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MOIST AIR REACTION WITH EXCESS UF₆

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MOIST AIR REACTION WITH EXCESS UF_6

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ABSTRACT

The moist air reaction with uranium hexafluoride (UF_6) has been studied at conditions simulating UF_6 hydrolysis during air inleakage in the cascade. In excess UF_6 , the reaction mechanism is more complicated than predicted by the simple gas-phase reaction of one UF_6 molecule with two water molecules to form uranyl fluoride and hydrogen fluoride. The initial UF_6 consumption is significantly greater than predicted, suggesting that a metastable uranium compound is formed during the hydrolysis reaction. This intermediate uranium compound may facilitate uranyl fluoride transport in the cascade.

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SUMMARY

The moist air reaction with uranium fluoride (UF_6) has been studied at conditions simulating UF_6 hydrolysis during cascade air inleakage. In excess UF_6 , the reaction mechanism is more complicated than predicted by the simple gas-phase hydrolysis of UF_6 and water (H_2O) to form uranyl fluoride (UO_2F_2) and hydrogen fluoride (HF):

The initial UF_6 consumption by H_2O is significantly greater than predicted by Reaction (1), suggesting that a metastable uranium product is formed during the hydrolysis reaction. Immediately after hydrolysis, this metastable species can associate with much more UF_6 than predicted by Reaction (1). The metastable intermediate(s) is probably more volatile than UO_2F_2 and may facilitate UO_2F_2 transport in the cascade. Eventually, the metastable species dissociates into UO_2F_2 , releasing the excess UF_6 .

INTRODUCTION

Air inleakage is an important concern in gaseous diffusion plant operation. The UO_2F_2 generated from UF_6 hydrolysis can adversely affect barrier performance.¹ Several cascade operations are performed in order to minimize and counteract UF_6 hydrolysis. Leak certification of cascade components and special compressor seals are used to minimize cascade air inleakage.² Cell treatments are used to remove UO_2F_2 produced by UF_6 hydrolysis.³

Although UF_6 hydrolysis is often observed, the hydrolysis mechanism is not well understood. Previous studies suggest that Reaction (1) may not describe the hydrolysis mechanism at cascade conditions.⁴ At cascade temperatures and pressures, a surface reaction may be responsible for UO_2F_2 formation, rather than the gas-phase reaction described by Reaction (1).⁴ The type of reaction mechanism can determine the extent of UO_2F_2 transport during hydrolysis. If hydrolysis involves a surface reaction, the hydrolysis rate will depend on system geometry, potentially allowing UO_2F_2 to be transported far from the leak site. On the other hand, at cascade conditions, a gas-phase hydrolysis reaction would probably be rapid, producing UO_2F_2 near the leak site.

Cascade observations of moist air inleakage do not conclusively establish the extent of UO_2F_2 transport. The mobility of UO_2F_2 seems to vary with the hydrolysis conditions. In massive inleakage, sizable UO_2F_2 deposits are found near the leak site. However, barrier permeability measurements suggest that some UO_2F_2 may be transported far from the leak source.

This report describes a laboratory study of the UF_6 hydrolysis reaction. The experimental procedure used to measure hydrolysis kinetics and stoichiometry is described

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in the next section. The results of these measurements and their implication to the hydrolysis mechanism and UO_2F_2 transport are then presented and discussed. The work is summarized in the final section of this report.

EXPERIMENTAL PROCEDURE

The laboratory reactor system previously used to simulate cell treatments was modified to measure UF_6 hydrolysis kinetics.⁵ The UF_6 hydrolysis reaction was performed in the infrared spectrometer cell used in that study. The cell was equipped with barium fluoride windows to minimize UF_6 reaction with cell surfaces. For these studies, the furnace and reactor were removed from the system. A gas bubbler filled with distilled water served as a moist air supply. The air humidity was controlled by varying the temperature of the bubbler. The resulting system is shown schematically in Fig. 1. The other components, including the pressure transducers, Fourier transform infrared spectrometer (FTIR) and gas handling equipment, were those used in the previous studies.⁵

