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# Chemical Conversion of Anhydrous Hydrogen Fluoride for Safe Disposal

**June 2018**

TA Blake  
CS Brauer

WJ Bachmann, Jr.



Prepared for the U.S. Department of Energy  
under Contract DE-AC05-76RL01830

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Richland, Washington 99352



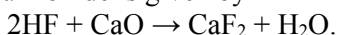
## Abstract

A procedure for the safe conversion of a small (~ 1 gram) quantity of anhydrous hydrogen fluoride to calcium fluoride is described. The purpose of the conversion is to put the toxic, corrosive, gaseous compound into a chemical form that is a less toxic solid (calcium fluoride) and easier to dispose of. The hydrogen fluoride, which was contained in a 50 cc metal sample cylinder, was drawn by a small mechanical vacuum pump through an all-metal gas manifold and into a metal trap containing alternating layers of calcium oxide powder and Teflon turnings. The anhydrous hydrogen fluoride reacts with the calcium oxide to produce calcium fluoride and water vapor. Because some of the calcium oxide powder was drawn out of the trap and into the vacuum tubing, it was not possible to quantify the amount of anhydrous hydrogen fluoride converted to calcium fluoride. However, it was noted that there was a temperature rise in the trap when the gas was flowing through it, and no HF gas was detected at the vacuum pump exhaust at this time using a colorimetric Dräger tube. The trap was sealed and disposed of as solid chemical waste.



## Summary

The report describes a procedure for chemically converting a small quantity (initially estimated to be 6 grams) of anhydrous hydrogen fluoride to a more benign material that can be more easily disposed of. The hydrogen fluoride was stored in a non-DOT-approved, 50 cc stainless steel sample cylinder and could not be easily transported off-site for disposal. It was decided by the researchers and PNNL Facilities and Operations personnel that the safest and most cost effective method for disposal would be treatment-by-generator. This treatment-by-generator procedure involves flowing the anhydrous hydrogen fluoride from its sample storage cylinder, into an all-metal gas manifold, and then through a trap containing calcium oxide where the HF reacts to form calcium fluoride and water vapor. A small vacuum pump on the downstream side of the trap would be used to pull the HF into the trap. The reaction between anhydrous hydrogen fluoride and calcium oxide is given by



A mass of 30 grams of calcium oxide was used in the trap. The reaction is exothermic, so a temperature rise and a mass change of the calcium oxide in the trap would be indicative of the desired chemical change. The mass of the trap was carefully measured before the reaction took place.

A detailed description of the gas manifold, trap, valves, pressure gauges, and vacuum system is given. The sample cylinder containing the anhydrous hydrogen fluoride was attached to the gas manifold and the gas was flowed through a needle valve to regulate the flow into the manifold and then into the trap. The needle valve was calibrated and set during the chemical conversion so that the trap would not overheat. The equipment was leak tested with a helium leak checker before the valve to the sample cylinder was opened. The lab and fume air were checked before and after the sample cylinder was attached to the manifold for trace hydrogen fluoride vapor using a colorimetric Dräger tube. No hydrogen fluoride was detected. The sample cylinder was checked for hydrogen before proceeding with the chemical conversion. This was done by opening the sample cylinder to the manifold, noting the pressure in the manifold and then cryopumping the gas back into the sample cylinder at liquid nitrogen temperature. Since all the gas in the manifold pumped back into the sample cylinder, we determined that there was no hydrogen present in the cylinder. We also noted that the pressure in the manifold, which has a volume of 676 cc, was 115 Torr at 21.5 °C. This is far less pressure than we anticipated for an HF sample of 6 grams.

Once these checks and tests were completed, the chemical conversion reaction was started. With the needle valve set to a minimum flow, the valve between the gas manifold and the calcium oxide trap open, and the system evacuated up to the shut-off valve just above the sample cylinder, the shut-off valve on the sample cylinder was opened. There was a slow rise in pressure at a thermocouple gauge just above the vacuum pump. The needle valve was opened slightly more and the pressure rose to a maximum 1500 mTorr. The temperature of the trap rose 1.5 °C above ambient. A Dräger tube reading was made at the outlet of the vacuum pump at this time and no HF was detected. Within 10 minutes of this surge in pressure and temperature rise, the pressure and temperature began to drop. The needle valve was opened further and the sample cylinder was pumped on for another two hours.

With the reaction complete, the sample cylinder was removed from the manifold and checked with a Dräger tube. No HF was detected in the tube. The sample cylinder was weighed and it was determined that the mass of HF in the cylinder had been 0.37 grams. The trap was weighed and it was determined that it had lost about 2.6 grams of mass. Some of the CaO/CaF<sub>2</sub> powder was found inside the vacuum tubing downstream of the trap. The trap was sealed and disposed of as solid waste.

The pressure surge accompanied by the temperature rise in the trap seemed to indicate that the conversion reaction had taken place. And the fact that no hydrogen fluoride vapor was detected by the Dräger tube readings at the vacuum pump exhaust at this time, suggests that there was complete conversion of the hydrogen fluoride.





