5	80	235
			RuF_5	101	70
			RhF_5		95.5
			RhF_6	70	73.5

The process would consist of oxidative fluorination of the spent fuel to produce volatile U, Pu, Np, and fission-product fluorides and non-volatile fluorides. The volatilized fluorides would be separated using a distillation column or selective sorption column(s).

Fundamental to *Fluoride Volatility Recycle* is the fluorination-oxidation reagent. Typical reagents such as F_2 and ClF_3 are highly toxic and reactive as provided in Table 2.

Table 2. NFPA Hazard Ratings

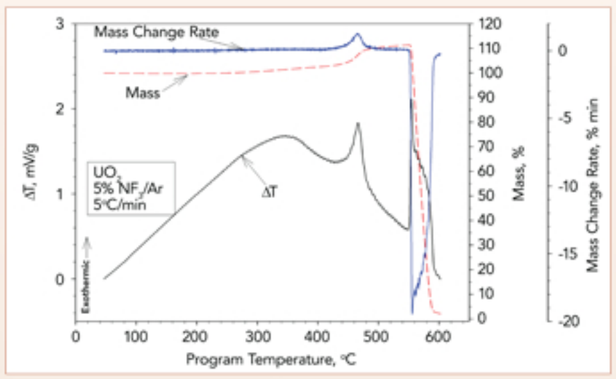
Reagent	Health	Fire	Reactivity	Special
F_2	4	0	4	Water reactive
ClF_3	4	0	4	Water reactive, oxidizer
NF_3	1	0	0	Oxidizer

NFPA hazard scale runs from 0 to 4 with 4 being the most hazardous

In our search for a fluorinating reagent to replace ClF_3 for removing U and Tc deposits in the Portsmouth Gaseous Diffusion Plant, we investigated the fluorinating-oxidizing reagent NF_3. NF_3 was attractive because of its low toxicity and negligible reactivity hazard at ambient conditions (Table 2).

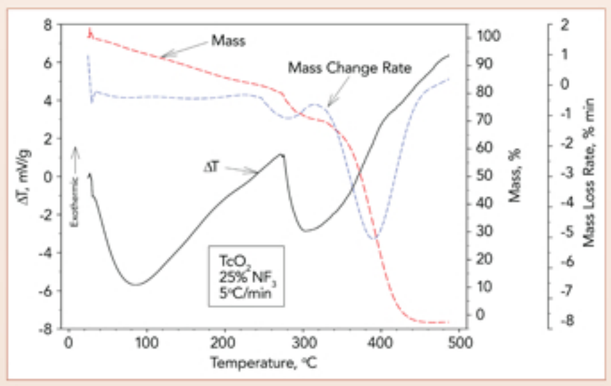
Using the simultaneous thermogravimetric and differential thermal analysis (TG/DTA) presented in Figure 1, we found that NF_3 could at elevated temperatures convert potential U and Tc deposit materials to volatile fluorides. This is illustrated by the TG/DTA of the fluorination-oxidation of UO_2 to $UF_{6(g)}$ in Figure 2 and TcO_2 to $TcF_{6(g)}$(?) in Figure 3.

Figure 1. Simultaneous TG/DTA/FTIR



NF_3 oxidizes and fluorinates UO_2 to UF_6 near 550°C

Figure 2. Conversion of UO_2 to UF_6 by NF_3



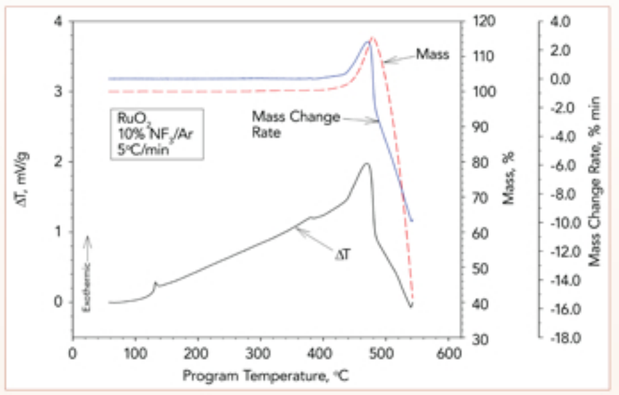
NF_3 fluorinates and oxidizes TcO_2 to volatile TcF_6 near 350°C

Figure 3. NF_3 Volatilization of TcO_2

Attractive qualities of NF_3 as the fluorinating-oxidizing reagent in *Fluoride Volatility Recycle* include

