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CHARACTERIZATION OF THE SOLID,
AIRBORNE MATERIALS CREATED WHEN
UF₆ REACTS WITH MOIST AIR FLOWING
IN SINGLE-PASS MODE

P. W. Pickrell

Materials and Chemistry Technology Department
Process Support Division

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Martin Marietta Energy Systems, Inc.
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Larry E. Williams
Authorizing Official

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SUMMARY

A series of experiments has been performed in which UF_6 was released into flowing air in order to characterize the solid particulate material produced under non-static conditions. In two of the experiments, the aerosol was allowed to stagnate in a static chamber after release and examined further but in the other experiments characterization was done only on material collected a few seconds after release. Transmission electron microscopy and mass measurement by cascaded impactor were used to characterize the aerosol particles which were usually single spheroids with little agglomeration in evidence.

INTRODUCTION

The work reported here was conducted as a part of the Plant and Long Range Technical Support (P&LRTS) environmental program at the Oak Ridge Gaseous Diffusion Plant. The goal of the work is to determine the chemistry and physics of the UF_6 -atmospheric moisture reaction under a variety of conditions so that information about resulting species and product morphologies is available for containment and removal (knockdown) studies as well as for dispersion plume modeling and toxicology studies. This report completes the milestone for reporting the information obtained from releases of UF_6 into flowing rather than static air.

EXPERIMENTAL

In all of the experiments UF_6 was released into a 5-inch I.D. Plexiglass pipe with ambient air flowing in the direction of the release at approximately 6 ft per sec 4 mph. The pipe was 12 ft long, therefore 2 sec elapsed before the aerosol plume left the containment of the pipe, i.e., aerosol particles were collected at the discharge end of the pipe no more than 2 sec after formation. Additionally, some samples were collected upstream of the discharge end of the pipe as near as 3 ft (1/2 sec) from the release point or after the discharged plume had been caught in a chamber and allowed to stagnate.

Figure 1 shows the UF_6 container used, for most of the releases, to hold the UF_6 and allow rapid release of the contents by pulling the Teflon plug from the container. An overwrap of Nichrome wire (not shown) was used as the heating element after a charge of 1/2 - 1 1/2 gm UF_6 was put in the container for each experiment. Samples for microscopy were collected on Formvar-coated microscope grids placed in the airstream or in the static chamber after plume collection. Particle size distribution measurement by mass microbalance was done by placing the collection probe at the discharge end of the pipe.

FIG. 1. PHOTOGRAPH OF CONTAINER USED TO ALLOW RAPID,
CONTROLLABLE UF_6 RELEASE

Since static release experiments show a correlation between aerosol particle morphology and the temperature of the UF_6 at time of release, three releases at UF_6 container temperatures of 75°C , 80°C , and 85°C were made. The critical temperature of UF_6 is 64°C . Relative humidities of the flowing air for these three releases were 55%, 52%, and 35% respectively. Evaporative cooling and concurrent solidification of the UF_6 in the container prevented the release of most of the UF_6 at 75°C and 80°C but at 85°C all of the material was expelled from the container. At 75°C 9% of the UF_6 was released and at 80°C 16% of the UF_6 was released. Figures 2 and 3 are transmission electron micrographs of material collected 12 ft (2 sec) downstream of the 75°C release. Very few particles were collected and most of these were larger, as large as 2 microns in diameter, and showed evidence of faceting unlike expected hydrolysis product particles. This suggests the collected material was condensed UF_6 particles rather than UO_2F_2 particles. This same observation was made in the 80°C releases. In micrographs of samples collected three ft (1/2 sec) and 12 ft (2 sec) downstream of the release point, most of the particles collected exhibit this non-hydrolysis product character. Figures 4 and 5 show such particles in addition to an obscuring, uniform film more evident in Figure 4. This film is thought to be UF_6 deposited before discrete particle formation. This film or deposit is more evident in samples collected from the 85°C release. Figure 6 is a micrograph of a control grid and Figure 7 is a micrograph of material collected 12 ft (2 sec) downstream of the release. Figure 6 has only 1/4 the exposure to the electron beam as Figure 7 which illustrates the thickness or obscuring effect of the film of UF_6 deposited. Most of the smaller UO_2F_2 particles cannot be resolved because of this film but the larger particles are more resolvable. Figure 8 is a micrograph of material collected 9 ft (1 1/2 sec) downstream of the release point which shows larger spheroids, which probably were originally condensed UF_6 rather than UO_2F_2 , as well as a thicker uniform film of " UF_6 ".

