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Tritiated Sulfur Hexafluoride Disposition Strategies

Raymond Belliveau
Amy Corona

June 2021
SRNL-STI-2021-00313, Revision 0

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EXECUTIVE SUMMARY

Tritium (T_2) is a radioactive isotope of hydrogen that is produced in nuclear fission reactions and is often used in nuclear fusion reactions and accelerator-based applications for medical isotope production. In applications where tritium is handled, tritium confinement is performed using different barriers to minimize releases to the environment. Primary tritium confinement barriers typically produce low volumes of high tritium concentrations of tritiated methane from carbon in steels or organic materials along with tritiated water/tritium oxide (e.g. HTO) and tritiated ammonia from reactions with oxygen and nitrogen. Tritium escaping primary confinement into secondary confinement atmospheres (e.g. gloveboxes) produce higher volumes of lower activity contamination than found in process piping. Tritium contamination also occurs by leaks or tritium permeation/diffusion through confinement materials.

Accelerator based processes for medical isotope production represent an atypical tritium contamination challenge. To create the large voltage differentials for accelerator operations, an electrical insulation medium is needed to prevent or rapidly quench electric discharges. A common electrical insulation medium utilized in accelerator applications is sulfur hexafluoride (SF_6) gas. SF_6 has a high dielectric strength and allows for the construction of smaller accelerator systems compared to other electrical insulation mediums such as air or dry nitrogen.

Tritium contaminated SF_6 creates a material without any obvious processes for managing the contamination, reuse, or disposal of the contaminated SF_6. This document will discuss possible management strategies for tritium contaminated SF_6 for accelerator-based processes for Molybdenum-99 (Mo-99) production. Potential strategies include liquefaction, hydrates, dissolution and caustic scrubbing based approaches which all have potential to remove tritium from SF_6 and its decomposition byproducts by sequestering the tritium in water, which may then be treated by water detritiation methods. These methods require a drying step for the SF_6 after treatment, such as drying over alumina. Separation of T_2 from SF_6 and its decomposition byproducts in the gas phase before other purification steps are taken is impractical due to the complex nature of SF_6 breakdown, the wide array of breakdown products, and the uncertainty with regards to the actual byproducts in the system. A caustic-based treatment process is discussed as a possible treatment process for removal of SF_6 decomposition byproducts. Bench- and pilot-scale testing to determine the degree of SF_6 byproduct generation and the efficiency of detritiation treatment methods is needed to make a recommendation on the best suited treatment method for accelerator-based Moly-99 production.

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LIST OF ABBREVIATIONS

B.P.	Boiling point
°C	Celsius
CANDU	Canada Deuterium Uranium
EPDM	Ethylene Propylene Diene Monomer
keV	Kilo-electron Volts
^3He	Helium-3
HF	Hydrogen Fluoride or Hydrofluoric Acid (aq)
ITER	International Thermonuclear Experimental Reactor
mmol	Millimole
Mo-99	Molybdenum-99
MPa	Megapascal
M.P.	Melting Point
N_2	Nitrogen
NBI	Neutral Beam Injector
NNSA	National Nuclear Security Administration
O_2	Oxygen
-OH	Hydroxyl
PSA	Pressure-Swing Adsorption
ppm	Parts Per Million (mg/L)
ppt	Parts Per Trillion (ng/L)
PTFE	Polytetrafluoroethylene
SF_6	Sodium Hexafluoride
SRNL	Savannah River National Laboratory
STP	Standard Temperature and Pressure
T_2 or ^3H	Tritium
HTO or T_2O	Tritiated Water
TFTR	Tokamak Fusion Test Reactor

1.0 Introduction

Tritium (T_2) is a radioactive isotope of hydrogen that is produced in nuclear fission reactions and is often used in nuclear fusion reactions and accelerator-based applications for medical isotope production. As a hydrogen isotope, tritium can readily bind to hydroxyl radicals (OH), forming tritiated water (HTO or T_2O), and to carbon atoms. Tritium decays to helium-3 (^3He) via beta-decay with max decay energy of 18.6 keV. While it is not an external radiation hazard, it can be an internal radiation hazard if tritium is inhaled, ingested, or absorbed through the skin.

In applications where tritium is handled, tritium confinement is performed using different barriers to minimize releases to the environment. For gaseous (elemental), liquid (oxide), and metal (hydride) tritium, process piping and components provide the primary confinement function. Secondary tritium confinement is typically provided by inert (i.e. non-flammable gases such as nitrogen, argon, or helium) gloveboxes which are connected to a tritium stripper system. Primary tritium confinement barriers typically produce low volumes of high tritium concentrations of tritiated methane from carbon in steels or organic materials along with tritiated water/tritium oxide (e.g. HTO) and tritiated ammonia from reactions with oxygen and nitrogen. Tritium escaping primary confinement into secondary confinement atmospheres (e.g. gloveboxes) produce higher volumes of lower activity contamination than found in process piping.

Tritium contamination also occurs by leaks or tritium permeation/diffusion through confinement materials. Tritium from inside primary confinement barriers will diffuse or leak out of the primary confinement barrier and usually into the air, if the system is inside an air hood or ventilated hot cell, or into the secondary confinement (e.g. glovebox) atmosphere which is either exhausted or stripped based on the function of the secondary confinement (glovebox) system.

Accelerator based processes for medical isotope production represent an atypical tritium contamination challenge. In medical isotope production, deuterium supply gas is ionized and accelerated to a tritium gas target to produce neutrons that are then used to produce the medical isotopes through additional nuclear fission reactions. To create large voltage differentials for accelerator operations, an electrical insulation medium is needed to prevent or rapidly quench electric discharges. A common electrical insulation medium utilized in accelerator applications is sulfur hexafluoride (SF_6) gas. SF_6 has a high dielectric strength and allows for the construction of smaller accelerator systems compared to other electrical insulation mediums such as air or dry nitrogen.