After the reactor system was stabilized with chlorine trifluoride (ClF_3) and evacuated, a known pressure of UF_6 was added to the system and circulated through the heated spectrometer cell. The UF_6 concentration was monitored by the FTIR and by pressure transducer (P_2). When these measurements indicated that the UF_6 concentration had stabilized, the spectrometer cell was isolated from the rest of the system by closing the appropriate valves shown in Fig. 1. The hydrolysis was initiated by adding a known amount of moist air to the cell. The reaction kinetics and stoichiometry were then evaluated by monitoring the concentrations of UF_6 , HF and H_2O using the FTIR. At the completion of the experiment, solid deposits on the cell windows were identified after the system was evacuated. The system was then cleaned and stabilized with ClF_3 prior to conducting additional hydrolysis experiments.

Calibration, control and blank experiments were performed to further characterize the hydrolysis results. Calibration experiments were performed to correlate partial pressures of UF_6 , HF and H_2O in diluent gases with absorption peaks. The control experiments were used to determine the effects of mixing and reactant diffusion in the spectrometer cell. Blank experiments were used to determine reactant and product stability in the spectrometer cell. Some hydrolysis experiments with ClF_3 and fluorine (F_2) were also performed to identify solid byproducts on the cell windows.

RESULTS

Typical infrared absorption spectra obtained during a UF_6 hydrolysis are shown in Fig. 2. The dashed line shows the spectrum before hydrolysis, while the solid line shows the infrared adsorption 5 min after hydrolysis. Major absorption features are indicated in the figure. As expected, UF_6 was consumed in the hydrolysis as HF and UO_2F_2 were generated. The carbon dioxide (CO_2) peak is from the moist air. The UO_2F_2 deposit remained on the cell windows after evacuation of the spectrometer cell but disappeared after ClF_3 treatment.

Figure 1

SCHEMATIC REPRESENTATION OF HEATED SPECTROMETER CELL USED FOR HYDROLYSIS STUDIES.
Pressure transducers are indicated by P₁ and P₂, the flowmeter is indicated by FM and thermocouples are indicated by TC₁, TC₂ and TC₃.

Figure 2

INFRARED SPECTRA BEFORE AND AFTER UF_6 HYDROLYSIS AT 65°C .

The dashed line is the infrared spectrum prior to hydrolysis while the solid line is the spectrum 5 minutes after hydrolysis. These results are from hydrolysis experiment, H17. Major peak assignments are indicated.

Hydrolysis kinetics were determined from the infrared absorption measurements taken at various times during the hydrolysis. Figure 3 shows the UF_6 pressure, $[\text{UF}_6]$, as a function of hydrolysis time, t , for two different hydrolysis experiments. Moist air was added to the cell at $t = 0$ when $[\text{UF}_6] = [\text{UF}_6]_0$. The absorption results are shown as relative pressure, $[\text{UF}_6]/[\text{UF}_6]_0$. The symbols are actual experimental measurements, while the solid and dashed lines were empirically drawn through the experimental data. Similar analyses were used to determine HF and H_2O pressures, $[\text{HF}]$ and $[\text{H}_2\text{O}]$, at various t after moist air addition.

Absorption measurements indicated the initial hydrolysis reaction occurred more rapidly than the cell contents could be analyzed. Water consumption was complete and almost instantaneous (<0.1 min) after moist air addition. Initial UF_6 consumption and HF production were also essentially instantaneous. However, the $[\text{UF}_6]$ continued to change after H_2O consumption was complete, indicating that secondary reactions were occurring.

Hydrolysis reaction stoichiometry was analyzed from $[\text{UF}_6]$, $[\text{H}_2\text{O}]$ and $[\text{HF}]$. Results from UF_6 hydrolysis experiments at 65°C are summarized in Table 1. The initial pressure of UF_6 added to the cell, $[\text{UF}_6]_i$, is listed in column 1, while the initial concentration of water introduced with the moist air, $[\text{H}_2\text{O}]_i$, is listed in column 2. These values were used to calculate the initial ratio of UF_6 to H_2O , $([\text{UF}_6]/[\text{H}_2\text{O}])_i$, in column 3. The UF_6 consumed at $t = 0$, $\Delta[\text{UF}_6]_0$, is listed in column 4. Since water consumption, $\Delta[\text{H}_2\text{O}]$, was complete and almost instantaneous, it was calculated from $[\text{H}_2\text{O}]_i$:

$$\Delta[\text{H}_2\text{O}] = [\text{H}_2\text{O}]_i. \quad (2)$$

Table 1. Summary of UF_6 hydrolysis stoichiometry at 65°C

$[\text{UF}_6]_i$ (torr)	$[\text{H}_2\text{O}]_i$ (torr)	$([\text{UF}_6]/[\text{H}_2\text{O}])_i$	$\Delta[\text{UF}_6]_0$ (torr)	$(\Delta[\text{UF}_6]/\Delta[\text{H}_2\text{O}])_0$	$\Delta[\text{HF}]_0$ (torr)	$(\Delta[\text{HF}]/\Delta[\text{H}_2\text{O}])_0$
0.00	11.1	0.00	0.00	0.00	2.5	0.23
0.95	10.7	0.09	0.95	0.09	2.2	0.21
2.14	10.3	0.21	1.92	0.19	4.0	0.39
4.97	9.8	0.51	2.66	0.27	4.9	0.50
10.10	10.2	0.99	3.02	0.30	5.8	0.57
25.3	10.4	2.44	6.3	0.61	6.3	0.61
52.8	10.1	4.89	13.3	1.32	7.0	0.69
90.7	11.4	7.96	22.9	2.01	7.9	0.69
97.0	9.5	10.21	15.5	1.52	7.0	0.74
100.9	3.0	33.63	14.1	4.70	4.8	1.60

The ratio of UF_6 to H_2O consumption, $\Delta[\text{UF}_6]/\Delta[\text{H}_2\text{O}]$, was determined at any t , from the time dependent $\Delta[\text{UF}_6]_t$ and from the time independent, $\Delta[\text{H}_2\text{O}]$. The consumption ratio at $t = 0$, $(\Delta[\text{UF}_6]/\Delta[\text{H}_2\text{O}])_0$, is listed in column 5 of Table 1. The ratio of UF_6 to H_2O consumption at other times was determined by substitution of the appropriate value for $\Delta[\text{UF}_6]_t$. The $[\text{HF}]$ formed at $t = 0$ $\Delta[\text{HF}]_0$, is listed in column 6

Figure 3

RELATIVE UF₆ PRESSURE, $[UF_6]/[UF_6]_0$, AS A FUNCTION OF HYDROLYSIS TIME, t .

UF₆ is exposed to moist air at $t = 0$. The circles are results from a hydrolysis at 31°C, while the squares are from a hydrolysis at 151°C. Open symbols are used for spectrometer measurements obtained prior to hydrolysis, while solid symbols indicate measurements after hydrolysis. The solid and dashed lines are empirical curves drawn through the appropriate experimental results.

of Table 1. The ratio of HF produced to H_2O consumed at $t = 0$, $(\Delta[\text{HF}]/\Delta[\text{H}_2\text{O}])_0$, is listed in column 7.

The hydrolysis results in Table 1 indicate a strong dependence of $(\Delta[\text{UF}_6]/\Delta[\text{H}_2\text{O}])_0$ with $([\text{UF}_6]/[\text{H}_2\text{O}])_i$. This is shown in Fig. 4 where the UF_6 to H_2O consumption ratio is plotted as a function of the initial ratio of UF_6 to H_2O . The open circles are the results from Table 1, while the solid line is an empirical representation of the experimental data obtained by polynomial regression.⁶ Consumption ratios obtained 5 and 10 min after the hydrolysis are shown by the dashed and dotted lines, respectively. Other measurements at $t > 1$ h produced the consumption behavior predicted as $t \rightarrow \infty$, which is indicated by the dotted/dashed line in the figure.

The results of UF_6 hydrolysis experiments performed at other temperatures are summarized in Table 2. For the hydrolysis temperature, T , shown in column 1, the $[\text{UF}_6]_i$ and $[\text{H}_2\text{O}]_i$ are shown in columns 2 and 3, respectively. The quantities, $([\text{UF}_6]/[\text{H}_2\text{O}])_i$, $(\Delta[\text{UF}_6]/\Delta[\text{H}_2\text{O}])_0$, $\Delta[\text{HF}]_0$ and $(\Delta[\text{HF}]/\Delta[\text{H}_2\text{O}])_0$ listed, respectively, in columns 4 through 7 were determined as in Table 1. The results in Table 2 show insignificant variations in reaction stoichiometry with hydrolysis temperature. Hydrolysis kinetics also appeared to be temperature independent.