## **Acknowledgments**

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## Acronyms and Abbreviations

atm	atmosphere
cc	cubic centimeters
°C	temperature, Celsius unit
CaF <sub>2</sub>	calcium fluoride
CaO	calcium oxide
CFM	cubic feet per minute
cm	centimeter
DOT	Department of Transportation
ΔT	temperature change
g	grams
H <sub>2</sub>	hydrogen
HF	hydrogen fluoride
H <sub>2</sub> O	water
ISO	International Organization for Standardization
K	temperature, Kelvin unit
kg	kilograms
kJ	kilojoule
K-type thermocouple	chromel-alumel thermocouple
L	liter
LSL2	Life Sciences Laboratory-2
MKS	MKS Instruments, Inc.
mTorr	milliTorr
N <sub>2</sub>	nitrogen
OD	outside diameter
PNNL	Pacific Northwest National Laboratory
P/N	part number
ppm	parts per million
psig	pounds per square inch gauge
PTFE	polytetrafluoroethylene
QF	Quick flange, a quick release ISO flange
T	temperature
TC	thermocouple

TWA	time weighted average
Torr	Torricelli, unit of pressure, 1 Torr = 1/760 atmosphere
VCR	a Swagelok, Inc. trademark name for a metal seal vacuum fitting

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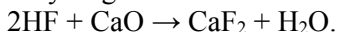
## 1.0 Introduction

This report describes a procedure for chemically converting a small quantity (6 grams; estimated by cylinder weight) of anhydrous hydrogen fluoride to a more benign material that can be more easily disposed of than the gaseous HF. The hydrogen fluoride is stored in a non-DOT approved, 50 cc stainless steel sample cylinder and could not be easily transported off-site for disposal. It was decided by the researchers and PNNL Facilities and Operations personnel that the safest and most cost effective method for disposal would be treatment-by-generator (see appendix A). This treatment-by-generator procedure involves flowing the anhydrous hydrogen fluoride from its sample storage cylinder, into an all-metal gas manifold, and then through a trap containing calcium oxide where the HF will react to form calcium fluoride and water vapor. [1, 2] A small vacuum pump on the downstream side of the trap would be used to pull the HF into the trap. See Fig. 1.1.



**Figure 1.1** This photo shows the gas manifold, sample cylinder and needle valve used for storing and flowing the anhydrous hydrogen fluoride from the sample cylinder into the trap (not shown). The manifold is located in a fume hood.

The reaction between anhydrous hydrogen fluoride and calcium oxide is given by



The 6 grams of HF is 0.3 moles of material reacting with 0.15 moles (8.4 grams) of calcium oxide to produce 0.15 moles (11.7 grams) of calcium fluoride and 0.15 moles (2.7 grams) of water. The trap will be filled with 30 grams of calcium oxide to ensure complete reaction of the hydrogen fluoride. The reaction is exothermic, so the flow of the HF through the trap will have to be controlled and the temperature of the trap monitored. The water vapor may react with the calcium oxide to produce calcium hydroxide. Using the heats of formation and the molar quantities given above, the heat of reaction will be -49.8 kJ. The heat capacity of stainless steel is 0.5 kJ/(kg K), so the temperature rise of the 0.85 kg stainless steel trap will be  $\Delta T = 49.8 \text{ kJ} / [(0.5 \text{ kJ}/(\text{kg K})) \times 0.85 \text{ kg}] = 117 \text{ K}$ . So the temperature rise would be considerable if all the HF were to be flowed through the trap at once. We will flow the HF at a rate that will allow convection to dissipate the heat from the trap. The temperature of the trap will be monitored with a thermocouple (Fluke 52 II, K-type thermocouple).

This report describes a procedure used to chemically react a small quantity of anhydrous hydrogen fluoride so that it may be disposed of safely. The equipment and procedure are described in

considerable detail. *However, this report should not be used as a “How to Manual” for chemical conversion and disposal of anhydrous hydrogen fluoride.* Each disposal scenario will depend on the amount of HF, the available gas handling equipment, the available first aid and monitoring equipment, the experience of the staff performing the work, and facility rules and regulations. *Anhydrous hydrogen fluoride is an extremely dangerous material.*

## 2.0 Equipment and Setup

The gas manifold where the chemical conversion will take place is located in the south wall fume hood in the LSL2 building, room 1432. The manifold body is made of stainless steel and has a volume of 676 cc. Connections to the manifold are made with ¼" VCR fittings and Monel ball valves (Whitey M-43VCR4). The exhaust port of the manifold, which leads to the mechanical vacuum pump via stainless steel flex tubing, is sealed with a welded bellows valve (Swagelok SS-8BK-VCR) with ½" VCR fittings. The manifold has a 150 psig pressure relief valve. A 15 psig pressure relief valve is below the exhaust valve to protect the vacuum pump inlet from overpressure. Both relief valves are Swagelok SS-RL3M4 and are adjusted and calibrated for their respective release pressures. Pressure in the manifold is measured with 10,000 and 1000 Torr capacitance manometers (MKS Instruments, Inc.) and a thermocouple gauge (MKS). One port on the manifold is connected to a nitrogen cylinder. Nitrogen is used to pressure test the tubing connections and to flush out the cylinders and manifold. The fume hood is a constant air volume hood with a nominal flow rate of 775 CFM.