Due to tritium permeation/diffusion through accelerator process and confinement materials, there is the possibility that tritium can contaminate the electrical insulation medium of the accelerator. Tritium contaminated SF_6 creates a material without any obvious processes for managing the contamination, reuse, or disposal of the used SF_6. This document will discuss possible management strategies for tritium contaminated SF_6 for accelerator-based processes for Molybdenum-99 (Mo-99) production.

2.0 Sulfur Hexafluoride Properties and Impurities

Sulfur hexafluoride (SF_6) is an inorganic, colorless, odorless, non-flammable, non-toxic, nonpolar gas. "Pure" SF_6 may contain small amounts of common impurities, such as oxygen (O_2), nitrogen (N_2), and water (H_2O) on the ppm scale (grade-dependent), but also commonly contains ppm-levels of carbon tetrafluoride (CF_4). SF_6 can decompose as a result of an electric discharge across or into SF_6 when used as an electrical insulator. Fortunately, most decomposed SF_6 quickly reforms back to SF_6, but some decomposition products such as highly toxic disulfur decafluoride (S_2F_{10}) are formed. Reactions with other impurities in the SF_6 and materials of construction of the gaseous confinement system can produce a wide array of secondary impurities, listed in Table 1. These impurities exist independent of exposure to tritium and when tritium is present, represent many mechanisms by which tritium can "contaminate" a gas that is typically treated as non-reactive.

2.1 Decomposition Byproducts

The mechanism of SF_6 decomposition in typical cases arises from electric discharge, resulting in dissociation of the SF_6 molecule via electron impact, producing various fragments.[1] The most common fragments produced are sulfur tetrafluoride (SF_4) and the sulfur pentafluoride (SF_5) radical, which is unstable in the presence of other gasses. The SF_5 radical may reform SF_6 or dimerize into S_2F_{10}. In the presence of oxygen and/or water it may oxidize into thionyl tetrafluoride (SOF_4), and then further oxide or hydrolyze to sulfuryl fluoride (SO_2F_2) or sulfur dioxide (SO_2). It may also undergo further fragmentation to the energetically stable SF_4.

Table 1: Properties and references for SF_6 and reported SF_6 decomposition byproducts.

Chemical Formula	Chemical Name	References	M.P. (°C)	B.P. (°C)	Phase at STP
HF	Hydrogen Fluoride	5, 6	-83.6	19.4	Gas
SOF_2	Thionyl Fluoride	5, 7, 8, 9	-130	-43.7	Gas
SOF_4	Thionyl Tetrafluoride	5, 7, 9, 10, 11	-100	-49	Gas
SF_4	Sulfur Tetrafluoride	5, 12, 13, 14	-125	-40	Gas
S_2F_{10}	Disulfur Pentafluoride	5, 12	-92	29	Gas/Liquid
SO_2F_2	Sulfuryl Fluoride	5, 7, 15	-137	-55	Gas
SO_2	Sulfur Dioxide	5, 7, 16	-10.0	-72.7	Gas
OF_2	Oxygen Difluoride	16, 17	-224	-145	Gas
H_2S	Hydrogen Sulfide	18, 19	-83	-62	Gas
SF_5CF_3	Trifluoromethyl Sulfur Pentafluoride	4	-87	-20.4	Gas
NF_3	Nitrogen Trifluoride	2, 20	-207.2	-129.0	Gas
F_2	Fluorine	6	-220	-188.1	Gas
COF_2	Carbonyl Fluoride	21, 22, 23	-114	-84.6	Gas
CF_4	Carbon Tetrafluoride	24	-187	-128	Gas
S_2OF_{10}	Bis(pentafluorosulfur) Oxide	2	-118.5	31	Gas
$S_2O_2F_{10}$	Bis(pentafluorosulfur) Peroxide	2	-95.4		Gas
$S_2O_3F_6$	Pentafluorosulfur Fluorosulfonate	2, 25	-105.1		Gas
SiF_4	Silicon Tetrafluoride	3	-97	-65	Gas
C	(Amorphous) Carbon	26			Solid
S_8	(Elemental) Sulfur	26	115	445	Solid
Al_2S_3	Aluminum Sulfide	26	1100	1500	Solid
FeS	Iron (II) Sulfide	26, 27	1193		Solid
Cu_2S	Copper (I) Sulfide	26	1100		Solid
CuF_2	Copper (II) Fluoride	26	836	1676	Solid
FeF_3	Iron (III) Fluoride	26, 27		987	Solid
FeF_2	Iron (II) Fluoride	26	970	1100	Solid
Fe_2O_3	Iron (III) Oxide	27	1539		Solid
AlF_3	Aluminum Fluoride	26	1040		Solid
SiO2	Silicon Dioxide	26	1713	2950	Solid

Table 1 lists SF_6 decomposition byproducts in order of formation reported in literature. However, in the presence of other gasses such as water, oxygen, and nitrogen different species may dominate as the primary decomposition byproduct. S_2F_{10} is known to be less favored as a byproduct in the presence of N_2 in the insulating gas, instead SO_2 becomes a primary byproduct. Bis(pentafluorosulfur) oxide (S_2OF_{10}), bis(pentafluorosulfur) peroxide ($S_2O_2F_{10}$), and pentafluorosulfur fluorosulfonate ($S_2O_3F_6$) are known to be produced in less relative concentrations in the presence of N_2.[2]

