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REPORT NO.: KY-795

**MARTIN MARIETTA**

FALLOUT OF URANIUM DURING UF<sub>6</sub> RELEASES (U)  
(Taken from KY/L-694, Part 11, 1/6/75 and  
KY/L-765, Part 2, 3/26/75, T. J. Mayo)

January 6, 1994

This document has been approved for release  
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MARTIN MARIETTA UTILITY SERVICES, INC.  
UNDER CONTRACT WITH  
THE UNITED STATES  
ENRICHMENT CORPORATION

DATE OF ISSUE: January 6, 1994

REPORT NO.: KY-795

FALLOUT OF URANIUM DURING UF<sub>6</sub>RELEASES  
(Taken from KY/L-694, Part 11, 1/6/75  
and KY/L-765, Part 2, 3/26/75,  
T. J. Mayo)

Prepared by  
Martin Marietta Utility Services, Inc.  
Paducah Gaseous Diffusion Plant  
for the  
United States Enrichment Corporation  
under Contract No. USECHQ-93-C-0001

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FALLOUT OF URANIUM DURING UF<sub>6</sub> RELEASES

Master: Marietta, PGDP

(T. J. Mayo, Laboratory)

When UF<sub>6</sub> is released to the atmosphere, it is quickly hydrolyzed to UO<sub>2</sub>F<sub>2</sub> and HF by atmospheric moisture. It is frequently believed that a large part of the UO<sub>2</sub>F<sub>2</sub> rapidly falls to the ground due to gravitational effects while the HF remains airborne. On the other hand, in atmospheric dispersion work it is generally assumed that aerosols (particle diameters less than 20 microns) remain airborne for long periods of time. The gaseous reaction of UF<sub>6</sub> and H<sub>2</sub>O frequently produces UO<sub>2</sub>F<sub>2</sub> particles of micron or submicron size or, in other words, well down in the aerosol range. There is, therefore, some question about the rapid fallout of UO<sub>2</sub>F<sub>2</sub>. There is also a possibility that HF, with its strong tendency to adsorb on practically any surface, would attach to the UO<sub>2</sub>F<sub>2</sub> particles and also be removed from the air should solids fallout occur.

In this project, the behavior of the UO<sub>2</sub>F<sub>2</sub> and HF resulting from the release of gaseous UF<sub>6</sub> to the atmosphere will be investigated.

CURRENT PROGRESS

The method chosen was to release known quantities of gaseous UF<sub>6</sub> and SF<sub>6</sub>, sample the atmosphere downwind, and determine the total U, F<sup>-</sup>, and SF<sub>6</sub> in the sample. Losses of either U or F<sup>-</sup> should be reflected in deviations of the ratios of U and F<sup>-</sup> to SF<sub>6</sub> from the known ratios which were released. Loss of either U or F<sup>-</sup> relative to the other would also be reflected, of course, in the U to F<sup>-</sup> ratio.

Approximately 215 grams of UF<sub>6</sub> and 14 grams of SF<sub>6</sub> were charged into a 5.6-liter Monel bulb with the amounts established to within 1-2%. The bulb was then heated to 230°F to vaporize the UF<sub>6</sub>. At this temperature the vapor pressure of UF<sub>6</sub> is about 76 psia. In the bulb employed, the actual UF<sub>6</sub> pressure was about 50 psia at 230°F with an additional 8 psi supplied by the SF<sub>6</sub>. The hot bulb was then carried into the field in an insulated box (also heated to 230°F) and the UF<sub>6</sub>-SF<sub>6</sub> gaseous mixture released. The mixture pressure was monitored to make certain that there was no UF<sub>6</sub> condensation before release. About 75% of the bulb contents, or approximately 160 grams of UF<sub>6</sub> and 10 grams of SF<sub>6</sub>, were released during each run. The releases were essentially complete in less than half a minute.

Sampling was done with four portable Bendix Model 15003 battery-operated air samplers. The air was pulled through two K<sub>2</sub>CO<sub>3</sub>-coated, membrane-type filters to trap the UO<sub>2</sub>F<sub>2</sub> and HF. The sampler discharge was then split and a known fraction (about 14%) trapped in a vinyl bag for SF<sub>6</sub> determination. Occasionally an uncoated filter was used in front of the two coated filters to trap particulates and determine the amount of adsorbed HF.

The U and F<sup>-</sup> analyses were performed by standard wet chemical methods. The SF<sub>6</sub> analyses were by chromatographic means using an electron capture detector.

