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PLANT

MARYNN MARIETTA

ARSENIC REMOVAL FROM GASEOUS STREAMS

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November 1989

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ABSTRACT

Uranium feed materials, depending on the production process, have been found to contain arsenic (As) as a contaminant. Analyses show the As to be present as As pentafluoride (AsF_5) and/or hexafluoroarsenic acid (HAsF_6) and enter the enrichment cycle through contaminated hydrogen fluoride (HF). Problems related to corrosion of cylinder valves and plugging of feed lines and valves have been attributed to the As. Techniques to separate AsF_5 from uranium hexafluoride (UF_6) using sodium fluoride (NaF) as a trapping media were successful and will be discussed. Procedures to significantly reduce (up to 97%) the level of As in HF will also be reported.

EXECUTIVE SUMMARY

The Paducah Gaseous Diffusion Plant (PGDP) enriches uranium supplied from different manufacturers. AsF_5 and HAsF_6 have recently been identified as contaminants in some UF_6 feed material and the cause of significant corrosion of materials of construction. Recent cylinder valve corrosion and valve and feed line plugging have been traced to these contaminants in the feed material. As fluorides are reported to complex with a number of metal fluorides, and it is theorized that the protective metal fluoride film is broken down in contact with AsF_5 allowing fluoride attack on the base metal. The proper removal and disposal of this material are also of concern related to the protection of the environment.

Corrosion of materials of construction and environmental impact are also of concern to the UF_6 feed manufacturers. As is a contaminant in fluorspar used to manufacture HF, which in turn is used in the manufacture of feed UF_6 . Early removal of this contaminant from the production cycle is of interest.

This report offers a means of separating the As contaminant from the feed UF_6 and the HF used in the manufacture of UF_6 . Tests have shown that by operating a NaF trap at elevated temperatures (above the dissociation pressure of the NaF- UF_6 complex), the UF_6 in low concentrations will pass through trapping only the As contaminant. Another method of operation could be to trap both the UF_6 and the As and then heat the bed to the normal UF_6 regeneration temperature of 600°F to 650°F, leaving behind the As. Tests show the As is driven off the NaF at an onset temperature of about 750°F to 800°F, well above the normal UF_6 regeneration temperature.

In the initial stages of this investigation, scoping tests were made to identify a trapping method for removing AsF_5 from UF_6 feed material. Seven potential trapping materials were tested. These materials are magnesium fluoride (MgF_2), calcium carbonate (CaCO_3), NaF, polyethylene chips, molecular sieve, activated alumina (Al_2O_3), and fluorspar [calcium fluoride (CaF_2)]. These scoping tests showed that only NaF, Al_2O_3 , and MgF_2 trapped significant amounts of the AsF_5 to warrant further investigation. Further, it was observed that more loading occurred as the bed temperature was increased from ambient to 400°F or 500°F. Through thermogravimetric analysis of the AsF_5 -exposed NaF, it became apparent that NaF at the proper temperature would allow UF_6 to pass through while trapping AsF_5 . Another option would be to trap both As and UF_6 , heat to the normal UF_6 regeneration temperature, remove the UF_6 , and leave behind the AsF_5 .

The second phase in testing dealt with removal of the As from HF. If the contaminant could be removed at this point, then it would not be a concern in the enrichment process. Significant reductions in the As level in HF were obtained by vapor feeding and condensing the HF (97%). Very little As was captured on the trapping media since most of the As remained in the feed cylinder. Of the three trapping media tested [NaF, sodium bifluoride (NaHF_2), and nickel (Ni) chips], the Ni chips had the best potential.

These methods can be used either by the enrichment industry or the feed supplier in removing As contamination from feed UF_6 . The last method may also have application with the HF industries in providing a product with less contamination, thus minimizing corrosion of exposed equipment and possibly environmental impacts.

EXPERIMENTAL

MATERIALS

The AsF_5 mixes used in the scoping tests and trapping studies were prepared from AsF_5 (500 g) purchased commercially. Most of the trapping agents evaluated in the scoping study were from materials on hand:

MgF_2 -- Cylindrical pellets prepared from high surface area powder at PGDP.

$CaCO_3$ -- Irregular size rock ~1/4 in. screened.

NaF -- Pellets processed from commercially obtained $NaHF_2$ pellets ~1/8-in. cylindrical.

Polyethylene chips -- ~1/4-in. chips cut from 1/4-in. tubing.

Molecular sieve -- ~1/16-in. round beads.

Al_2O_3 -- Spherical pellets ~1/8-in. diameter.

CaF_2 -- ~1/4- to 1/8-in. flakes commercially obtained.

SYSTEM DESIGN

The trapping system is shown in Figure 1. The flow system is housed in a 170°F heated cabinet that contains a manifold for sampling (trap inlet and outlet gas streams), evacuation, and nitrogen (N_2) purging. The flow system contains separate orifice systems for metering up to three flows. Controllers on each orifice system maintain the flows at set levels. Ports are available for attaching three gas supplies; however, on these tests generally only two were used. N_2 or HF was passed through System 1, and a mixture (AsF_5 and N_2 or an AsF_5 - UF_6 and N_2 mixture) was passed through System 2. The desired final concentration fed to the trapping materials was obtained by adjusting the N_2 flow and mixture to achieve the value. Checks between the calculated concentrations based on flow measurements and those obtained by gas analysis were used as a basis to conclude that the calibration of the orifice flow systems was correct and that the desired flows were being obtained. In low system pressure tests, a metal bellows pump and air ejector were used.