The calcium oxide trap consists of a 5" long stainless steel nipple with QF40 ISO flanges. The inside diameter of the nipple is 1-3/8". The trap is shown in Fig. 2.1. Each end of the nipple has a QF40 to QF25 reducing adapter. The reducing adapters are held in place with centering rings with Viton O-rings and clamps. The trap is packed, starting at the bottom, with a wad of copper wool 2 cm thick (see Fig. 2.2), Teflon (PTFE) chips 1 cm thick (see Fig. 2.3), 15.0 grams of calcium oxide, lightly packed, Teflon (PTFE) chips 1 cm thick, 15.3 grams of calcium oxide, lightly packed, Teflon (PTFE) chips 1 cm thick, and finally another wad of copper wool 2 cm thick at the top. The top side of the trap is connected to the exhaust port valve on the manifold by an 18" length of ½" OD stainless steel flex tubing with a swage fitting at each end.



**Figure 2.1** The assembled trap with calcium oxide, copper wool and Teflon chips. The total mass, prior to running the reaction, is 908.55 grams.

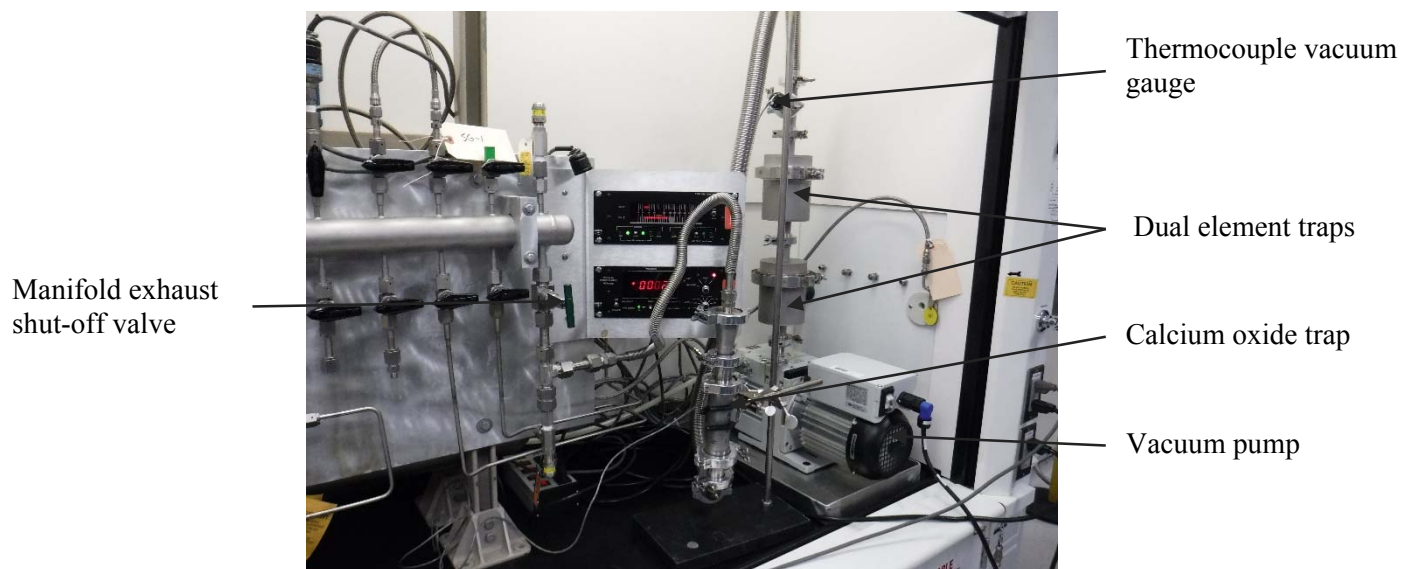


**Figure 2.2.** Copper wool. The copper wool was taken from an unused vacuum trap (MDC Vacuum Products, Corp. P/N 433055).



**Figure 2.3** Teflon (PTFE) turnings. The Teflon was purchased from McMaster-Carr as a 2" diameter rod, 1 foot long, and was turned on a lathe in a PNNL machine shop. The turnings were washed in acetone and then isopropyl alcohol baths and allowed to dry. The turnings were then cut into 1 cm lengths using scissors. The resulting chips were used in the trap.

The exhaust side of the calcium oxide trap is connected to the mechanical vacuum pump (Leybold Trivac D8B, nominal pumping speed 6.9 CFM) by a 6' length of 1" ID, stainless steel flex tubing with NW25 flanges. This tube connects to a stack of two exhaust traps (MKS P/N 433060) on top of the vacuum pump. These traps are dual element activated charcoal and fiberglass that are used primarily to prevent back-streaming of pump oil back into the calcium oxide trap and the manifold.