This apparent UF_6 film seen at lower temperatures was also seen in a release when the UF_6 temperature at time of release was 100°C , the air temperature was 24°C and the relative humidity was 22%. Micrographs of samples collected at 3 ft (1/2 sec), 6 ft (1 sec), 9 ft (1 1/2 sec), and 12 ft (2 sec) downstream of the release point are shown in Figures 9, 10, 11, and 12, respectively. The film on the grid at 3 ft is so thick that resolution of particles is impossible although some particles approaching 1 micron in diameter are evident. The deposit film gets progressively thinner but is still in evidence on the 12 ft samples but is not thick enough to prevent good resolution of the UO_2F_2 particles. Agglomeration of the airborne particles has begun in the material shown in Figure 12. Mean diameters of 741A, 987A, and 991A were obtained by measuring Figures 12, 11, and 10 respectively neglecting the two largest agglomerates in Figure 12. This shows the influence of the larger, condensed UF_6 particles nearer the point of release. A release at a UF_6 temperature of 100°C in which a constricting valve was used to control the UF_6 release showed only the UO_2F_2 particulate material and not the uniform film of UF_6 and the larger, condensed UF_6 spheroids. This was because the valve restriction required much longer (30 sec vs 3 sec) for release completion. Figure 13 shows the lack of any continuous film or

deposit and the size range (300A to 500A) of UO_2F_2 single spheroids collected 12 ft (2 sec) from this release.

Two experiments in which the release plumes were caught in a chamber and allowed to stagnate were used to get information about the aerosol particles under both dynamic and static conditions. One release, in which the UF_6 container was at 100°C at time of release, did not occur as planned when a plug developed in the UF_6 container. Because of this plug, which later broke free, this release was not continuous and only a portion of the total release plume was caught in the stagnation chamber. Samples were collected 12 ft (2 sec) from the release point and at various times in the static chamber. Air temperature was 24°C and relative humidity was 28%. Sampling of the aerosol as it was discharged from the pipe into the static chamber was also done to obtain an aerodynamic particle size distribution of the aerosol 2 sec after release. A cascaded quartz crystal microbalance was used for this measurement and the distribution obtained is shown in Table 1. Also shown are distributions obtained at various times from the static aerosol.

Table 1. Aerodynamic particle size distributions of aerosol samples collected at different times after UF_6 release

Diameter, μ	Wt% of collected particles at various elapsed times			
	2 sec	20 min	3 1/2 hr	6 hr
18	2	0	0	3
9	1	0	0	0
4.5	2	0	1	2
2.2	1	5	2	6
1.1	1	0	5	7
.56	2	0	35	21
.28	3	71	47	11
.14	7	15	9	46
.07	70	9	1	4
.035	11	0	0	0

The distributions obtained at longer times, i.e. samples from the static chamber are typical of such aerosols showing initial agglomeration to larger airborne entities with decrease in size as the aerosol particles fallout leaving smaller particles airborne. The distribution obtained from the two second sample appeared to indicate the uniform, non-particulate film seen in earlier experiments might be artificially showing the presence of very large particles. No such film or large particles could be seen in the micrographs of material collected on grids 2 sec after release, as shown in Figures 14 and 15, however, and a later experiment in which such a film was very obvious from micrographs but not measured by the aerodynamic particle size technique did not support this thinking.

Particle size measurement of Figures 14 and 15 in which some agglomeration is evident gives average particle diameters of 712A and 878A, respectively, which agrees with the aerodynamic measurement very well. Although the micrographs of the two-second sample indicate no uniform film or deposit is present on the collector grids, micrographs of material collected by gravitational setting of samples of aerosol removed from the chamber show localized heavy deposits or shadowing associated with most collected particles even for long time periods after the release. This may be the result of continued hydrolysis of UF_6 associated with hydrolyzed particles but the thickness of the deposit is great and it seems unlikely that continued hydrolysis would produce such a large effect. The method of sampling may be introducing this anomaly. Figures 16, 17, 18, and 19 are micrographs of material removed from the static chamber at 5 min, 20 min, 3 1/2 hr, and 6 hr after the release showing typical chainlike agglomerates of small UO_2F_2 spheroids and the unexplained deposit associated with areas of particle-substrate contact.

In the other experiment in which the release plume was caught in a static chamber a higher aerosol particle density was achieved when all the contents of the UF_6 container was released in a single surge lasting 5 sec. The UF_6 container was at 100°C and the air temperature and relative humidity were 22°C and 61%. The plume was caught and allowed to stagnate as previously. Of the uranium released from the container, 55% was caught in the static chamber. An aerodynamic particle size distribution was obtained on the plume 12 ft (2 sec) downstream of the release point and is shown in Table 2.

Table 2. Aerodynamic particle size distribution of aerosol particles collected 2 sec after release

Diameter, μ	Wt% of collected particles
18	0
9	0
4.5	0
2.2	0
1.1	9
.56	26
.28	46
.14	8
.07	6
0.35	5

Figures 20 and 21 are micrographs of material collected 2 sec after release and show the deposit or film of UF_6 seen in some other releases. The particles of UO_2F_2 or unhydrolyzed UF_6 are unagglomerated spheroids which are larger than those seen in other releases of this type and the

film has itself developed structure, presumably hydrolysis after deposit. The spheroids appear to be greater than $1/2 \mu$ in diameter although a mean particle size from the micrographs was not obtained because of the obscuring effect of the film. Figures 22, 23, 24, 25, and 26 are micrographs of material collected from the static chamber at varying times. The average particle diameter obtained from the first 12 minute sample (Fig. 22) is 1.04μ which is in agreement with earlier static release experiments with similar aerosol concentrations. Particle diameters were not obtained from other samples because of the non-equant nature of the particles but the micrographs show the typical trend of growth by agglomeration followed by size decrease or segregation as fallout continues. Table 3 gives values for the aerosol uranium content as fallout occurred.