The trap is housed in an oven for heating the bed during some of the runs. The cylindrical 1-in. OD by 15-in.-long Monel reactor stands vertically in the oven, with the inlet at the bottom and the outlet at the top. In every case, the reactor was filled to a depth of 12 in. Positioned in the cross-sectional center of the bed material are four thermocouple wells located every 4 in.

TRAPPING SYSTEM SCHEMATIC

Figure 1

Breakthroughs were monitored with an infrared analyzer with an approximate lower limit of detection (LLD) of 30 ppm AsF_5 . Bubblers containing approximately 500 mL of distilled water (two in series) followed by chemical analysis for As were used on the outlet stream to determine the outlet concentration prior to breakthrough and below the detection limit of the infrared. Other system designs were used and will be discussed in the "Results" section.

PROCEDURE

The trap material was weighed, placed in the reactor, and heated to the desired temperature. During the scoping runs, tests were made at 80°F to 400°F. At the beginning of a run, flows were established bypassing the reactor and gas samples were taken for analysis to determine the inlet concentration. Once this was completed, the flow was diverted through the bed and timing of the run was started. Outlet gas samples were analyzed and, periodically, additional inlet samples were taken to confirm the inlet concentration during the run. Once the run was terminated, the bed was unloaded, weighed, and sent for As analysis. Estimated As loading factors were calculated at the time of breakthrough and termination of the run based on the inlet concentration, total flow, and time.

As mentioned above, efforts were made to use bubblers in the off gases from the traps to determine concentrations below the 30 ppm detection limit of the infrared. Initially, the inlet concentration was fed to two glass bubblers in series and, at one time, four plastic bubblers in series. Smoke was observed coming through the series of bubblers. Comparing the total As trapped in the set of bubblers to the infrared analysis, it was determined that the bubblers were only about 80% efficient. It is obvious that the As compound is not easily hydrolyzed and could not be effectively scrubbed out in a scrubber system. Visual indication of smoke in the bubblers, however, has been observed to be a good indicator of breakthrough in the test traps. Smoke was noted at the same time 30 ppm AsF_5 was measured by infrared analysis.

The procedure for the closed system tests will be discussed in the "Results" section.

RESULTS

AsF_5 SEPARATION FROM UF_6

Scoping Study

Before the purchased cylinder of AsF_5 had been received, a scoping test was made with a gas mixture containing approximately 3.6% AsF_5 taken from the gas over solid removed from a contaminated UF_6 feed cylinder. The gas was removed from the feed cylinder into a 67-L Ni cylinder and resulted in a cylinder working pressure of approximately 325 mm Hg. Therefore, the trapping test was made at subatmospheric pressure and ranged from approximately 30 mm Hg to 120 mm Hg with the aid of a metal bellows pump and air ejector.

Initially the scoping tests were made at ambient temperature, which has ranged from about 106°F to 140°F due either to heat transfer from the heated flow system or heat of reaction. As breakthrough occurred on some of the materials, the temperature was increased to determine if additional loading could be obtained.

MgF₂ was used as the trapping media in the first scoping test. Initially 100.1 g of the pellets were loaded in the reactor which, after drying at 200°F and treatment with F₂, showed a pretrapping bed weight of 92.0 g. The bed was operated at room temperature for about 30 min, after which the temperature was gradually increased to 200°F for the remainder of the run.

The run was continued for 3 hr. Breakthrough occurred after 2.7 hr. Prior to breakthrough, AsF₅ could not be detected in the off-gases by infrared analysis. Following the run, the bed was divided into three equal sections and sent for As analyses. These analyses showed 1.6% As (3.6% AsF₅) at the inlet end of the trap, 1.5% As (3.4% AsF₅) in the mid-section, and 1.2% As (2.8% AsF₅) in the outlet section. Average bed analysis and weight gain measurements showed an AsF₅ loading of 3.3% and 3.7%, respectively. The loading experienced with the MgF₂ is considered low.

For the remaining scoping runs, which are shown in Table 1, a mixture of AsF₅ and N₂ was prepared in a 67-L Ni cylinder at a concentration of 0.7%. The mixture was then blended with a N₂ stream to achieve an inlet concentration going to the trap of approximately 550 ppm AsF₅. Total flow to the traps was approximately 3.5 L/min in the 1-in. OD by 12-in.-long bed.

Table 1. Summary of scoping studies.

Conditions: 550 ppm AsF₅ in N₂, 800 mm Hg pressure, and ~0.5 ft/sec velocity.

Material	Temperature °F	Calculated ^a Loading, %	Bed Analysis, %
MgF ₂	106 - 118	0.7	1.3
CaCO ₃	123 - 200	0	-
NaF	124 - 145	2.9	-
NaF	140 - 200	4.6	5.0
Polyethylene Chips	107	0	-
Molecular Sieve	122 - 131	1.7	-
Molecular Sieve	200	1.7	-
Al ₂ O ₃	125 - 131	4.5	-
Al ₂ O ₃	200	10.9	-
Al ₂ O ₃	300	12.9	-
Al ₂ O ₃	400	14.6	11.8
CaF ₂	106 - 200	0	-

a. g AsF₅/g initial bed material x 100 at breakthrough time.