**Figure 2.4** Photograph of the fume hood interior with manifold, vacuum line, traps and vacuum pump.

The 50 cc sample cylinder with welded bellows valve (Swagelok SS-4BRW-WY4) containing the anhydrous hydrogen fluoride is attached to the gas manifold through a needle valve (Swagelok 4BMRW-VCR; regulating stem tip),  $\frac{1}{4}$ " VCR fittings, and a Monel ball valve. The manifold, trap, valves and vacuum pump are shown in Fig. 2.4. The sample cylinder and its needle valve and shut-off valve are shown in Fig. 2.5. To test the flow of gas from the sample cylinder through the valves, the trap and out the pump, we replaced the sample cylinder containing the HF with an identical, empty cylinder. We put 1 atm of air into the sample cylinder, set the opening on the needle valve to a certain setting, evacuated the manifold, and then opened the valve on the sample cylinder and started a timer. The time for the pressure in the manifold to drop back to zero as indicated on a 1000 Torr MKS Baratron was noted. The peak pressure and number of turns on the needle valve were also noted. The micrometer on the needle valve is marked off in divisions of  $\frac{1}{25}$ <sup>th</sup> of a turn, and one division corresponds to 0.001 inch of travel of the valve stem. With the needle valve set at zero turns the regulating tip provides shut-off service and the sample cylinder is sealed from the manifold.

With the needle valve opened 5 divisions and the sample cylinder filled with 739 Torr of air ( $\sim 0.050$  L atm of air), the manifold pressure peaks at 12.5 Torr when the cylinder valve is opened and the pressure drops to 0.0 Torr in 30 seconds. With the needle valve open 4 divisions, the pressure in the manifold peaks at 9.7 Torr when the cylinder valve is opened and pumps to 0.0 Torr in 39 seconds. With the needle valve open 3 divisions, the pressure in the manifold peaks at 5.7 Torr when the cylinder valve is opened and pumps to 0.0 Torr in 1 minute, 30 seconds. With the needle valve open 2 divisions, the pressure in the manifold peaks at 0.2 Torr when the cylinder valve is opened and pumps to 60 mTorr in 10 minutes. For this last arrangement, much of the air was still in the 50 cc sample cylinder after 10 minutes.

The burden of HF (6 grams, 0.3 moles) in the sample cylinder at 20 °C is 7.2 L atm. The boiling point of HF is 19.5 °C and the typical temperature in the lab is 20 °C, so the vapor pressure of the HF is 783 Torr. If we set the needle valve to 3 divisions open, the time to pump out the 7.2 L atm would be about 3.6 hours.





**Figure 2.5** A photograph of the 50 cc sample cylinder, shut-off valve and needle valve. Connections between components are made using 1/4" Swagelok VCR fittings with nickel gaskets.

### 3.0 Procedure

Anhydrous hydrogen fluoride is an extremely dangerous and toxic material. The first aid and safety procedures for handling HF are given in Appendix B of this report. This information comes from the Chemical Process Permit for the laboratory space (LSL2/1432). Read this permit before handling hydrogen fluoride. Call the single point of contact 375-2400 if there is an exposure to HF or if there is a release of HF in the lab or in the fume hood. Release of HF to the environment is regulated and, depending on the amount, may be reportable.

When anhydrous HF is released into the air, a white cloud is formed. When this cloud is seen in the fume hood, close the fume hood sash, evacuate the lab space and call 375-2400. If the cloud is seen in the lab space, evacuate the lab immediately and call 375-2400. For eye exposure, flush the eyes with water immediately. There are safety showers in the hallways of LSL2. For skin exposure, apply calcium gluconate gel to the affected area (Calgonate). A tube of Calgonate gel is kept near the manifold.

There is no affordable, reliable continuous air monitoring system for hydrogen fluoride. The odor threshold for the compound is 0.04 ppm. The Time Weighted Average (TWA) for HF is 0.5 ppm. Spot monitoring of HF is performed using Dräger colorimetric tubes. A Dräger Accuro Gas Detector Pump along with Dräger gas tubes (Part no. 8103251, HF 0.5 to 90 ppm detection levels) are used to monitor the fume hood and room air for HF before and at intervals during the chemical conversion. See Appendix B for further details.

A Dräger tube reading is to be made of the lab and fume hood before the HF cylinder is brought into the lab. The sample cylinder containing the HF is carried from its ventilated/sprinklered cabinet in LSL2/1339 to LSL2/1432 using a rubber, bucket-type bottle carrier. Above the valve on the cylinder a ¼" VCR male plug is screwed into the ¼" VCR female fitting on the valve. Remove the plug and connect the cylinder to the manifold as shown in Fig. 2.5. Use a new nickel gasket for this connection.

Leak check the manifold and the connections to the sample cylinder using a helium leak detector. Once the leak testing is complete, make another Dräger tube reading of the fume hood.