Table 2. UF_6 hydrolysis at various temperatures, T

T (°C)	$[\text{UF}_6]_i$ (torr)	$[\text{H}_2\text{O}]_i$ (torr)	$([\text{UF}_6]/[\text{H}_2\text{O}])_i$	$(\Delta[\text{UF}_6]/\Delta[\text{H}_2\text{O}])_0$	$\Delta[\text{HF}]_0$ (torr)	$(\Delta[\text{HF}]/\Delta[\text{H}_2\text{O}])_0$
65	90.3	7.2	12.56	2.16	7.0	0.97
90	92.3	7.8	11.83	2.30	6.7	0.86
116	90.2	8.6	10.44	2.61	10.9	1.25

DISCUSSION

KINETICS

If Reaction (1) were an elementary reaction describing the gas-phase hydrolysis of UF_6 , the UO_2F_2 formation rate would be

$$d/dt [\text{UO}_2\text{F}_2] = k_1 [\text{UF}_6] [\text{H}_2\text{O}]^2, \quad (3)$$

where k_1 is the reaction rate constant.⁷ As written, Reaction (1) is a third order reaction, first order in $[\text{UF}_6]$ and second order in $[\text{H}_2\text{O}]$. When there is a large excess of UF_6 , the $[\text{UF}_6]$ doesn't change during hydrolysis and can be considered constant. Under these conditions, the reaction half-life, $t_{1/2}$, is given by

$$t_{1/2} = 1/(k_1 [\text{UF}_6]_0 [\text{H}_2\text{O}]_0). \quad (4)$$

Figure 4

UF_6 CONSUMPTION PER MOLE H_2O , $\Delta[\text{UF}_6]/\Delta[\text{H}_2\text{O}]$, AS A FUNCTION OF INITIAL UF_6 TO H_2O CONCENTRATION, $([\text{UF}_6]/[\text{H}_2\text{O}])_i$.

The open circles are the results from measurements at 65°C immediately following the hydrolysis ($t = 0$). The solid line is an empirical representation of the results obtained by regression. The dashed and dotted lines are empirical representations of results obtained at $t = 5$ and $t = 10$ min after hydrolysis, respectively. The dotted/dashed line is an estimate of the UF_6 consumption as $t \rightarrow \infty$.

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Equation (4) indicates that the reaction half-life is inversely proportional to $[UF_6]$ and $[H_2O]$ at $t = 0$.

Unfortunately, the kinetic measurements reported in the previous section indicate that the hydrolysis mechanism in excess UF_6 is more complicated than predicted by Reaction (1). Water consumption and HF production are essentially complete instantly (<0.1 min), but changes in $[UF_6]$ can continue for many minutes. If the UF_6 hydrolysis were described by the gas-phase mechanism in Reaction (1), then changes in $[UF_6]$ would coincide with changes in $[H_2O]$.

Since the experimental conditions (cell diameter and reactant pressures) were selected to minimize reactant and product diffusion times (<30 s), the time dependence in Fig. 4 is probably from secondary reactions of an intermediate hydrolysis product(s). The kinetic results suggest that UF_6 hydrolysis proceeds with a rapid reaction of H_2O forming HF and a metastable uranium oxyfluoride. This metastable uranium oxyfluoride slowly liberates UF_6 during its conversion to UO_2F_2 . Figure 4 indicates that the conversion of this metastable uranium oxyfluoride into UO_2F_2 is essentially complete in an hour and has a half-life ~ 10 min when $[H_2O]_0 = 10$ torr and $[UF_6]_0 = 100$ torr.