Breakthroughs occurred at 45 min running time for MgF_2 , 4 min for CaCO_3 , and 335 min for NaF. The temperature of the bed during the MgF_2 test ranged from approximately 106°F to 117°F and was above ambient due mainly to heat transfer from the heated flow system. Breakthrough with the CaCO_3 was essentially instant and, as a result, it was decided to increase the bed temperature to determine if a higher temperature would cause the material to trap the AsF_5 . No AsF_5 was trapped to a temperature of 200°F. On starting the NaF test, the oven was still warm from the CaCO_3 test. The NaF test was initiated and continued with the trap ranging from 145°F to about 130°F. On reaching 130°F and after feeding for 210 min, breakthrough occurred with the NaF. It was then decided to increase the bed temperature and, on reaching 140°F to 200°F, the outlet concentration was again below the detection limit and remained such until a total time of 335 min had elapsed.

NaF and Al_2O_3 were obviously the best performers of the seven materials evaluated. A loading factor of 2.9% AsF_5 was calculated at the time of breakthrough on the NaF at ambient temperature and 4.6% at breakthrough at 200°F. Al_2O_3 showed a loading of 4.4% at ambient temperature, a total loading of 10.6% at 200°F, 12.6% at 300°F, and 14.6% at 400°F. Some problems of sensitivity with the infrared analyzer were encountered at higher temperatures and may affect the accuracy of the calculated loading factors during this test. Instant breakthroughs were observed with CaCO_3 and polyethylene, and moderate increases in temperature had no effect on AsF_5 removal. Very low loading was observed with MgF_2 at ambient temperature. The bed temperature was not increased in this test and may need to be repeated at some future time.

Thermogravimetric analyses were performed on ground subsamples of the bed materials removed from the NaF and Al_2O_3 tests. Weight losses with respect to temperature were measured at a scan rate of 20°F/min in N_2 . These scans are shown in Figure 2. The onset of the major weight loss curve with NaF occurred at approximately 750°F to 800°F. Total weight loss ranged from 5.6% to 6.4% in two tests on reaching 1000°F to 1200°F. Only about 0.16% weight loss occurred at 600°F to 650°F, which is the normal UF_6 regeneration temperature for NaF. Analysis of the sample from one of the tests showed only 0.24% AsF_5 remaining on the material (the starting material contained 5% AsF_5) after heating to 1000°F. It became obvious at this point that NaF might be used to selectively remove AsF_5 from UF_6 . The Ni sample boat used to contain the sample gained approximately 20 mg during the first test and about 8 mg in the second, showing apparent reaction with the AsF_5 . The onset for weight loss with the exposed alumina material occurred at ~300°F and continued up sharply at higher temperatures.

UF_6/AsF_5 in N_2 Studies

The trapping tests and thermogravimetric analyses of the exposed NaF indicated that AsF_5 may be selectively removed from the feed UF_6 by possibly two methods. One method was to heat the bed above the dissociation pressure of the NaF- UF_6 complex and trap the AsF_5 , allowing the UF_6 to pass through. If AsF_5 was trapped preferentially to UF_6 on NaF, then perhaps the higher temperature is unnecessary. The second method would be to trap both materials and then regenerate the bed at 600°F to 650°F, leaving behind the As which appeared to start coming off at about 750°F to 800°F.

TG ANALYSIS ALUMINA - SODIUM FLUORIDE

HEAT RATE: 20 °F/MINUTE

Figure 2

Three trapping runs were made to evaluate these methods. The data from these runs are summarized in Table 2. The inlet gas concentrations were approximately the same for all three runs: ~1000 ppm AsF_5 and ~500 ppm UF_6 in N_2 with a total flow of ~3550 sccm.

Table 2. UF_6/AsF_5 in N_2 studies -- NaF.

Temperature	400°F	500°F	200°F
<u>Inlet Gas Concentration</u>			
AsF_5 , ppm	973	932	980
UF_6 , ppm	439	525	555
Total Flow, sccm	3536	3552	3550
<u>Breakthrough Time (BT)</u>			
AsF_5 , hrs	18	13	15
UF_6 , hrs	.25	.08	2.33
<u>Estimated Loading at BT</u>			
AsF_5 , %	22.1	15.9	19.4
<u>Total Run</u>			
Time, hrs	19	14	16
Estimated Loading AsF_5 , %	23.4	17.2	20.7
<u>Bed Analyses^a</u>			
AsF_5 , %	24.2	16.4	20.3
UF_6 , %	0.6	0.7	19.2

a. Based on initial bed weight.

AsF_5 breakthrough occurred on the 400°F run after 18 hr of running time. The calculated loading factor was 22.1% AsF_5 based on the initial bed weight. The run was continued beyond breakthrough for 1 hr, and bed analysis showed 24.2% AsF_5 based on the initial bed weight. Analysis showed UF_6 concentrations matching the inlet concentrations very soon after the run was started. Bed analysis at the end of the run showed only 0.6% UF_6 remaining on the material.