Initially, releases were made in the early afternoon, and dispersion was so great that detectable amounts of uranium and fluoride were generally not obtained. Later releases were made in late afternoon in the last 30 minutes before dark. At this time, when the sky is clear and wind speeds low, the atmosphere becomes very stable at the lower levels as an inversion builds up. Gravitational effects should be greatest at this time. Results of the runs are summarized in table 1.

In runs 4, 5, and 6, four samples were taken at a single distance in each run with the intention of going to greater distances later. Variation of the ratios was such that this approach did not appear encouraging. In runs 7 and 8, the procedure was changed to take two samples at each of two distances.

The results to date have not been entirely unambiguous, but some general observations can be made. There are no indications of major, rapid losses of uranium from the atmosphere at distances up to 400 yards. This is based on observation of the clouds which are quite visible initially as well as the data in the table. The U/F ratios in runs 7 and 8 suggest a little loss of uranium with distance, but the U/SF<sub>6</sub> ratio gives opposite indications in one case (run 7). This may be at least partly due to sampling problems. For example, in run 7 it can be seen that more material was found at the greater distance. The site of this release was rather rolling terrain cut somewhat by ditches. This roughness caused the cloud to rise over the first samplers almost missing them completely before returning to envelope the more distant samplers.

The only serious problem with the program occurred in run 6 when it appears that a sampling and/or analytical problem resulted in low SF<sub>6</sub> values. Thus, both the U/SF<sub>6</sub> and F/SF<sub>6</sub> are unreasonably high, but the U and F data do provide some information relative to the disposition of HF.

To determine whether, in fact, free HF was present in the cloud during runs 6, 7, and 8, one of the samplers had an extra, untreated filter in front of the K<sub>2</sub>CO<sub>3</sub>-treated papers. This untreated paper would catch only the UO<sub>2</sub>F<sub>2</sub> with the free HF being caught in the K<sub>2</sub>CO<sub>3</sub>. In the three runs, 36, 42, and 50% of the fluoride was found on the untreated paper. Since one would expect 33% of the fluoride to be as UO<sub>2</sub>F<sub>2</sub>, it is clear that very little of the HF is adsorbed on the UO<sub>2</sub>F<sub>2</sub> or other dust particles in the atmosphere.

The U/SF<sub>6</sub> data also gives some information about the particle size of UO<sub>2</sub>F<sub>2</sub> in the cloud. The untreated filters used had hole sizes of 0.8 microns, and the fact that the expected or higher U/SF<sub>6</sub> ratio was usually found indicates that all the uranium was caught on the filter. This means that the predominant UO<sub>2</sub>F<sub>2</sub> particle size or particle agglomerate

Table 1  
FALLOUT OF  $UO_2F_2$

Run	Sampler	Sampling Distance, yds	Sample Size, $\mu$	Total U Found, $\mu$ g	Weight Ratio Found		
					U/F	U/SF <sub>6</sub>	F/SF <sub>6</sub>
4	1	125	42	500	2.5	12	4.7
	2	125	45	580	2.5	12	4.7
	3	125	49	470	2.5	11	4.5
	4	125	49	330	2.4	10	4.2
				Ratio Released		2.09	10.2
5	1	120	43	59	2.4	16	6.9
	2	120	45	47	2.1	14	6.3
	3	120	47	52	2.2	13	5.8
	4	120	48	102	2.2	13	5.7
				Ratio Released		2.09	10.4
6	1	153	51	125	1.9	84	44
	2	153	60	80	2.0	61	31
	3*	153	62	22	2.0	43	21
	4	153	70	8	2.0	41	21
				Ratio Released		2.09	10.9
7	1	92	59	108	2.5	14	5.6
	2	92	65	24	2.7	5.1	1.9
	3*	212	85	488	2.0	20	9.9
	4	212	99	535	2.2	22	9.9
				Ratio Released		2.09	9.90
8	1	190	39	27	2.7	17	6.3
	2*	190	37	22	2.8	17	6.2
	3	380	55	13	2.6	14	5.4
	4	380	59	10	2.0	9.7	4.9
				Ratio Released		2.09	10.2

\*Uncoated filter used ahead of normal coated filters.

was greater than 0.8 microns. If many submicron particles are present, they represent an insignificant portion of the total uranium released.

Finally, a word about the atmospheric stability. While it was intended to obtain data during stable conditions (Pasquill's F), it was obvious at the time of the release of the  $UF_6$ - $SF_6$  mixtures that only in runs 4 and 7 were stable conditions present. In the other runs, the stability was probably D or neutral. The limited amount of data available does not indicate any effect from the different stabilities, but this question needs further consideration.