Hydrogen fluoride may react with the metal in the cylinder, and this build-up of  $H_2$  is a safety concern (see Appendix C). Before converting the HF, the sample cylinder should be opened to the manifold, with the exhaust valve closed, and the pressure noted. If the pressure is much greater than 790 Torr at room temperature, there may be hydrogen in the cylinder. If this is the case, several freeze-pump-thaw cycles should be performed on the sample cylinder using liquid nitrogen. If the pressure is not above an atmosphere, freeze the HF back into the sample cylinder using liquid nitrogen. Warm the cylinder back to room temperature.

Now the conversion reaction can be started. Turn the needle valve two and a half divisions counter clockwise and tighten the set screw on the valve's sleeve to lock the valve at this setting. Open the exhaust valve on the manifold. When the pressure in the manifold drops below 30 mTorr open the valve on the sample cylinder and start the digital timer. Monitor the pressure in the manifold and in exhaust line (thermocouple gauge above the vacuum pump), and the temperature on the calcium oxide trap. If the pressure above the pump climbs above 300 mTorr or the temperature on the trap rises more than 5 °C above ambient close the needle valve by one division. If there is no rise in pressure or temperature, open the valve by one division or more as needed. Every 20 minutes or so take a Dräger reading in the fume hood and at the exhaust port of the vacuum pump. When the pressure in the manifold and above the traps on the vacuum pump have dropped below 30 mTorr and the temperature of the calcium oxide trap has returned to ambient temperature the reaction is done and the hydrogen fluoride has been converted. Close the exhaust valve on the manifold and fill the manifold and sample cylinder with about 3 to 4 atmospheres of dry nitrogen and pump the nitrogen away. Repeat this two more times.

Close the exhaust valve on the manifold. Close the valve on the sample cylinder and disconnect this from the manifold. Take Dräger tube readings at the inlet of the needle valve and the fitting on the sample cylinder. With the sample cylinder in the fume hood slowly open the valve on the sample cylinder and take Dräger readings at the fitting on the sample cylinder. If no white cloud appears and there is no

positive reading on the Dräger tube, then the tube is empty and the process is complete. If there is a white cloud or there is a positive reading for hydrogen fluoride, reconnect the sample cylinder and continue to flush, pump, and test the cylinder.

When the sample cylinder is empty and clean, close the exhaust valve on the manifold, turn off the vacuum pump, and vent the vacuum line. Disconnect the calcium oxide trap and weigh the trap. Cap the ends of the trap and put it in a waste container and label as regulated waste. Calcium oxide may have gotten into the flexible vacuum line. Rinse the line out with water. Oil in the vacuum pump should now be emptied by a millwright. Inform the millwright of the chemical exposure to the pump. The process is now complete.



## 4.0 Results

The chemical conversion was conducted on April 20, 2018. Dräger tube readings of the lab air and air in the fume hood were made and no HF was detected. The HF sample cylinder was moved from LSL2/1339 to the fume hood in LSL2/1432 using the rubber, solvent bottle carrier. The male plug in the cylinder's valve fitting was removed and the cylinder was connected to the inlet of the needle valve on the gas manifold. A new nickel gasket was used to make the connection. Another Dräger reading was made of the interior of the fume hood. The exhaust valve to the manifold was closed, the vacuum pump shut off, the thermocouple (TC) pressure gauge above the dual element traps was removed and a flex tube was connected between TC port and a helium leak detector. The vacuum pump was started, the exhaust valve opened, and the helium leak detector started. The manifold, traps and vacuum lines were leak tested with helium gas. No leaks were found. The leak detector and pump were shut off and the leak detector was disconnected from the TC port and the TC gauge connected back to its port. The vacuum pump was restarted and the manifold, traps and vacuum line evacuated below 30 mTorr.

Next, we closed the exhaust valve on the manifold and opened sample cylinder to manifold. The pressure in manifold was 115 Torr. No substantial amount of hydrogen was present in the cylinder. A Dräger tube reading inside the fume hood was made and no HF was detected. The ambient temperature in the lab was 21.5 °C. Given the volume of the manifold, 676 cc, the measured pressure, and lab temperature, the amount of HF in the sample cylinder is on the order of 0.1 gram, not 6 grams. We cryo-trapped the HF back into the sample cylinder using liquid nitrogen. The valve on the cylinder was then closed and we then warmed the cylinder back to room temperature using a heat gun, being careful to not overheat the cylinder.

The needle valve was turned 2.5 divisions counter clockwise from its closed position and locked in place using the set screw in the valve's micrometer sleeve. The exhaust valve on the manifold was open to the traps and vacuum line. The sample cylinder valve was opened and a timer started. The time, the opening on the needle valve, the pressure at the TC gauge above the dual element traps in the vacuum line, and the temperature of the calcium oxide trap, as measured by a K-type thermocouple, were noted and the results given in Table 4.1.