Higher bed temperatures may be required to get above the dissociation pressure, depending on the UF_6 concentration; thus, a run was made at 500°F. Breakthrough occurred after 13 hr, giving a calculated loading factor of 15.5% AsF_5 . Bed analysis after a total of 14 hr showed 16.4% AsF_5 and 0.7% UF_6 based on the initial bed weight. These two runs show that AsF_5 can be selectively removed while allowing UF_6 to pass through the trap at low partial pressures of UF_6 .

The third test involved loading a NaF trap at 200°F with both AsF₅ and UF₆ and regenerating the bed to see if the UF₆ and AsF₅ could be separated. The gas mixture, which averaged 980 ppm AsF₅ and 555 ppm UF₆, was fed into the test trap heated at 200°F. Very low levels (~13 ppm) of UF₆ were seen exiting the trap by IR after 2:20, and low concentrations remained in the effluent of the trap for several hours: 22 ppm after 10:00, 50 ppm after 12:00, and 119 ppm after 14:00. This is shown in Figure 3. During previous tests involving only UF₆ and N₂, the UF₆ concentration in the outlet increased at a much more rapid rate after breakthrough than observed in the presence of AsF₅. AsF₅ breakthrough occurred at 15:00 with a level of 39 ppm and a UF₆ concentration of 169 ppm. The test lasted for 16 hr, with a final outlet concentration of 61 ppm AsF₅ and 197 ppm UF₆. The 113.6 g initial bed weight had increased 41.3%. Estimated loading at breakthrough based on inlet concentration, time, and initial bed weight was 19.4% AsF₅. The estimated feed for the entire run was 23.5 g AsF₅ and 27.6 g UF₆.

At the conclusion of the test, a regeneration was performed with a system setup as shown in Figure 4. A N₂ purge with ~2% F₂ was fed through the test trap heated at 600°F. The outlet stream was sent through an IR cell, a second clean NaF trap (operated at ambient temperature), and two liquid bubblers in series. The test trap was heated at 600°F for ~4 hr. No AsF₅ was detected in the off-gases by the infrared. At the conclusion of the regeneration, the bubblers were analyzed and showed the outlet gas concentration from the second trap to contain <2 ppb AsF₅ and UF₆ in the low ppb range. The bed material from the test trap was analyzed to contain 20.2% (22.9 g) AsF₅ and 0.09% (0.11 g) UF₆, and the material from the receiver trap contained 0.01% (0.01 g) AsF₅ and 19.08% (26.4 g) UF₆. This work shows that UF₆ and AsF₅ can be separated in the regeneration phase.

AsF₅ in UF₆ Studies

The next set of tests was directed at high concentrations of UF₆ containing low levels of As. As a source of material to perform this work, ten 800-cc Monel cylinders were filled from a 14-ton contaminated feed cylinder. This feed material was reported to have significant levels of AsF₅ and HAsF₆. The ten small containers were taken in the same liquefaction of the feed cylinder. Each of the small cylinders were liquid sampled for As analysis, and the results are summarized in Table 3.

Table 3. As analysis of subsamples from a feed cylinder.

Sample Order	Transfer Number	First Sample μg As/g U	Second Sample μg As/g U
1	447058	2.7	2.4
2	447059	3.9	
3	447060	3.9	
4	447061	2.9	2.3
5	447062	3.3	
6	447063	2.8	
7	447064	6.2	2.7
8	447065	5.7	
9	447066	3.7	
10	447067	8.0	6.7

UF_6/AsF_5 TRAPPING ON NaF AT 200°F

Figure 3

4 HR REGENERATION AT 600 °F

ORIGINAL TRAP
 (22.9g) 20.2% As F₅
 (0.11g) 0.09% UF₆

RECEIVER TRAP
 (0.01g) 0.01% As F₅
 (26.4g) 19.08% UF₆

200°F NaF TEST - REGENERATION

Figure 4

These data show a concern in feed cylinder sampling. The last containers drawn from the feed cylinder had higher levels of As than the first. This suggests a possible sampling system conditioning problem. Liquid resamples of the small cylinders for As were in fair agreement as indicated in the table.

At an earlier date and different liquefaction, two small cylinders were drawn from the same feed cylinder as the ten cylinders just discussed and were liquid-sampled for As. These analyses showed 9.4 and 7.8 $\mu\text{g As/g U}$.

Duplicate trapping tests were conducted at NaF bed temperatures of 200°F, 400°F, and 550°F using selected cylinders from those listed in Table 3. As shown in Figure 5, the contents of one of the selected containers were transferred through a NaF trap and collected in a second clean cylinder. The supply cylinder was placed in a heated water bath, and the UF_6 flow was maintained at 650 sccm with a system pressure of 200 mm Hg. The flow was directed through a NaF trap (at 200°F, 400°F, or 550°F) and collected in the receiver cylinder cooled in a Freon/dry ice slush. The feed cylinder was liquid-sampled for As prior to the test, and the receiving cylinder was liquid-sampled after the test. The NaF trap material was ground, blended, and sent for analysis also after the test. A sample of clean NaF (unused) was sent for As analysis and was found to contain a background level of 4.29 $\mu\text{g As/g}$.