Depending on the presence of other materials in the system, other species may be formed. The presence of silicates (possibly in the form of dust from ceramics or glass) can lead to silicon tetrafluoride (SiF_4) being produced. SiF_4 is readily hydrolyzed and produces hydrogen fluoride (HF) and silicon dioxide (SiO_2) as a result.[3] Plastics, organic insulator materials, epoxies, or other carbon sources may provide material to produce carbonyl fluoride (COF_2) or CF_4. SF_5 radicals will attack carbon which has been fluorinated by the HF produced in many of these reactions to form trifluoromethyl sulfur pentafluoride (SF_5CF_3), a long-lived and potent greenhouse gas.[4]

Oxyfluoride production in the case of SF_6 decomposition has been well studied.[1, 2, 7, 27, 28, 29] Table 2 details reaction pathways for SF_x (where x = 2 to 5) fragments to react with oxygen, water, or other fragments and byproducts to produce some of the decomposition byproducts listed in Table 1. The reactions with oxygen are reportedly much faster than the reactions with water, and are considered to take place after the SF_6 fragmentation has occurred, the fragments have reacted, and the initial byproducts have diffused away from the electrical discharge.[1, 28]

Table 2: Reaction pathways for SF_6 fragments and decomposition byproducts with oxygen and water.

Reaction	Rate Constant k_{298} (cm^3/s)	Reference
$SF_5 + OH \rightarrow SOF_4 + HF$	1.1×10^{-12}	29
$SF_5 + O \rightarrow SOF_4 + F$	2×10^{-11}	7
$2\ SF_4 + O_2 \rightarrow 2\ SOF_4$	n/a	
$2\ SF_4 + O_2 \rightarrow 2\ SOF_2 + 2\ F_2$	n/a	
$2\ SF_3 + O_2 \rightarrow 2\ SOF_2 + F_2$	n/a	
$2\ SF_2 + O_2 \rightarrow 2\ SOF_2$	$\leq5\times10^{-16}$	1
$2\ SF_4 + 2\ OH \rightarrow 2\ SOF_2 + F_2 + 2\ HF$	n/a	
$SF_3 + OH \rightarrow SOF_2 + HF$	n/a	
$2\ SF_3 + O_2 \rightarrow 2\ SO_2F_2 + F_2$	n/a	
$SF_2 + O_2 \rightarrow SO_2F_2$	$\leq5\times10^{-16}$	1
$SF_4 + H_2O \rightarrow SOF_2 + 2\ HF$	1.5×10^{-19}	1
$SOF_4 + H_2O \rightarrow SO_2F_2 + 2\ HF$	2.0×10^{-21}	1
$SOF_2 + H_2O \rightarrow SO_2 + 2\ HF$	1.2×10^{-23}	1
$SF_5 + SF_5 \rightarrow S_2F_{10}$	1.8×10^{-12}	1
$S_2F_{10} + H_2O \rightarrow SOF_2 + SF_6 + 2\ HF$	n/a	5
$F + H_2O \rightarrow OH + HF$	9.0×10^{-12}	1

In addition to the gas-phase reactions, metal surface reactions may take place in which metal fluorides are produced as a result of bombardment by short-lived fluoride ions (if within the electric discharge field) or by HF attacking the surface.[7] Solid decomposition byproducts are reported to present as a powder with particles typically 10 microns in size or smaller.[26, 27] These powders are often reactive (FeF_2) or soluble in water (CuF) and pose a serious toxic inhalation risk. Iron (II) sulfide is reactive to acids such as HF and will produce iron (II) fluoride and hydrogen sulfide as a result.[26]

2.2 Relative Concentrations of SF_6 Impurities

Production rates of many SF_6 decomposition byproducts have been tabulated in Reference 1, and a portion of them are shown in Table 2. Byproduct production rates generally increase in proportion to the power dissipated into the SF_6, except SO_2F_2, which decreases.[27] Production rates vary with the concentration of O_2 and H_2O available for oxyfluorides. N_2 concentration significantly alters the production of some byproducts, also providing nitrogen to produce nitrogen trifluoride (NF_3).

The presence of water in particular may result in a very different profile of stable decomposition byproducts than comparatively pure SF_6 due to hydrolysis of many of the decomposition species. SOF_2, SOF_4, SF_4 readily undergo hydrolysis to SO_2, SO_2F_2, SOF_2 respectively.[9, 14] SO_2 vapor in the presence of water vapor will slowly form sulfuric acid. The rates for some of these hydrolysis reactions are given in Table 2.

Data in References 1, 7, and 28 show that variations in O_2 and H_2O concentrations below 1% of the bulk gas have only a small effect on the production of SOF_2, SOF_4, and SO_2F_2. O_2 concentrations between 1% and 2% actually decrease oxyfluoride production. O_2 concentrations higher than 2% show a strong positive influence on the production of SOF_4, but only weak influences on SOF_2 or SO_2F_2 production.[7] At low oxygen and water concentrations, it is expected that SOF_2 is the dominant oxyfluoride species produced, followed by SOF_4 and SO_2F_2.

The influence of trace amounts of N_2 is not reported in literature, however the influence of high concentrations of N_2 for the purposes of replacing pure SF_6 with a SF_6/N_2 mixture has been the subject of several studies.[2, 29, 30] In general, N_2 decreases production of S_2F_{10}, while having little effect on other typical byproducts. If N_2 and O_2 are both present in the system, it results a decrease in byproduct production (including NF_3) except for SOF_4, which increases. The effect of trace amounts of N_2 is therefore unknown, but modest effects of >80% N_2 concentrations indicate that it can be expected that HF, SOF_4, SO_2F_2, and SOF_2 would remain the primary decomposition byproducts.