There was an initial rise in exhaust pressure when the valve was first opened, but this was small. So we opened the needle valve to 2.75 divisions and the exhaust pressure rose substantially 1500 mTorr and the trap temperature rose from 21.5 °C to 23 °C. Within a few minutes the pressure dropped back down below 150 mTorr. We continued to open the needle valve, but there wasn't another surge. We kept opening the needle valve and pumping on the sample cylinder through the calcium oxide trap. After 2 hours and 8 minutes of pumping, we stopped pumping, flushed the cylinder and manifold out with dry nitrogen, and then disconnected the cylinder from the manifold and checked with the Dräger tube as described in the Procedure section. No HF was detected.

We then disconnected the calcium oxide trap. Some of the calcium oxide powder leaked through the Teflon chips and copper wool and into the flex tubing. So we lost some weight from this. When we weighed the trap after the chemical conversion it weighed 905.96 grams (loss of 2.59 grams). So it would not be possible to determine the amount of calcium fluoride generated. The trap body was capped and disposed of as regulated waste. The vacuum tubing was cleaned of calcium oxide powder.

Initially, we estimated the weight of the HF in the cylinder by weighing the cylinder and then weighing an identical cylinder that was empty. The difference was 5.90 grams. When the HF cylinder was empty and flushed out, we weighed it and found that its weight was 447.64 grams. The weight of the empty cylinder that we used for the tare weight earlier was 442.11 grams. The difference is 5.53 grams. So the actual amount of HF in the cylinder was 0.37 grams.

No HF gas was observed by the Dräger tube, either in the fume hood or at the exhaust of the vacuum pump. Based on our exhaust pressure and trap temperature measurements, much of the small quantity of HF in the cylinder was converted within the first few minutes of opening the cylinder valve.

**Table 4.1** Time and conditions for HF chemical conversion. Time, needle valve opening as measured by divisions on the valve's micrometer, calcium oxide trap temperature as measured with a K-type thermocouple gauge, and the pressure in the vacuum line above the dual element traps as measured using a thermocouple pressure gauge.

Time	Needle Valve Open	CaO Trap Temp. °C	Exhaust TC Press. mTorr	Comment
13:43	2.5 div.	21.5	30	Start
13:44	"	"	60	Open valve on cylinder; heat w/ heat gun
13:47	2.75	"	1500	
13:51	"	23.0	150	
14:00	3.0	"		Open needle valve to 3 divisions
14:04	4.0	22.0	60	Open needle valve to 4 divisions
14:05	5.0	21.9	58	Open needle valve to 5 divisions
14:19	10.0	22.0	35	Open needle valve to 10 divisions
14:20	25.0	22.2	30	Open needle valve to 25 divisions
14:28	"	22.5	25	
15:07	"	22.5	20	
15:21	"	21.8	17	
15:52	"			Cylinder valve closed
15:55	"			Cylinder and manifold flushed w/ N <sub>2</sub>
16:02	"			Cylinder disconnected

## 5.0 References

1. Muttenthaler M, F Albericio and PE Dawson. 2015. "Methods, Setup and Safe Handling for Anhydrous Hydrogen fluoride Cleavage in Boc Solid-Phase Peptide Synthesis." *Nature Protocols* 10(7):1067-1083.
2. Mort AJ. 1983. "An Apparatus for Safe and Convenient Handling of Anhydrous, Liquid Hydrogen Fluoride at Controlled Temperatures and Reaction Times. Application to the Generation of Oligosaccharides from Polysaccharides." *Carbohydrate Res.* 122:315-321.



# Appendix A

## Treatment-by-Generator Request Form

### Treatment-by-Generator Request Form

This form is to be completed by the generator before treating any hazardous waste and submitted to an FSR.

#### Section 1 – General Information

Generator: Tom Blake Work Package: N18204 #833 Hazardous Waste Training? ☒ Yes ☐ No  
Area/Building/Room: LSL/1432 Building has current Building Emergency Plan? ☒ Yes ☐ No  
Waste Identification: Anhydrous Hydrogen Fluoride Treatment

Description of waste stream: 50cc stainless steel containing 6 grams of Anhydrous Hydrogen Fluoride gas will be discharged through a calcium oxide trap by pulling a vacuum through a manifold. This treatment would produce calcium fluoride when the gas comes in contact with the calcium oxide and Teflon shavings (used as packing material) in the trap. The waste generated will consist of calcium oxide /calcium fluoride pellets with Teflon shavings in a trap.

#### Section 2 – Original Composition

Composition	Wt%
Anhydrous Hydrogen Fluoride gas	100

Isotope (if rad)	Ci

pH: N/A

☐ Contains listed or tank waste  
☐ Volumetric Released waste (attach copy of release data form)

Volume to be treated: 0.006 L per (check one below)  
☐ day ☐ wk ☐ mon ☐ qtr ☒ one-time

#### Section 3 – Treatment Process

Storage container type / size: HDPE/1 Liter poly

Description of proposed treatment process and chemical(s) to be used: 6 grams of Anhydrous Hydrogen Fluoride gas will be discharged through a calcium oxide trap (containing calcium oxide pellets and Teflon shavings) by pulling a vacuum through a manifold. This treatment would produce calcium fluoride when the gas comes in contact with the calcium oxide and Teflon shavings used as packing material in the trap. Waste: 50.0 grams of Calcium/fluoride Oxide pellets, 40 grams of Teflon shavings.