Table 4 presents the data from the cylinder tests. Prior to these tests, the system was conditioned with fluorine, purged with N_2 , and a blank run was made with clean UF_6 ($<0.1 \mu\text{g As/g U}$) through an empty trap at 200°F and into a clean cylinder. The analysis of the receiving vessel showed 3.6 $\mu\text{g As/g U}$ or 0.0037 g As, thus indicating a contamination problem from the flow system (used in the previous AsF_5 trapping tests) even after the fluorine treatment. The contamination problem appeared also in the first three runs, with more material caught than was fed as evidenced in the material balance column of the table. The problem appeared to be abating by the third run with only 0.00001 g As in the cold trapped material. After the tests, another blank run was made with clean UF_6 and only 0.2 $\mu\text{g As/g U}$, or 0.00017 g As was found in the cold trap, the same amount as was found in the last test conducted at 200°F. The last three runs showed a drop in the material balance with each successive run and cannot be explained unless the As was being lost to the system.

Table 4. Summary of trapping tests using contaminated feed UF_6 .

Test Sequence	Temp. °F	Feed g As	Cold Trap g As	NaF Trap		As Reduction %
				g As	g U	
1	200	0.0061	0.0044	0.0091	96.3	27.8
2	400	0.0056	0.0010	0.0065	96.6	82.1
3	550	0.0085	0.00001	0.0125	104.7	99.9
4	550	0.0047	0.00032	0.0028	99.6	93.2
5	400	0.0037	0.00043	0.0012	94.5	88.4
6	200	0.0028	0.00017	0.0009	88.1	93.9

CONDITIONS

SYSTEM PRESSURE: 200 MM Hg
 FLOW: 650 SCCM
 NaF TRAP TEMPERATURES: 200°F; 400°F 550°F

ANALYSIS

FEED MATERIAL - PRIOR TO TEST
 BED MATERIAL - AFTER TEST
 COLLECTOR MATERIAL - AFTER TEST

AsF₅ IN UF₆ STUDIES - CLOSED SYSTEM

Figure 5

The percent reduction shown in Table 4 is a ratio of the difference of the As in the feed minus the amount in the cold trap divided by the amount in the feed. The reduction is significant in the later runs with an average of about 91% of the As being removed from the UF_6 .

It appears that the NaF will trap As even when loaded with UF_6 . The NaF was loaded with UF_6 in the first few minutes of these tests but appeared to trap As through much of the run. Operating temperature of the bed did not appear to have much effect.

AsF₅ SEPARATION FROM HF

AsF₅/N₂ Mix in HF

After the UF_6/AsF_5 trapping studies, efforts were made to see if NaF would trap AsF_5 in HF. Prior to these experiments, clean HF was passed through the flow system in an attempt to remove any As deposited in the flow system from previous tests. In three tests, performed at temperatures of 200°F, 600°F, and 400°F, a mixture of 5.8% AsF_5 in N_2 was blended with HF in the flow system for a final estimated inlet gas concentration of ~500 ppm AsF_5 and superficial velocities of 0.62, 1.0, and 0.81 ft/sec, respectively. Total flows were constant in these runs and, thus, the different bed temperatures caused the velocity to change. The first test was conducted at 200°F, but had a temperature excursion of 187°F early in the test as the NaF was being converted to NaHF_2 . The run lasted 5 hr and the trap material had a weight gain of 42.9%. Theoretical weight gain for conversion of NaF to NaHF_2 is 47.6%. An estimated 1.57 g of As was fed based on flow system measurements, concentration of the inlet gas, and time of the run. The NaF bed at the conclusion of the run was analyzed to contain 0.95 g or 60% of the estimated As fed. Some of the As may have been deposited in the flow system piping and valves before reaching the trap.

The second test was conducted at 600°F with the same gas composition as in the previous run but a higher (1.0 ft/sec) superficial velocity. There was no temperature excursion and only 0.2% weight gain on the bed at the conclusion of the test. The run lasted for 11 hr with an estimated 3.45 g of As fed and 1.99 g trapped on the NaF or ~58% of the estimated As fed.

After this test, an attempt was made to clean the flow system. A 1.5% F_2 in N_2 gas was passed through the system and empty trap at 200°F. The outlet stream was scrubbed through two liquid bubblers in series, each containing ~500 mL of water. The F_2 purge lasted for 1 hr, and 7.5 mg of As was found in the bubblers. Then a 2.1% ClF_3 in N_2 purge was used for 1 hr and 290 mg of As were retained in the bubblers. Finally a 1% UF_6 in N_2 purge removed 12 mg of As. So in all, 310 mg of As were removed from the flow system with 94% being removed by ClF_3 , thus suggesting that ClF_3 is a better cleaning gas than F_2 or UF_6 for As.

The third test in this series was conducted at 400°F, again with the same inlet gas concentration as in the previous two tests. A temperature increase of 79°F was incurred and a weight gain of 44.7% was experienced due to conversion to NaHF_2 . The run was terminated after 5.26 hr due to plugging in the bed which was believed to be caused by the pellets swelling on conversion to NaHF_2 . Analysis showed 0.71 g As trapped on the bed, as compared to an estimated 1.65 g feed, for a 43% removal efficiency. Trouble maintaining

flow levels occurred during this run due to the plugging, so the estimated feed may be low; or the fact that the flow system was clean prior to this test may have resulted in more As being lost back to the flow system.