CLASSIFICATION CHANGED TO

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1-6-98

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(Signature of Person Verifying Change) (Date)

Martin Marietta, PGDP FALLOUT OF URANIUM DURING UF<sub>6</sub> RELEASES

(T. J. Mayo, Laboratory)

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In this project, the behavior of the UO<sub>2</sub>F<sub>2</sub> and HF resulting from the release of gaseous UF<sub>6</sub> to the atmosphere will be investigated.

#### CURRENT PROGRESS

Since the last report,<sup>1</sup> four additional releases have been made from a five-liter bulb containing known quantities of UF<sub>6</sub> and SF<sub>6</sub>. The SF<sub>6</sub> serves as an internal standard and any decrease in the U/SF<sub>6</sub> or F/SF<sub>6</sub> ratio was intended to indicate a loss of uranium or HF from the plume. The UF<sub>6</sub> and SF<sub>6</sub> mixtures were made up so that the weight ratios in the released mixtures were 9.8 for U/SF<sub>6</sub>, 4.7 for F/SF<sub>6</sub>, with the U/F ratio in UF<sub>6</sub> being 2.1. The results of the four new runs along with the previous runs where samples were obtained at two distances are given in table 1.

All these releases were made in the late afternoon just before dark under clear skies with winds of 5 mph or less. The aim was to release during very stable atmospheric conditions corresponding to a Pasquill F stability category. Observation of the clouds of released material showed that this condition did not always exist and that stabilities actually ranged from stable to neutral or Pasquill categories F to D.

Examination of table 1 shows that while the ratios generally decrease with distance there are cases, runs 7 and 11, where the reverse is true. It will also be noted that more often than not the ratios exceed the known release values. Because of such problems, no further work is planned by this method.

There are, however, some worthwhile observations which can be made. Because of the variability of the data, probably the best way to look at it is from the standpoint of overall averages which are summarized in table 2. Considering the ratios in the order presented, the U/F

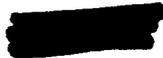


Table 1

SUMMARY OF UF<sub>6</sub>-SF<sub>6</sub> RELEASE RESULTS

Run	Sampling Distance, yards	Ratios		
		U/F	U/SF <sub>6</sub>	F/SF <sub>6</sub>
7	90	2.6	10	3.8
	210	2.1	21	9.9
8	190	2.8	17	6.3
	380	2.3	12	5.2
9	240	2.7	15	4.9
	480	-	10	-
10	70	2.1	29	14
	440	1.6	17	10
11	70	1.5	12	7.9
	440	2.0	11	5.4
12	70	2.1	14	6.5
	440	1.9	9	4.7
Theory		2.1	9.8	4.7

Table 2

SUMMARY OF AVERAGE RESULTS

Sampling Location	U/F	U/SF <sub>6</sub>	F/SF <sub>6</sub>
Near	2.19	15.9	7.58
Far	1.98	13.3	7.11
% Decrease	9.6	16.4	6.2



[REDACTED]

ratio change from the near to the far sample point indicates a small loss (9.6%) of uranium relative to the fluoride. The fluoride here is defined as the fluoride in the  $UO_2F_2$  plus HF from the hydrolysis. A similar loss of uranium (16.4%) is indicated by comparison to the internal standard  $SF_6$ . Only a minor loss (6.2%) of fluoride is indicated. At best, these values can only be considered as semiquantitative estimates because of the obviously poor precision of the data. It is concluded that some loss of uranium does occur downwind from an outside release during relatively stable weather conditions. The extent of the loss is not well defined, but it is probably small and almost certainly does not exceed 20-25% in a quarter of a mile.

During three of the releases, run 7 in table 1 and runs 4 and 6 reported previously, the clouds produced by the 160-gram  $UF_6$  releases were visible for at least a half mile. The atmosphere was very stable, and the clouds stayed near the ground permitting the extended observation. Neither this nor observations in the vicinity of the release points suggest a large loss of material. These observations appear to support the previous conclusion that it cannot be assumed a large portion of the uranium will quickly fall out of the cloud.

Two additional determinations were made concerning HF adsorbed on  $UO_2F_2$  or other atmospheric particles. This was done by placing an uncoated filter in front of the  $K_2CO_3$ -coated filters in the sampling heads. In a total of five determinations from 36 to 50 percent of the total fluoride was found on the uncoated filter. The average value was 43 percent. Since 33 percent of the fluoride would be present as  $UO_2F_2$ , this indicates that about 15 percent of the remaining fluoride, presumably as HF, was adsorbed on material trapped by the first filter. It is thus indicated that 85 percent of the HF was not adsorbed.

#### REFERENCE

- <sup>1</sup> Mayo, T. J., *Paducah Plant Development Progress Report, November 1974*, KY-L-694-11, January 6, 1975.
- [REDACTED]

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