Waste tracking references (LRB, procedures, etc): LSL-1432-CPP-192620

IWMS# 193180

#### Section 4 – Treated Composition

Frequency of treatment: ☒ One time ☐ Recurring batch ☐ Continuous

Composition	Wt%
Calcium oxide	30
Calcium fluoride	30
Teflon shavings	40

Isotope (if rad)	Ci
N/A	

pH: N/A

☐ Sewer disposal requested

Volume to be disposed: 0.1kg per (check one below)  
☐ day ☐ wk ☐ mon ☐ qtr ☒ one-time

#### Section 5 – Signatures

To the best of my knowledge, the compositions listed above include all constituents and radionuclides (if applicable) that are reasonably expected to be present in my waste stream.

Generator Signature: Thomas A. Blake Date: 4/4/18

FSR: William J. B. [Signature] Received Date: 4-4-18

(12/16)



## Appendix B

# Pacific Northwest National Laboratory Hydrogen Fluoride First Aid, Handling and Monitoring

### Hydrofluoric Acid (HF)

#### First aid for EYE contact with HF:

1. **Do not apply calcium gluconate gel to the affected EYE.**
2. Flush the affected EYE with copious quantities of water or dilute saline solution for at least 15 minutes while holding eyelids open.
3. Obtain immediate medical attention and treatment.

Hydrofluoric acid (HF) is very corrosive and presents a special hazard because of its unique health hazard properties. Hydrofluoric acid solution can produce serious health effects by any route of exposure. These effects are due to the fluoride ion's aggressive and destructive penetration of tissues. HF readily penetrates the skin and can cause both local cellular destruction of deep tissue layers (including the bone) as well as systemic toxicity by hypocalcemia. Unlike other acids which neutralize rapidly, this process may continue for days if untreated. Both liquid and vapor can cause severe burns to all parts of the body and quickly destroy the corneas of the eyes. Do not breathe HF acid vapor even for a very short time; the fumes can cause severe damage to the respiratory system. Therefore, all work with HF, including opening new packages, must be performed inside a fume hood and away from worker's breathing zone to minimize inhalation. Wear Chemical Goggles and Flexible Laminate Silver Shield gloves for maximum protection (Neoprene or Nitrile Gloves as minimum personal protective equipment (PPE) to reduce skin exposure).

If you are exposed to HF, regardless of the concentration, rinse the affected area with copious quantities of water for at least 15 minutes. Exposure to even a dilute concentration of HF may result in serious and delayed symptoms and **REQUIRES IMMEDIATE TREATMENT WITH CALCIUM GLUCONATE GEL/CREAM** and prompt medical attention from a health provider for advanced treatment (e.g., intravenous injection with 10% solution of sodium gluconate or its administration using a nebulizer). Dilute solution of HF allows deeper penetration of the non-dissociated HF acid, more severe burn, and delayed injuries and symptoms. Calcium gluconate gel/cream is an antidote that helps neutralize the HF acid burns on the skin. All lab users must read and thoroughly understand this information and the hazards associated with HF as well as discuss the hazards with the cognizant space manager (CSM) before working in this space. Please contact the CSM for location of container of calcium gluconate gel.

Note: Establish a designated work area (e.g., fume hood, section of the lab, or the entire lab) and post a "Danger" sign for [Hydrofluoric Acid](#).

#### **Additional severity and extent of risk information:**

\*\*\*\*\*  
FIRST AID STEPS AND ADDITIONAL MEDICAL INSTRUCTIONS FOR HF EXPOSURE  
\*\*\*\*\*

#### SKIN CONTACT

1. Move victim immediately under safety shower or other water source and flush affected area thoroughly

with large amounts of running water.

2. Call 375-2400 ASAP. Communicate the following information to 375-2400:

- a. Report a potential life-threatening HF skin exposure
- b. Request an immediate 911/ambulance response

3. Remove all contaminated clothing while continuing to flush with water.

4. After five minutes stop rinsing the affected area. Don surgical gloves, then apply calcium gluconate gel to affected skin area. Massage gel into the skin continuously until emergency medical assistance arrives.

#### INHALATION

1. Immediately move victim to fresh air

2. Call 375-2400 ASAP. Communicate the following information to 375-2400:

- a. Report a potential life-threatening HF inhalation exposure
- b. Request an immediate 911/ambulance response

3. Keep victim warm, quiet and comfortable until medical assistance arrives.

4. The Hanford/Richland Fire Departments carry calcium gluconate nebulizers.

#### EYE CONTACT

1. Immediately flush the eyes for at least 15 minutes with large amounts of gently flowing water. Hold the eyelids open and away from the eye during irrigation to allow thorough flushing of the eyes.