Fourier Transform Infrared Spectrophotometer (FTIR) Identification of As Compounds

Attempts were then made to identify As compounds in high concentrations of HF with the use of an FTIR. After the FTIR was conditioned for AsF_5 , HF was introduced. As the HF concentration increased, the AsF_5 level decreased and a peak identified as HAsF_6 increased (at certain concentrations, both As compounds were apparent). As the HF concentration continued to increase, the AsF_5 disappeared and eventually the HAsF_6 peak also disappeared. No other peaks, indicating another compound, were found except a window band that increased in size.

Segregated Bed

The next experiment was with a segregated bed. The trap bed was divided into five zones separated by screens. Each zone was weighed before and after the test. The run was conducted at 600°F , with an inlet concentration estimated at 50 ppm AsF_5 in HF and a superficial velocity of 1 ft/sec. The test lasted for 14.5 hr. Analysis, as shown in Table 5, revealed 76% of the As trapped was in the inlet zone and 0.4% was in the outlet zone. The amount of As trapped was 98% of the estimated feed.

Table 5. As in HF -- segregated NaF bed.

Zone	Wt., g	ppm As	g, As	% Total
Inlet	22.3	15,746	0.3511	75.8
2	23.6	4,044	0.0954	20.6
3	20.4	430	0.0088	1.9
4	21.4	270	0.0058	1.2
Outlet	21.4	90	0.0019	0.4
TOTAL:				0.4631

NOTE: A segregated NaF bed test was made at 600°F , 3500 sccm flow, and estimated inlet concentration of 50 ppm AsF_5 in HF.

Estimated total As fed based on 50 ppm inlet concentration is 0.4733 g.
Amount trapped is 97.8% of estimated fed.

Closed System Tests

Due to apparent analytical problems and/or system conditioning problems which were giving inconsistent material balances, it was decided to perform closed system tests as shown below:

- Mix of approximately 100 ppm AsF_5 in HF was prepared in a Monel cylinder.
- A liquid sample of the mix was taken and sent for analysis.
- The mix was transferred through a NaF trap to a cold trap (liquid N_2 temperature) at a controlled flow rate.
- The receiving cold trap was liquid-sampled for analysis and the NaF trap ground, blended, and sent for analysis.
- A blank run with HF only was made at the beginning and end of the series of tests.
- Tests were made at bed temperatures of 200°F and 600°F with NaF and NaHF_2 .
- During the 200°F runs, the NaF was converted to NaHF_2 during the first 40 min of run time with bed zone temperatures increasing by approximately 100°F or more.

A summary of the tests is shown in Table 6.

Table 6. Closed system tests.

Run No.	23	24	25	26	27 ^b
Temp., °F	Blank	200	600	600	200
Flow, sccm		3500	3500	2152	3500
Pressure, mm Hg		~760	~760	~760	~760
Velocity, ft/sec		0.62	1.0	0.62	0.62
Initial Bed Wt. g		114.5	113.6	113.4	111.4
Wt. Change, %		+43.8	-3.9	-2.8	+46.2
Start HF, ppm As ^a	<20	130	160	126	577
Final HF, ppm As ^a	66 ^d	26	29	22 ^d	22 ^d
% Removal		80	82	83	96
Bed, ppm As		16	160	103	4.7 ^c
Expected Bed Conc., ppm As		320	671	492	1651
Material Balance, %		22	38	35	3

a. By weight.

b. Sample sent for feed analysis was passed through a 60-micron, sintered, stainless steel filter.

c. 4.3 ppm of As is background level on NaF.

d. No As compounds were detected by IR analysis.

In the blank or first run, clean HF was flowed through the system and an empty trap at 200°F. The HF contained 66 ppm As at the conclusion showing As was being removed from the system by HF. Run 24 was conducted at 200°F and a superficial velocity of 0.62 ft/sec. For the first 40 min of the test, the cold trap was valved off as the HF was being absorbed on the bed and the NaF was being converted to NaHF₂. Analyses of the starting and ending HF showed concentrations of 130 ppm and 26 ppm As, respectively, or an 80% removal. The NaF bed contained only 16 ppm for a 22% material balance.

The next run (No. 25) was at 600°F and a superficial velocity 1 ft/sec. The starting HF contained 160 ppm of As and the cold trap at the conclusion contained 29 ppm of As, for an 82% removal. The material balance was again low, accounting for only 38% of the total As. The third test (No. 26) was also conducted at 600°F, but the velocity was lowered to 0.62 ft/sec by decreasing the total flow. The feed HF contained 126 ppm of As and the receiver HF contained 22 ppm of As, for a reduction of 83%. The material balance was 35%.

In the next test (No. 27), the feed was subsampled through a 60-micron, sintered, stainless steel filter. The As level in the feed was expected to be lower based on information from a feed producer that by filtering feed cylinder samples the As was reduced. However, the As concentration in this mix was actually much higher than the previous three mixes. After the test the cold trap material contained 22 ppm As for a reduction of 96%, but the material balance was only 3% because little or no As was detected on the NaF. Cylinder washings of three of the feed cylinders used in this series of tests contained 49 mg to 70 mg of As, which accounts for much of the material imbalances. Apparently the AsF_5 is combining with the HF or with the metal fluoride surfaces of the cylinder, leaving behind a low-volatile As compound.