Table 3. Uranium content of aerosol samples withdrawn at various times after release

Sample time	U (as UF_6), g/m ³
0 min	3.7
8	2.8
26	2.2
44	1.8
130	0.4

CONCLUSIONS

In all the experiments, the particulate material produced by releasing UF_6 into flowing air and observed within 2 sec of release consisted almost entirely of unagglomerated spheroids which varied in diameter from several hundreds of angstroms to several thousands of angstroms, i.e., a factor of ten. The formation of the larger particles was generally promoted by increased concentration of UF_6 and moisture as higher relative humidity air. These larger spheroids consisted of unhydrolyzed UF_6 as well as UO_2F_2 . Another factor contributing to larger particle formation was temperature of UF_6 at time of release, lower temperatures more readily allowing UF_6 condensation before hydrolysis. In aerosols caught and allowed to stagnate for much longer periods of time than 2 sec these spheroidal particles did not continue to grow as individuals but formed agglomerates with other spheroids. These agglomerates varied with increasing particle concentration and relative humidity from tenuous chainlike particles several microns in major dimension to denser, highly coalesced non-equant particles also several microns in major dimension. Also observed on the flowing air collectors was evidence that in the time frame of observation, UF_6 which had not condensed into discrete particles or reacted with moisture was deposited as a relatively homogeneous film. Therefore, all the materials observed by microscopy would be expected to have long (several hours) airborne life especially if dispersion from the release point prevented continued agglomeration.

JX-4291

30,000 X

FIG. 2. MATERIAL COLLECTED 2 SEC AFTER RELEASE AT 75°C

JX-4290

30,000 X

FIG. 3. MATERIAL COLLECTED 2 SEC AFTER RELEASE AT 75°C

FIG. 4. MATERIAL COLLECTED ONE-HALF SEC AFTER RELEASE AT 80°C

JX-4306

30,000 X

FIG. 5. MATERIAL COLLECTED 2 SEC AFTER RELEASE AT 80°C

FIG. 6. CONTROL UNEXPOSED GRID

7341

30,000 X

FIG. 7. MATERIAL COLLECTED 2 SEC AFTER RELEASE AT 85°C

FIG. 8. MATERIAL COLLECTED 1 1/2 SEC AFTER RELEASE AT 85°C

JX-3896

30,000 X

FIG. 9. MATERIAL COLLECTED 1/2 SEC AFTER RELEASE AT 100°C

JX-3902

30,000 X

FIG. 10. MATERIAL COLLECTED 1 SEC AFTER RELEASE AT 100°C

JX-3915

30,000 X

FIG. 11. MATERIAL COLLECTED 1 1/2 SEC AFTER RELEASE AT 100°C

JX-3934

30,000 X

FIG. 12. MATERIAL COLLECTED 2 SEC AFTER RELEASE AT 100°C

JX-3175

30,000 X

FIG. 13. MATERIAL COLLECTED 2 SEC AFTER RELEASE AT 100°C

FIG. 14. AEROSOL PARTICLES COLLECTED 2 SEC AFTER RELEASE

8197

30,000 X

FIG. 15. AEROSOL PARTICLES COLLECTED 2 SEC AFTER RELEASE

8173

30,000 X

FIG. 16. AEROSOL PARTICLES COLLECTED 5 MIN AFTER RELEASE

FIG. 17. AEROSOL PARTICLES COLLECTED 20 MIN AFTER RELEASE,
STEREO PAIR

8310

30,000 X

FIG. 17. AEROSOL PARTICLES COLLECTED 20 MIN AFTER RELEASE,
STEREO PAIR

8327

30,000 X

FIG. 18. AEROSOL PARTICLES COLLECTED 3 1/2 HR AFTER RELEASE

8329

30,000 X

FIG. 19. AEROSOL PARTICLES COLLECTED 6 HR AFTER RELEASE

8718

30,000 X

FIG. 20. AEROSOL PARTICLES COLLECTED 2 SEC AFTER RELEASE

8723

7500 X

FIG. 21. AEROSOL PARTICLES COLLECTED 2 SEC AFTER RELEASE

FIG. 22. AEROSOL PARTICLES COLLECTED FIRST 12 MIN AFTER RELEASE

FIG. 23. AEROSOL PARTICLES COLLECTED FOR 7 MIN ENDING
21 MIN AFTER RELEASE

FIG. 24. AEROSOL PARTICLES COLLECTED FOR 16 MIN ENDING
37 MIN AFTER RELEASE

8775

7500 X

FIG. 25. AEROSOL PARTICLES COLLECTED FOR 27 MIN ENDING
64 MIN AFTER RELEASE

39/40

8748

7500 X

FIG. 26. AEROSOL PARTICLES COLLECTED FOR 21 HRS ENDING
24 HR AFTER RELEASE

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