Of the primary reactions in the production of SF_6 decomposition byproducts, almost all of them produce HF. Stainless steel can act as a sink for low levels of vapor-phase HF, as the steel surface reacts to form a pacifying fluoride layer.[26] Additionally, ceramic, glass, and silicon components may act to remove HF from the system by forming silicon tetrafluoride (SiF_4). Hydrocarbons such as polycarbonate may become fluorinated. Depending on the length of time that the SF_6 has decomposed and on the presence of these HF sinks, the upper bound of relative HF concentration will be comparable to the sum of all other SF_6 decomposition byproducts, and the lower bound of relative concentration would be negligible, as the HF sinks act to remove all of the acid present. The HF that accumulates over time would concentrate in any condensed water or on surfaces with a significant presence of adsorbed water.

Table 3 shows relative concentrations of the primary decomposition byproducts, including HF.[5] The conditions used to generate these values may not be directly translatable to the conditions in an accelerator, however provide a useful reference for scale for the following discussions. Absolute concentrations of decomposition byproducts cannot be determined without analytical investigation of the system, but typical concentrations of byproducts from sparking and corona discharge indicate that these byproducts are produced on the ppt to ppm scale.[2, 7, 27, 28, 29, 30]

Table 3: Relative concentrations of major decomposition byproducts of SF_6.

Decomposition Byproduct	Approx. Relative Concentration (%vol)
SOF_2	0.5
SOF_4	0.085
SF_4	0.085
S_2F_{10}	0.025
SO_2F_2	0.006
SO_2	0.002
HF	1.0

2.3 Fate of Tritium in the SF_6 System

Tritium migration into the SF_6 reservoir may isotopically exchange into the impurities, or beta decay energy may fragment SF_6 or its impurities and bond with the fragments to produce tritiated impurity compounds. Potentially tritiated byproducts include tritiated analogs of hydrofluoric acid, sulfuric acid, hydrogen sulfide, and water. Of the listed SF_6 byproducts, the potential for tritium contamination lies primarily in HF. This will be the most common byproduct that may contain tritium atoms. HF is readily soluble in water, and it can be expected that any moisture in the system will accumulate the HF over time. HF present in the system as a vapor may react with the solid materials, fluorinating those materials and releasing hydrogen (or tritium). Thus it may be expected for tritium that has entered into the SF_6 reservoir to exist as TF vapor, HT or T_2 gas, T^+ ions in any condensed or sorbed water, T_2O or THO, and it may occur as a hydrogen sulfide isotopologue if that byproduct is formed. In Section 3.0, strategies for isolating tritium in these forms from the SF_6 and listed decomposition byproducts are discussed. In Section 4.0, a concept for treating tritiated SF_6 is described.

3.0 Treatment Options

SF_6 purification is a well-established technology and there are several commercially available purification methods that SF_6 users can choose from to meet their purification needs for non-radioactive decomposition products.[31, 32, 33] Detritiation technologies are also widely studied, however tritium systems are much less common in industry.[34] The overlap of the two technologies is confined to a series of publications on the International Thermonuclear Experimental Reactor (ITER) Neutral Beam Injector (NBI) system and the Tokamak Fusion Test Reactor (TFTR) Neutral Beam source.[35, 36] In these cases, the motivation of the publishing authors is to discuss small amounts of in-leakage of SF_6 into tritium processing systems. The effect of SF_6 contamination on detritiation systems of the ITER NBI system is detailed by Kobayashi, et al. in which the detrimental effect of SF_6 decomposition byproducts on platinum-based catalysts are reported.[35, 37] HF and SO_2 were posited to be the relevant decomposition byproducts. Tritium-induced SF_6 decomposition products in the Torus Cleanup System of the TFTR were determined to be SO_2 (which may form sulfuric acid in the presence of moisture), SiF_4, and HF. These decomposition products were acknowledged to corrode metal and glass surfaces and components in the system.[36]

To date there has been no published study or account of the effects of a tritium in-leakage to a majority-SF_6 gas. The published effects of SF_6 in-leakage to tritium systems, and the industry-typical approaches to SF_6 clean-up suggest that efficient approaches to SF_6 detritiation will target traditional purification methods which remove impurities from bulk SF_6, and that process will also remove any tritiated species. Therefore, the following sub-sections will discuss SF_6 purification methods found in literature to be employed at-scale and evaluate the potential of each method to remove tritiated SF_6 decomposition species.

Potential methods to detritiate contaminated SF_6 gas can be classed into several approaches. Liquefaction, cryogenic distillation, and freezing approaches leverage the differences in melting and boiling points for SF_6, SF_6 decomposition impurities, and any tritiated species. Section 3.7 details the use of sorption separation, where adsorbents and getter materials such as zeolites, activated carbon, or alumina may be used to separate SF_6 and any impurities. The solubilities of the gases may be used to separate tritiated components from the bulk gas by using a washing or scrubbing method. Washing or scrubbing with a caustic solution may be used to react the various species into forms more easily managed. SF_6 can be selectively trapped as a hydrate to achieve separation. Each of these approaches are discussed in this section, along with the potential impact to the current method of SF_6 treatment proposed, which is described in Section 3.1.

3.1 Routine Treatment of Decomposed SF_6

Treatment of SF_6 containing impurities from electrical discharges under normal operation consists of a separation step, a drying step, and a physical filtration step. In the Enervac E736A Gas Cart (Enervac International ULC, Cambridge, ON, Canada), these steps are performed by liquefying the SF_6 under pressure, then passing it through an activated carbon filter, an activated alumina filter, and a particle filter, respectively (Figure 1). The purified SF_6 is then stored in tanks and is re-evaporated as needed.[38] This process is not expected to remove T_2 or HT from the SF_6, leaving the tritium in the purified SF_6.