The only other time-dependent process observed during these UF_6 hydrolysis studies was the slow decrease in $[HF]$. Control experiments indicated that these decreases were due to HF reaction with system surfaces. {These HF surface reactions also apparently cause the ratio $(\Delta[HF]/\Delta[H_2O])_0$ in Table 1 to be <2 as predicted by Reaction (1)—See the following subsection.} Although the apparatus had been stabilized, reactions with nickel surfaces limited the half-life of HF to ~ 6 h. Hydrolysis experiments using HF and dry air mixtures indicated that UF_6 hydrolysis kinetics were not changed by HF reaction with system surfaces.

The formation of a metastable reaction product during UF_6 hydrolysis complicates mathematical analysis of the reaction kinetics. The rate law and half-life expressions given in Eqs. (3) and (4), respectively, are not valid if a metastable intermediate is formed. Although expressions for rate and half-life can be derived, their form depends on the proposed reaction mechanism. For that reason, further analysis of hydrolysis kinetics is postponed until potential reaction mechanisms are discussed later in this report.

STOICHIOMETRY

Reaction stoichiometry provides additional evidence that a metastable uranium oxyfluoride compound may be produced during hydrolysis in excess UF_6 . If Reaction (1) described the UF_6 hydrolysis mechanism, each mole of water would consume 0.5 mole of UF_6 [i.e., $(\Delta[UF_6]/\Delta[H_2O])_0 = 0.5$], while generating 2 moles of HF [i.e., $(\Delta[HF]/\Delta[H_2O])_0 = 2.0$]. The results in Table 1 indicate that neither UF_6 consumption nor HF production agree with values predicted by Reaction (1). As $([UF_6]/[H_2O])_i$ increases, although $(\Delta[HF]/\Delta[H_2O])_0 \rightarrow 2.0$, as expected, $(\Delta[UF_6]/\Delta[H_2O])_0$ appears to increase without limit. One value of $(\Delta[UF_6]/\Delta[H_2O])_0$ in Fig. 4 is an order of magnitude greater than predicted by Reaction (1).

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The excess UF_6 consumption suggests that hydrolysis initially produces an intermediate, metastable uranium compound which can temporarily complex with UF_6 . Since the HF production is rapid and approaches predicted values as the UF_6 is increased [i.e., $(\Delta[\text{HF}]/\Delta[\text{H}_2\text{O}])_0 \rightarrow 2.0$], this metastable compound probably does not contain HF. This metastable intermediate may be a uranium oxyfluoride compound with chemical composition, $\text{UO}_2\text{F}_2 (\text{UF}_6)_n$. The results in Fig. 4 suggest that n may be ≥ 3 . Attempts to identify metastable uranium oxyfluoride intermediates by infrared analysis of window deposits were unsuccessful. Although several unknown solid species were deposited on the spectrometer cell windows during UF_6 hydrolysis, the adsorption bands were too weak to quantify.

One more interesting feature of Fig. 4 is the substoichiometric consumption of UF_6 when excess UF_6 is added, i.e., $\Delta[\text{UF}_6]/\Delta[\text{H}_2\text{O}] < 0.5$ when $([\text{UF}_6]/[\text{H}_2\text{O}])_i \ll 0.5$. Experimental measurements indicated that when insufficient UF_6 was present in a hydrolysis experiment, the excess H_2O reacted with system surfaces. This was a result of the ClF_3 stabilizations used to coat system surfaces with nickel fluoride. When no UF_6 is present, excess H_2O can convert nickel fluoride into nickel hydroxide or nickel oxide. The H_2O reaction with nickel fluoride is very slow and therefore, unimportant when excess UF_6 is present.

TEMPERATURE DEPENDENCE

The results in Table 2 indicate that reaction stoichiometry and kinetics were similar at all hydrolysis temperatures examined between 65 and 120°C. This result is in apparent disagreement with earlier UF_6 hydrolysis experiments at British Nuclear Laboratories (BNL).⁸ In the BNL studies, hydrolysis kinetics were determined by chemical analysis of uranium deposits collected on a series of heated, packed beds. Analysis of these deposits indicated that reaction kinetics were significantly different at 120°C than at lower temperatures. These results led the BNL researchers to conclude that, at higher temperature, either the reaction mechanism was different or the hydrolysis products were slightly volatile.