Two-Trap Tests

The two-trap tests were conducted to determine if a reduction of As levels could be achieved in the receiver cold trap greater than those obtained by a single trap. In an effort to condition the system, the feed cylinder and the entire flow system up to the trap inlet were pretreated with 1% AsF_5 in N_2 mixture prior to the mixing and start of these tests. The results of these two runs are shown in Table 7. The first test was made by feeding a cylinder containing 194 ppm of As (liquid-sampled) in HF through two NaF traps in series at 600°F. The run was terminated when the system pressure was too low to maintain a feed rate of 3500 sccm. At the end of the run, the two NaF traps were evacuated to ~200 mm Hg with a vacuum pump. There was an 89% cleanup of the As from the HF in one pass through the trapping system.

The next test was similar to the previous except NaHF_2 was used instead of NaF and was heated to only 200°F. The run was terminated before the system pressure fell below 760 mm Hg. The primary and secondary traps showed 15 ppm and 10 ppm of As as shown in Table 7. Several samples of unused NaHF_2 pellets from different batches and drums were sent for As analysis, and the average value was 7.8 ppm As. Therefore, very little As was either getting to the traps or the trapping media was not effective in removing this material. Reduction in the As level in the HF based on liquid samples was 96%.

Empty Trap Tests

Since very little As was found on the trapping materials, it appeared that the trapping media was not instrumental in As removal. Therefore in the next two tests, runs were made with the trap empty. The feed cylinder was placed in a water bath at ~100°F and the HF was fed through the flow system at 3500 sccm to a receiver cold trap. A liquid subsample of the feed was made prior to the test, and a liquid subsample of the receiver was made at the conclusion of the run. A summary of these two runs is shown in Table 8. The feed cylinder was rinsed with water at the end of the test, and the rinse was found to contain 54% of the As originally present in the feed cylinder based on the liquid sample analysis. Therefore, a majority of the As never left the feed container. The material balance, including the cylinder wash, was 67%.

Table 7. Results from two-traps in series tests.

Trap Media	Trap Temperature °F	Feed Liquid (ppm As) g As	Primary Trap (ppm As) g As	Secondary Trap (ppm As) g As	Receiver Liquid (ppm As) g As	As in HF Reduction %	Material Balance %
NaF ^a	600	(194) 0.0892	(220) 0.0238	(40) 0.0043	(21.7) 0.0099	89	43
NaHF ₂ ^b	200	(184) 0.0777	(15) 0.0024	(10) 0.0015	(7.5) 0.0031	96	9

a. NaF -- Arsenic background level - 4 ppm.

b. NaHF₂ -- Arsenic background level - 8 ppm.

Table 8. Results from empty trap tests.

Test No.	Trap Temperature °F	Run Time Minutes	Feed Liquid (ppm As) g As	Receiver Liquid (ppm As) g As	Rinse Feed Cylinder g As	As in HF Reduction %	Material Balance %
30	200	180	(83) 0.0507	(11) 0.0068	0.0273	87	67
31	200	0	(66) ^a 0.0386				
		45	(98) 0.0416				
		90	(159) 0.0298				
		125		(4) 0.0017	0.0193	96	104

a. At timed intervals, liquid samples of the feed were tested for arsenic levels.

The second run of this series was conducted as the prior run except intermediate subsamples of the feed cylinder were made at timed intervals during the run. As shown by the feed concentrations in Table 8, the As remained behind while the HF was being vapor fed. These tests would indicate that the As and HF are forming a low-volatile compound that is left in the feed container when the HF vapor is fed. The compound is soluble in HF since the As appears in the liquid subsamples.

At the conclusion of the run, the cold trap contained only 4 ppm of As, or a reduction of 96%. After rinsing the cylinders and deducting the material lost for subsampling, the material balance was 104% with 50% of the As initially found in the feed cylinder (based on the liquid subsample) being present in the feed cylinder rinse at the conclusion of the run.

Cylinder-to-Cylinder (No Trap) Tests

The next two tests were conducted in a manner similar to the previous tests, except the HF was fed directly to a cold trap in an effort to reduce the system's total surface area. These results are shown in Table 9. In the first test, the water bath containing the feed cylinder was at $\sim 82^{\circ}\text{F}$. After feeding for 3 hr the system pressure was down to 750 mm Hg, the cold trap was removed, and a fresh cold trap was installed. The feed material was then flowed through a NaF trap at 200°F to the new cold trap. The objective of this test was to attempt to evacuate the As from the feed cylinder after the HF had been fed. Analysis showed 27 ppm As in the first trap, 15 ppm As on the NaF trap material, and an insignificant amount of As in the second cold trap. The effective As removal for the run was 97%. The feed cylinder rinse contained 175% of the amount of As originally present in the cylinder based on the initial liquid sample. The evacuation did not remove the As from the feed cylinder. Apparently the liquid sample did not represent all of the As in the cylinder. Since the feed cylinders in these current tests have higher levels of As than in the earlier work, perhaps this indicated that the As solubility level has been exceeded.

The second test was operated in the same manner as the previous except NaHF_2 was used as a trapping media after the system pressure was below ~ 760 mm Hg and, also at that point, the temperature of the water bath holding the feed cylinder was increased to 136°F in order to attempt to remove more As. At the conclusion of the test, the first cold trap contained 13.6 ppm As and the feed cylinder rinse contained 119% of the original amount of As calculated to be in the feed at the onset based on the liquid sample analysis. This shows an effective removal of 96% of the As from the feed HF. The NaHF_2 contained 15 ppm As. Once again the As could not be removed from the cylinder by evacuation. Perhaps if the feed cylinder was heated to a higher temperature than was possible in the current setup, the As could be evacuated.