Figure 1: Reference photo of an Enervac E736A Gas Cart.

The Enervac cart employs polytetrafluoroethylene (PTFE), ethylene propylene diene monomer (EPDM) rubber, and other polymeric materials in the gas transfer functions of the system.[39] Tritium may permeate through these materials at appreciable rates resulting in additional components and areas susceptible to tritium contamination.[40] Due to the tritium incompatible materials used in the construction of the SF_6 clean-up cart, detritiation of the SF_6 should occur prior to the routine gas treatment.

3.2 Freezing SF_6

The simplest approaches to separating SF_6 from any impurities may be by cooling the SF_6 to induce a phase change. An approach to purifying SF_6 by solidification is described by Kim, et al.[31] In that approach, SF_6 gas is first pretreated with an adsorbent filter to remove solids, moisture, and possibly other impurities. Then the SF_6 is frozen using liquid N_2 as a coolant. The remaining gas-phase species are vented, then the purified SF_6 is thawed. Some practical considerations of this approach are discussed by Perona, et al., in which a 'desublimer' is described based on a past application of the method to purifying UF_6.[41] This method requires a finned tube that can collect SF_6 ‘snow’ as it is cooled and can maintain an efficient removal of heat from the system without becoming blocked by solid condensate.

Figure 2 shows the melting and boiling points of SF_6 and several decomposition byproducts in order of melting point. At the melting point of SF_6 (-63.8 °C), F_2, F_2O, NF_3, CF_4, COF_2, and SiF_4 will remain as gasses, SF_6 and S_2F_{10} will solidify, and the remaining compounds will liquefy. In this case, without prior removal, water would also freeze. Of the potentially tritiated compounds, tritium fluoride (TF) (in water) could be removed in a pretreatment step similar to what is described by Kim et al., and if there is tritiated hydrogen sulfide present it could be separated out at this point in liquid form. If moisture is not removed prior to freezing, the SF_6 could be separated from the solid water by heating the SF_6 above its boiling point, but not past the melting point of water, then venting the purified SF_6. This would allow the SF_6 gas to be separated from any potentially tritiated water. This may be complicated by the presence of hydrates, which are discussed in Section 3.4. The vapor pressure of SF_6 at its melting point still leaves a relatively large fraction (~4%) of the SF_6 in the gas phase.[31] Repeated cycles of freezing the SF_6, removing the gas-phase fraction, evaporating the purified SF_6, then re-freezing the gas-phase fraction may be necessary to achieve the desired degree of overall purification.

This method is likely to be able to remove any tritiated species from SF_6. Tritiated water or tritiated hydrofluoric acid can be removed in a pretreatment step. Gas-phase tritiated impurities such as T_2 can be separated from the remaining SF_6 by repeated freezing processes. However, this approach may prove impractical for detritiating a contaminated volume of SF_6 gas due the logistical efforts of managing the liquid-solid phase change, the time required for repeated freezing cycles to reach the desired level of SF_6 purity, and the need to cool the bulk gas well below room temperatures to remove the many order of magnitude smaller amount of the impurity(ies).

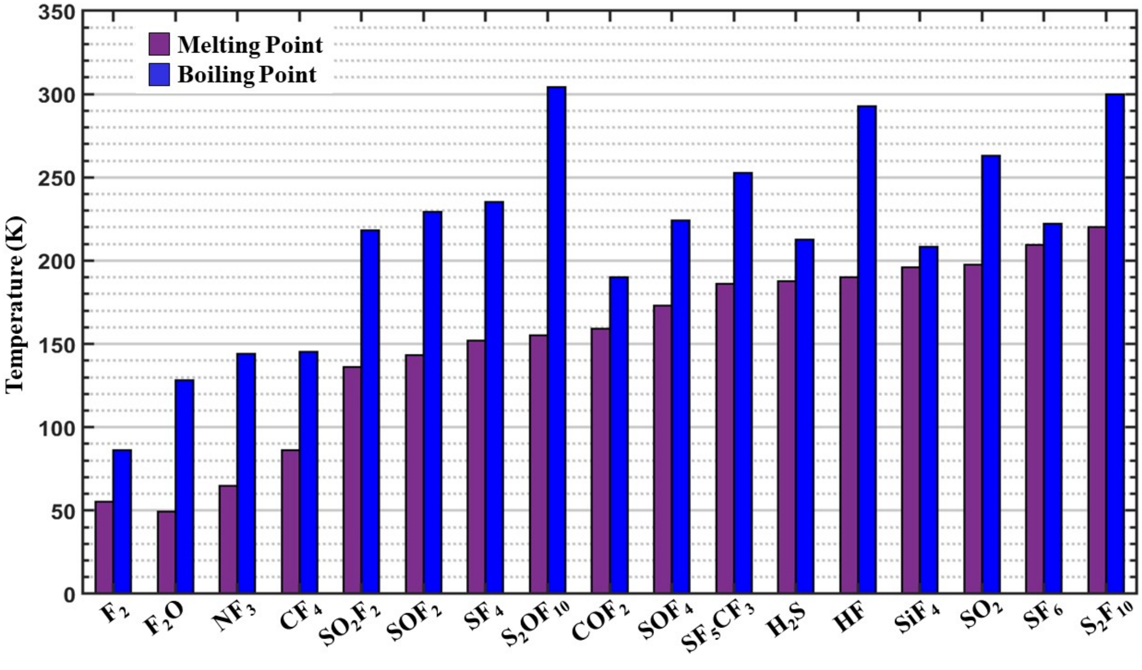

Figure 2: Boiling and melting points of SF_6 and its decomposition impurities. The compounds are ordered according to the melting point. Species which would remain gasses at the freezing point of SF_6: F_2, F_2O, NF_3, CF_4, COF_2, and SiF_4. S_2F_{10} is the only species which would solidify with the SF_6. The remaining species would exist as liquids, allowing for separation.