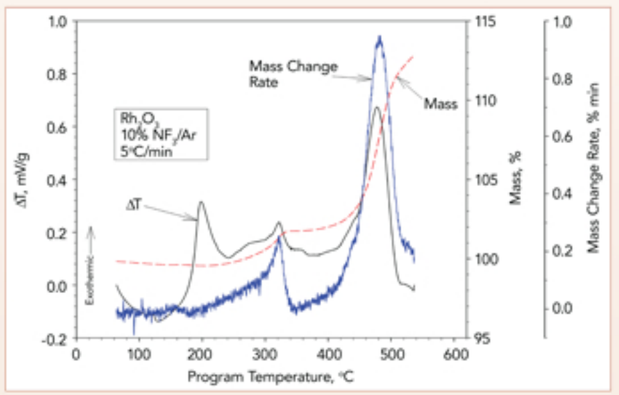
- NF_3 improves worker safety relative to other fluorinating reagents;
- NF_3 has a significant established manufacturing base (>4000 ton a^{-1});
- NF_3 is used by the silicon chip and laser manufacturing industries;
- NF_3 has a variable thermal reaction sensitivity which might be leveraged for separating different fuel constituents.

On this basis, we began investigating NF_3's reactions with spent nuclear fuel constituents using TG/DTA with the support of PNNL's Sustained Nuclear Power Initiative.



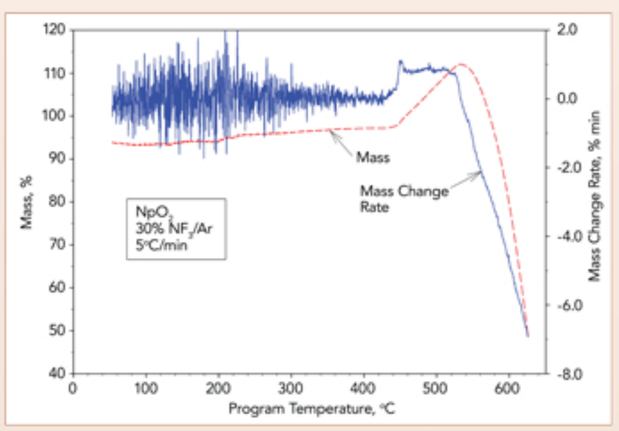
NF_3 fluorinates and oxidizes RuO_2 to volatile RuF_5 or RuF_6 at ≤ 500°C

Figure 4. Fluorination-Oxidation of RuO_2 by NF_3



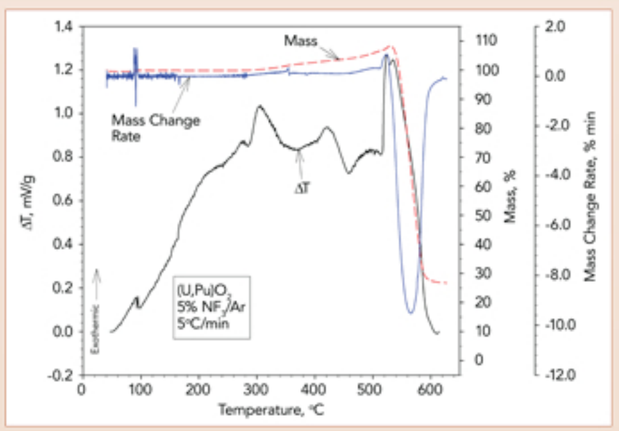
NF_3 does not convert Rh_2O_3 to the volatile RhF_5 or RhF_6 at temperatures up to 550°C

Figure 5. Fluorination of Rh_2O_3 by NF_3



NF_3 can oxidize and fluorinate NpO_2 to volatile NpF_6 when heated to 580°C

Figure 6. Fluorination-Oxidation of NpO_2 by NF_3



NF_3 will oxidize and fluorinate a 25% Pu/U mixed oxide and effectively separate the U from the mixed oxide.

Figure 7. Separation of U from $(U,Pu)O_2$ by NF_3

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For more information about the science you see here, please contact:

Randy Scheele
Pacific Northwest
National Laboratory
P.O. Box 999, MSIN P7-25
Richland, WA 99352
(509) 376-0956
randy.scheele@pnl.gov

Conclusions

NF_3 is potentially an attractive fluorinating-oxidizing reagent for use in *Fluoride Volatility Recycle*.

- NF_3 is less hazardous than other candidate reagents.
- Differences in the thermal sensitivities of reactions of fission product and actinide oxides with NF_3 may be exploited for separations.
  - U, Ru, Mo, Tc, and Np react and volatilize at different temperatures.
  - Rh does not volatilize when heated to 550°C.
  - Pu volatilization is slow at 600°C.
- NF_3 can separate U from Pu in mixed (75% U, 25% Pu)O_2.

Acknowledgements

- PNNL's Sustained Nuclear Power Initiative
- Gert Patello, Manager Radiochemical Processing and Engineering Group
- U.S. Department of Energy

PNNL-SA-72697