The major difference between the BNL experiments and the present study is the method of evaluating hydrolysis. The BNL experiments evaluated hydrolysis by determining the quantity of uranium deposits in a flowing gas system, while the current study measured UF_6 consumption in a closed system. As indicated by its authors, the BNL experiments are susceptible to reaction product volatility. Because UO_2F_2 is not volatile at 120°C, the BNL studies suggest that hydrolysis involves a metastable intermediate product having a higher vapor pressure than UO_2F_2 .⁸ This volatile intermediate product may be the metastable uranium oxyfluoride proposed earlier in this section.

REACTION MECHANISM

It is not surprising that Reaction (1) does not accurately describe UF_6 hydrolysis kinetics. It is improbable that the reaction would proceed by simultaneous gas-phase collision of two H_2O molecules and one UF_6 molecule. Reactions involving more than

two reactant molecules generally proceed by a series of elementary reaction steps.⁹ A series of elementary reactions is generally necessary because (1) simultaneous three-body collisions are extremely rare and (2) conservation of energy and momentum make the reaction probability of such collisions small.

Assuming that a series of elementary reactions is required to produce UO_2F_2 , a hydrolysis mechanism can be proposed which is consistent with the experimental results. Initially, a water molecule probably reacts with UF_6 to form HF and an intermediate uranium compound, UF_5OH :

In excess UF_6 , UF_5OH probably reacts forming another HF and the intermediate uranium oxyfluoride, $(\text{UF}_5)_2\text{O}$:

Because the energetics are favorable,¹⁰ Reactions (5) and (6) probably occur rapidly in the gas phase. This is consistent with the almost instantaneous appearance of HF after moisture inleakage.

Although $(\text{UF}_5)_2\text{O}$ may be produced rapidly during hydrolysis, its subsequent reaction in excess UF_6 is evidently slow, as indicated by the time delays seen in Fig. 4. If the reaction rate is sufficiently slow, $(\text{UF}_5)_2\text{O}$ may condense on system surfaces. Subsequent $(\text{UF}_5)_2\text{O}$ reactions may occur in the gas phase or on surfaces, depending on the $(\text{UF}_5)_2\text{O}$ vapor pressure at the hydrolysis temperature.

In order to produce UO_2F_2 in excess UF_6 , two $(\text{UF}_5)_2\text{O}$ molecules must either react directly:

or $(\text{UF}_5)_2\text{O}$ must convert to another species and react indirectly. One possible indirect reaction involves the formation of uranium oxide tetrafluoride, UOF_4 :

followed by

The existence of UOF_4 and its importance to UF_6 hydrolysis have been the subject of several previous studies.^{11,12}

Neither Reaction (7) nor Reaction (9) would be rapid in excess UF_6 , indicating that either $(\text{UF}_5)_2\text{O}$ or UOF_4 may be metastable at these hydrolysis conditions. In principle, it is possible to distinguish the direct hydrolysis mechanism depicted by Reactions (5), (6)

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and (7) from the indirect hydrolysis mechanism described by Reactions (5), (6), (8) and (9). Each mechanism obeys slightly different stoichiometry and kinetics. Analysis of the reaction stoichiometry indicates that $(\Delta[\text{UF}_6]/\Delta[\text{H}_2\text{O}])_0 = 0.5, 1.0$ and 2.0 when the initial hydrolysis products are UO_2F_2 , UOF_4 and $(\text{UF}_5)_2\text{O}$, respectively. Although the current data are insufficient to distinguish between the two reaction mechanisms, the results in Fig. 4 $[(\Delta[\text{UF}_6]/\Delta[\text{H}_2\text{O}])_0 > 1.0]$ suggest that neither Reaction (7) nor Reaction (8) is rapid, making $(\text{UF}_5)_2\text{O}$ a metastable hydrolysis product.