3.3 Liquefaction of SF_6

Liquefaction of SF_6 is less energy intensive compared to freezing SF_6, however many of the same issues are faced in both methods. Kim et al. describes two liquefaction methods. The first employs a pressure-swing adsorption (PSA) step, where the SF_6 and the impurities are cooled and condensed on activated carbon. This is very similar to the process used in the Enervac E736A Gas Cart. The purified SF_6 is desorbed by lowering the pressure in the system using a vacuum pump, while retaining impurities and a fraction of the SF_6 on the adsorbent. The remaining SF_6 and impurities are desorbed together and reprocessed by repeating the adsorption then pressure swing steps. It can result in very high purity (99.999%) SF_6, but is reported to be very slow.[31] Kim et al. also report a second liquefaction method, which only uses compression and cooling of the SF_6 to -10 °C to achieve separation. Similar to the freezing and PSA methods, after the desired phase change, the gas-phase fraction remaining is removed. The condensed fraction is vaporized and stored. The fraction containing the impurities are then processed again until the desired purity of SF_6 is achieved. The vapor pressure of SF_6 at -10 °C is around an order of magnitude higher than at the melting point of SF_6. Kim et al. reported that the gas-phase fraction of SF_6 after compression and cooling to -10 °C was 27%. This suggests multiple refinement cycles are necessary for a high degree of separation. Despite this, it was reported to be twice as fast as the PSA method.[31] Perona et al. reports liquefaction of SF_6 with 1% impurities at -45 °C, condensing 88% of the SF_6.[41] The gas-phase fraction (40% SF_6) was then processed using activated carbon.

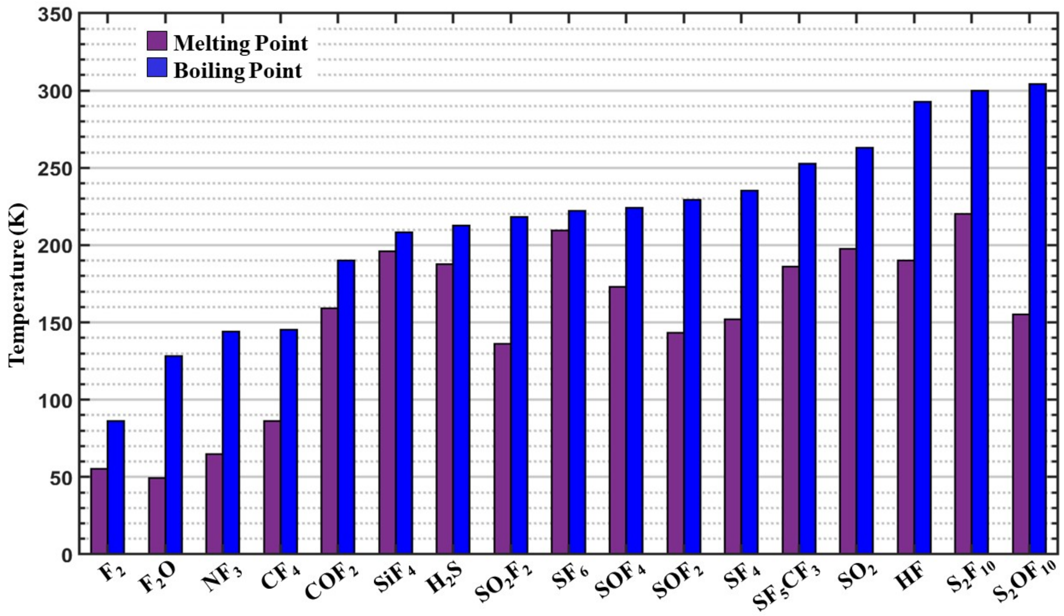

Figure 3: **Boiling and melting points of SF_6 and its decomposition impurities. The compounds are ordered according to the boiling point. Species which would remain gasses at the boiling point of SF_6: F_2, F_2O, NF_3, CF_4, COF_2, SiF_4, H_2S, and SO_2F_2. S_2F_{10} is the only species which may solidify at the boiling point of SF_6. The remaining species would exist as liquids.**

It can be expected that many of the same impurities will be in the same phase as SF_6 in the liquefaction method as in the SF_6 freezing method (Figure 3). Based on the boiling points of the SF_6 and the impurities, the following species will remain as gasses: F_2, F_2O, NF_3, CF_4, COF_2, H_2S, SO_2F_2, and SiF_4. The remaining compounds will liquefy with the SF_6. Small amounts of moisture in the system may stay dissolved in the liquid SF_6, however significant amounts may freeze. This poses the problem of potentially tritiated versions of molecules in the gas phase (H_2S), in the liquid phase (HF), and in the solid water. Similarly to freezing SF_6, it may be more efficient to use an adsorbent to dry and remove impurities such as HF prior to condensing SF_6.