Nickel Test

This experiment was conducted with the same setup as the other closed-system tests except Ni chips were used as the trapping media. The trap was loaded with 37.7 g of Ni U-shaped porous metal pieces. The test was

conducted at 600°F with a gas velocity of ~0.5 ft/sec. The feed HF contained 543 ppm As (0.1893 g) based on a liquid sample prior to the experiment. The flow began to decrease after 2:48 of run time, and the test was terminated at 3:28 with 200 mm Hg of system pressure. The results are shown in Table 10.

At the conclusion of the run, the receiver was analyzed to contain 72.8 ppm As (0.0249 g) or 13% of the As originally in the feed cylinder. The material balance was 90% for the test. A water rinse of a portion of the used Ni trap material showed an insignificant amount of As. This indicates that the Ni-As complex is not soluble in appreciable quantities in water. Therefore, it appears that the As rinsed from the feed cylinders after the HF has been vaporized in previous experiments is not complexed with the Ni in the cylinder walls like the As on the Ni trap material.

Filter Test

The objective of the filter investigation was to determine if an in-line filter would reduce the As level in a liquid sample. In the first sampling, a 60-micron stainless steel filter was placed in-line and the manifold was rinsed three times with the HF prior to taking a liquid sample. After taking the sample, the filter was viewed through a microscope. Large areas of white material could be seen on the inner surface (the outer surface was relatively clean). The liquid feed sample passing the filter contained 430 ppm As.

The last sample was taken through a 5-micron Ni filter placed in-line. The manifold was again rinsed three times with the material prior to subsampling. After sampling, many of the pores on the inlet side of the filter were clogged with a beige color material, a few white irregular chunks, and two long strands of white material. The filter was almost plugged. The outlet side of the filter appeared relatively clean. Analysis of the material on the filter showed uranium and Ni products. The liquid feed sample contained 431 ppm As. Therefore, it appears that the As complex is not a particulate but is soluble.

CONCLUSIONS

Some general conclusions and observations on the behavior of AsF_5 from the scoping tests were made. NaF and Al_2O_3 appeared to be the most promising trapping agents for As. Generally, the As loading was affected by temperature with higher loadings at higher temperatures. The water bubblers were not effective for scrubbing out AsF_5 with only up to an 80% efficiency. White smoke in the bubblers was a good indicator of AsF_5 breakthrough of the trap.

In a gas stream of UF_6 (low partial pressure) and AsF_5 in N_2 , the gases can be separated by a NaF trap (operated at temperatures of 400°F to 500°F) by allowing the UF_6 to pass through and retaining the AsF_5 . Regenerations at 600°F show that on NaF beds loaded with both UF_6 and AsF_5 , the UF_6 can be removed and the AsF_5 will remain on the NaF .

Table 9. Results from cylinder-to-cylinder tests.

Test No.	Feed Cylinder >760 mm Hg		Trap Media	Feed Cylinder <760 mm Hg			As in HF Reduction %
	Feed Liquid (ppm As) g As	Receiver Liquid (ppm As) g As		As in Trap (ppm As) g As	Rinse Secondary Receiver g As	Rinse Feed Cylinder g As	
32	(360) 0.180056	(27) 0.011752	NaF	(15) 0.00203	0.00036	0.313508	97
33	(295) 0.14574	(13.6) 0.006537	NaHF ₂	(15.3) 0.00234	0.00049	0.173217	96

Table 10. Results from Ni trapping media tests.

Test No.	Feed Liquid (ppm As) g As	Receiver Liquid (ppm As) g As	Trap Media	As in Trap (ppm As) g As	Rinse Feed Cylinder g As	As in HF Reduction %
34	(543) 0.1893	(2.65) 0.0011	Ni saddles	(403) ^a 0.0150	0.1447	99

a. Water rinse of trap material after exposure did not remove the arsenic from the Ni.

The AsF_5/UF_6 tests using actual contaminated feed material showed that low As levels in UF_6 could be significantly reduced by employing a NaF trap. As deposits in the flow system and lines from previous tests was a contamination concern in this investigation. As trapping appeared to continue even after the NaF was loaded with UF_6 .

Removing all of the As in gaseous HF with chemical traps was not entirely successful, but vapor feeding liquid HF from one container and condensing in another can result in significant separation, with up to 97% of the As remaining in the feed cylinder. Discrepancies in the As levels in initial liquid subsampling of feed and the water rinse after the HF had been fed indicate that in HF with high levels of As, the liquid subsample was not truly representative of all of the As in the cylinder and that perhaps the As solubility limit had been exceeded. Evacuation of the feed cylinder after the vapor transfer of the HF does not remove the As remaining in the cylinder. Heating the cylinder while evacuating may be effective if done at higher temperatures than were possible with the experimental setup in this study. A water rinse was capable of removing the As from a cylinder after feeding. Ni trap material removed some As from the gaseous AsF_5/HF mixture stream.

Liquid sampling of the AsF_5/HF mix through 5- and 60-micron filters did not reduce As levels in the samples, indicating the As to be in solution.

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