2. Call 375-2400 ASAP. Communicate the following information to 375-2400:

- a. Report an HF eye exposure
- b. Request an immediate 911/ambulance response

A small (50 cc) storage cylinder of anhydrous hydrogen fluoride (corrosive and toxic) is located in a ventilated and sprinklered cabinet located in the LSL2/1339 near the laboratory, LSL2/1432.

There is no affordable, reliable, continuous air monitoring system for hydrogen fluoride. The odor threshold for hydrogen fluoride is 0.04 ppm. The odor is described as strong, pungent and irritating. Symptoms of HF exposure include irritation of the eyes, skin, nose, and throat, eye and skin burns, rhinitis, bronchitis, pulmonary edema (fluid buildup in the lungs), and bone damage. The ACGIH Threshold Limit Value-Time Weighted Average (TLV-TWA) for HF is 0.5 ppm. The ACGIH Threshold Limit Values-Ceiling. (TLV-C) is 2.0 ppm. Personnel shall not be exposed to concentrations above this ceiling under any circumstance.

Real-time exposure monitoring for HF gas is REQUIRED during the initial hookup of the HF to the gas manifold. Modification or repair of the system with the potential to release more than trace quantities of HF gas is not allowed unless real-time HF monitoring is being performed.

During normal operations and in the absence of real-time HF monitoring, HF odor detection or the presence of a white fog (caused by HF aerosols in the air) will alert personnel to a hydrogen fluoride leak. The presence of HF odor or a white HF aerosol cloud is NOT expected and is NOT within the work scope of this permit.



Upon sensing the odor or seeing the cloud the lab space should be immediately evacuated and 375-2400 should be called. If possible and if it is safe to do so, the valve on the hydrogen fluoride cylinder in the cabinet in the Service Corridor should be closed.

Tubes of calcium gluconate are at the hydrogen fluoride gas handling manifold in room 1432, near the gas cabinet in room 1339. The gluconate is for skin contact. A sheet with HF first aid measures shall be placed near the work area and in the vicinity of the calcium gluconate supplies



## Appendix C

# Lessons Learned for Anhydrous Hydrogen Fluoride Cylinders



### Pressurization of Anhydrous Hydrogen Fluoride Cylinder

Lawrence Berkeley National Laboratory Lessons Learned

LL-2005-02

**Concern Statement:** Aging anhydrous hydrogen fluoride (AHF) cylinders can potentially explode. AHF cylinder over two years old should be returned to the vendor.

**Applicable to:** All Lab staff that works with anhydrous hydrogen fluoride.

**Incident:** In July 2005, an anhydrous hydrogen fluoride lecture bottle spontaneously exploded in a UC Santa Barbara laboratory. No one was injured, but the lab was extensively damaged. The photograph (below) shows that the lecture bottle had split along its seam. Its cap and valve assembly are located to the immediate left.

**Cause:** The explosion was caused by hydrogen gas pressure build up in the cylinder. AHF comes in carbon steel cylinders as a liquefied gas under a pressure of 0.9 psi @ 70°F (i.e., the vapor pressure of the liquid). Though cylinders should be passivated with fluorine, which forms a protective coating, over time AHF may slowly react with the iron in a cylinder to form iron fluoride and hydrogen gas. The generation of hydrogen gas may produce cylinder pressures as high as several hundred psi.



#### Recommended Actions:

- The recommended safe storage time for AHF is two years. Contact the vendor for pick up and disposal for cylinders older than two years in age. (You should also return unneeded gas, even if it has been less than two years since you obtained it.)
- If the cylinder is less than two years old and you wish to keep it, then:
  - Check the pressure of the cylinder. It must be within the maximum pressure stamped on neck of the bottle. If the pressure is at or above the cylinder's maximum pressure, contact the vendor for pick up and disposal. Do not attempt to move the cylinder yourself.
  - If below the cylinder's maximum pressure, vent excess pressure through an appropriate medium such as Puracarb® available at <http://www.purafil.com/> (KOH impregnated activated carbon). Use a two-person team. Conduct venting in a fume hood. Control all ignition sources during venting since most of the vent gas will be H<sub>2</sub>. At a minimum, wear chemical goggles, nitrile gloves, and a lab coat for protection against gaseous HF. Keep an HF exposure kit on hand (available free of charge from Health Services, Ext. 6266). An eyewash and safety shower must be readily accessible (within a ten second travel distance). Any skin, eye or respiratory irritation may be indicative of a possible exposure. Follow the first aid procedures listed on the exposure kit. Report all HF exposures to Health Services (Ext. 6266).

#### Further Information:

- Air Products published a safety bulletin on this AHF cylinder hazards. It can be accessed at the following link: [http://www.airproducts.com/Responsibility/EHS/ProductSafety/ProductSafetyInformation/safety\\_bulletins\\_PotentialPressurization.htm](http://www.airproducts.com/Responsibility/EHS/ProductSafety/ProductSafetyInformation/safety_bulletins_PotentialPressurization.htm).
- Contact Larry McLouth at extension 5286 ([ldmclouth@lbl.gov](mailto:ldmclouth@lbl.gov)) if you have any questions.

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