3.4 Separation using SF_6 Hydrates

SF_6 hydrates are a phase of SF_6 trapped in solid water formed under high pressure and low temperatures. Ahn et al. reports the formation of SF_6 hydrates for the purpose of separating SF_6 from N_2 and O_2 by cooling gas mixtures to 0 °C under pressure (up to 1.1 MPa).[32] N_2 and O_2 impurities are concentrated in the gas-phase fraction is separated. Both the purified and impurity fractions must be dried, and if used, surfactants must be separated out. Ko et al. report a similar method in a 2021 paper, and also detail a scheme of using a hydrate-based purification step to purify low-concentration SF_6 gas mixtures up to 80% SF_6, and then using liquefaction to purify the SF_6 further.[42]

This technology is fairly new. SF_6 hydrates for purification are not used on the industrial scale yet. A 2017 publication by Kim et al. details the use of an SF_6 hydrate pilot-scale reactor for the Korea Electric Power Corporation.[31] Partially decomposed SF_6 (80% purity) containing decomposition impurities (in the 100s of ppm range) and air components (16% N_2) was processed at 2 - 4 °C and 0.2 - 0.5 MPa without a pretreatment step to remove particulates or moisture. The post-refinement purity of the SF_6 is reported to be 90% after this process.

While the current technology focus on SF_6 hydrates is for separation of SF_6 and N_2, many SF_6 decomposition byproducts are soluble in water or easily hydrolysable. After forming SF_6 hydrates, the gas-phase fraction may contain any HT or T_2 that was present in the SF_6, however HF, H_2S, and any previously accumulated tritiated water may all be expected to remain in the hydrate reactor water after refining. During the hydrate formation process, some HT or T_2 gas will also undergo isotopic exchange with the solid and liquid water, removing that tritium from the gas phase. Further detritiation processing may be necessary to remove tritium from the gas-phase fraction.

3.5 Dissolution Separations

Dissolution of the SF_6 impurities in water is a straightforward method, the benefits of which are similar to what is described in the use of SF_6 hydrates in Section 3.4. A bubble column system, recirculating water loop system, or a spray-nozzle type system such as a Venturi Scrubber (Figure 4) may see tritiated analogs of HF and H_2S, as well as most of the major decomposition byproducts (SO_2, SOF_4, SOF_2, SO_2F_2), and any previously accumulated tritiated water separate from the SF_6 gas into the water either by dissolution or hydrolyzation to a soluble species.[5, 9, 13, 43, 44] This technology is widely used to remove SO_x, NO_x, CO_2, and other impurity gases from air.[44, 45] Venturi designs are typically targeted for particulate removal, but also show success at removing gas-phase contaminates, depending on the application. Many of the solid impurities are also water soluble or may simply be captured as residue in the liquid water. This method will not remove tritium gas or HT gas, however, it may provide opportunity for those gasses to undergo isotopic exchange with the water.[46] Because of the low water solubility of SF_6 and high affinity of the impurities for water, this method can be expected to be a viable approach to removing decomposition and tritiated impurities from SF_6.

Dissolved impurities will lower the pH of the water over time as the impurities produce a combination of hydrofluoric acid and sulfuric acid. Regular exchange of water into the treatment system, or neutralization methods may be used to address this. This is discussed further in Section 3.6.

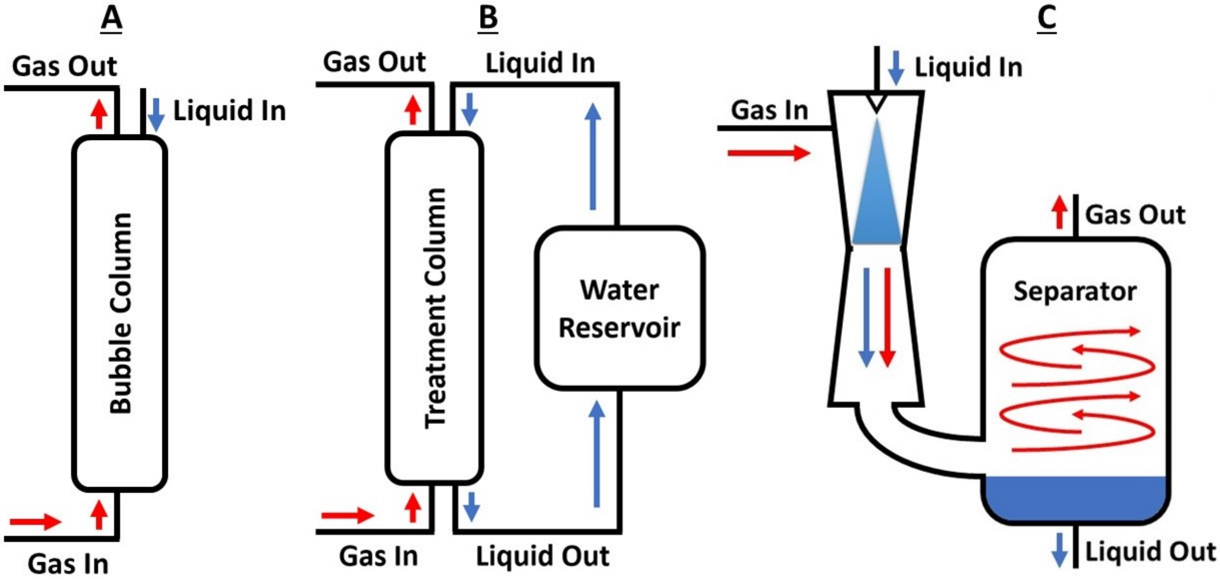

Figure 4: Dissolution-based SF_6 impurity removal concepts. These designs are common for the use of scrubbing SO_x and NO_x species from industrial exhaust gasses. Impurities are removed from the gas to the liquid water. Process water may be removed for treatment, and fresh water can be exchanged into the system as needed. A - bubble column. B - recirculating single loop scrubber. C - Venturi scrubber.