Mathematical expressions for the hydrolysis kinetics can be derived for these reaction mechanisms. The derivation is simplified because HF formation is much more rapid than UO_2F_2 formation. In this study, Reactions (5) and (6) were >80 times faster than either the direct formation of UO_2F_2 [via Reaction (7)] or the indirect formation of UO_2F_2 [Reactions (8) and (9)]. In excess UF_6 , this means that

$$[(\text{UF}_5)_2\text{O}]_0 \approx [\text{H}_2\text{O}]_0. \quad (10)$$

For the direct hydrolysis mechanism, the initial rate of UO_2F_2 formation is given by

$$d/dt([\text{UO}_2\text{F}_2])_0 = k_7 ([\text{H}_2\text{O}]_0)^2, \quad (11)$$

where k_7 is the rate constant for Reaction (7). The rate expression for the indirect mechanism is similar:

$$d/dt([\text{UO}_2\text{F}_2])_0 = k' ([\text{H}_2\text{O}]_0)^2, \quad (12)$$

but the rate constant, k' , is a complex expression of rate constants which depends on the relative rates of Reactions (8) and (9).

One important consequence of Eqs. (11) and (12) is that UO_2F_2 formation is independent of $[\text{UF}_6]$ and second order in $[\text{H}_2\text{O}]_0$ for both mechanisms. As a result, the half-life of metastable uranium oxyfluoride intermediate for both mechanisms is given by

$$t_{1/2} = 1/(K [\text{H}_2\text{O}]_0), \quad (13)$$

where the proportionality constant $K = k_7$ or k' for the direct and indirect mechanisms, respectively.⁷ Equation (13) indicates that the smaller the leak, the greater the intermediate half-life.

PROCESS IMPLICATIONS

Although the results of this study are insufficient to confidently predict the hydrolysis reaction mechanism, they are sufficient to correct several misconceptions concerning UF_6 hydrolysis. In excess UF_6 , the formation of HF is quite rapid, but the formation of UO_2F_2 is quite slow. The conversion of UF_6 into UO_2F_2 probably proceeds through the formation of a uranium oxyfluoride intermediate, possibly UOF_4 or $(\text{UF}_5)_2\text{O}$, in agreement with earlier speculation.¹² In excess UF_6 , the formation of this intermediate is a gas-

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phase reaction, but its conversion into UO_2F_2 may be either a gas-phase or a surface reaction. These results, together with the BNL experiments,⁸ suggest that the intermediates have appreciable volatility at temperatures above 70°C , which may contribute to the apparent transport of UO_2F_2 away from the source of a moisture leak.

Operating cascades can experience both major and minor leaks. Major leaks may have an excess of H_2O , while minor leaks are characterized by a large excess of UF_6 . Equation (13) predicts that the UO_2F_2 formation rate is strongly dependent on the leak size (i.e., $[\text{H}_2\text{O}]_0$).

If a leak is sufficiently massive (excess H_2O), UO_2F_2 formation may be quite rapid. In this case, most UO_2F_2 deposits are localized near the leak source.

Minor leaks, similar to those examined in this study, are more prevalent in cascade operation. Examples include pinhole openings in weld joints and cracks in expansion bellows. Minor leaks may go undetected and unrepaired for many years. In such leaks, the UF_6 excess may be such that $([\text{UF}_6]/[\text{H}_2\text{O}])_i > 200$. Under these conditions, UO_2F_2 formation should be quite slow. The metastable uranium oxyfluorides shown in Fig. 4 are quite stable having a half-lives > 8 min. Equation (13) suggests that the half-life should increase further as $[\text{H}_2\text{O}]_0$ decreases.

CONCLUSION

The moist air reaction with UF_6 has been studied at conditions simulating hydrolysis during cascade air inleakage. In excess UF_6 , the reaction mechanism is more complicated than predicted by the simple gas-phase hydrolysis of UF_6 and H_2O to form UO_2F_2 and HF shown in Reaction (1). The initial UF_6 consumption by H_2O is significantly greater than predicted by Reaction (1), suggesting that a metastable uranium product is formed during the hydrolysis reaction. Immediately after hydrolysis, this metastable species can associate with much more UF_6 than predicted by Reaction (1). Two possible intermediate products are $(\text{UF}_5)_2\text{O}$ and UOF_4 . These metastable products are long lived, with half-life inversely proportional to $[\text{H}_2\text{O}]$. These intermediates are probably also more volatile than UO_2F_2 apparently facilitating UO_2F_2 transport and dispersion in the cascade. Eventually (depending on $[\text{H}_2\text{O}]_0$), the metastable products dissociate into UO_2F_2 and UF_6 .

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