Alternatively, SF_6 is soluble in alcohols and non-polar solvents.[24] Dissolution into non-aqueous solvents may have the added benefit of removing CF_4 from the system, which is otherwise very difficult to remove from SF_6. SF_6 and CF_4 are both very soluble in Freon-113 (1,1,2-trichloro-1,2,2-trifluoroethane), which may be more suitable to this application than organic solvents as there are no hydrogen atoms available to undergo isotopic exchange in Freon-113.[47] However, solubility data on the decomposition byproducts of SF_6 with Freon-113 are not available.

3.6 KOH Scrubbing

The addition of basic compounds to the gas scrubber systems described in Section 3.5 has been widely used for a variety of applications.[6, 18, 44, 45, 48, 49, 50, 51] Notably, the addition of sodium hydroxide (NaOH) or potassium hydroxide (KOH) to wet scrubber systems for the removal of H_2S and SO_2 can greatly increase the efficiency of these systems.[44, 50] KOH is particularly suitable for the removal of HF and F_2, capturing the fluorine as soluble potassium fluoride (KF) for easier handling.[6] Table 4 shows the reaction pathways for many of the SF_6 decomposition byproducts under a KOH treatment. A combination of KOH-assisted hydrolysis and acid-base reactions produces mostly water, KF, potassium sulfite (K_2SO_3), potassium sulfate (K_2SO_4), and potassium hydrosulfide (KSH) at pH 7 through 12.[52] SF_6 is unreactive in these conditions. The presence of F_2 will also produce O_2 as a byproduct in this reaction scheme.[6] The potassium salts produced by this treatment method are readily soluble in water, and are generally non- or low-toxicity compounds.

Table 4: Reaction pathways of SF_6 decomposition byproducts treated with KOH.

Species	Reaction	Reference/Notes
F_2	$F_2 + KOH \rightarrow OF_2 + 2KF + H_2O$ $OF_2 + KOH \rightarrow H_2O + O_2 + 2KF$ **Net:** $\mathbf{F_2 + 2KOH \rightarrow 2H_2O + O_2 + 4KF}$	6
HF	**Net:** $\mathbf{HF + KOH \rightarrow KF + H_2O}$	6
H_2S	$H_2S + KOH \leftrightarrow KSH + H_2O$ $KSH + KOH \leftrightarrow K_2S + H_2O$	KSH will be favored at pH 7-12. 52
SO_2	$SO_2 + KOH \leftrightarrow KHSO_3$ $KHSO_3 + KOH \leftrightarrow K_2SO_3 + H_2O$	K_2SO_3 will be favored at pH>7. 52
SOF_2	$SOF_2 + KOH \rightarrow SO_2 + HF + KF$ $HF + KOH \rightarrow KF + H_2O$ **Net:** $\mathbf{SOF_2 + 2KOH \rightarrow K_2SO_3 + 2KF + H_2O}$	9
SO_2F_2	$SO_2F_2 + 2KOH \rightarrow H_2O + KSO_3F + KF$ (Fast) $KSO_3F + KOH \rightarrow HF + K_2SO_4$ (Slow) $HF + KOH \rightarrow KF + H_2O$ **Net:** $\mathbf{SO_2F_2 + 4KOH \rightarrow 2H_2O + 2KF + K_2SO_4}$	15
SOF_4	$SOF_4 + KOH \rightarrow SO_2F_2 + HF + KF$ $SO_2F_2 + 2KOH \rightarrow H_2O + KSO_3F + KF$ $KSO_3F + KOH \rightarrow HF + K_2SO_4$ $HF + KOH \rightarrow KF + H_2O$ **Net:** $\mathbf{SOF_4 + 6KOH \rightarrow 2H_2O + 4KF + K_2SO_4}$	9, 10
SF_4	$SF_4 + KOH \rightarrow SOF_2 + HF + KF$ $SOF_2 + KOH \rightarrow SO_2 + HF + KF$ $HF + KOH \rightarrow KF + H_2O$ $SO_2 + KOH \leftrightarrow KHSO_3$ $KHSO_3 + KOH \leftrightarrow K_2SO_3 + H_2O$ **Net:** $\mathbf{SF_4 + 6KOH \rightarrow K_2SO_3 + 3H_2O + 4KF}$	K_2SO_3 will be favored at pH>7. 14, 52

With regards to SF_6 detritiation, this method sequesters tritium within tritiated versions of water, KOH, and potentially in KSH (depending on if H_2S is produced during the SF_6 decomposition process). At pH values over 7, virtually no potassium bisulfite ($KHSO_3$) may be formed, suggesting the presence of tritiated potassium bisulfite ($KTSO_3$) is unlikely to occur.

The 1960 report by J. B. Ruch at Oak Ridge National Laboratory goes into considerable detail on practical design considerations using a KOH spray nozzle scrubbing system.[6] The scrubber described in that report is designed to remove HF and F_2 to 2 and 1 ppm (respectively) from 3000 cfm of contaminated air. It is similar in construction to the Venturi scrubber described in Section 3.5, consisting of a spray chamber and a condensate separation stage after. KOH was elected over NaOH due to two facts: that the reaction products of KOH with fluorine, fluorides, and carbonates such as carbon dioxide (CO_2) are much more soluble in water, and that the fluorine byproduct oxygen fluoride (OF_2) hydrolyzes slowly in NaOH (and slower still in neutral water), but reacts quickly in the presence of KOH.

This method requires a similar level of capital investment as liquefaction and hydrate methods in terms of tanks, pumps, space, etc. However, it is a more complete treatment method, as it addresses the issue of continuous acidification of the clean-up water used in other methods. It also has the benefit of reacting the most common SF_6 byproducts into safer, easier to handle forms.

3.7 Sorption Separation

Gas-phase separations using solid sorbents are based on both physical and chemical characteristics of the species under treatment. Molecular sieves contain pores sized to capture molecules of a specific size or smaller, and also rely on dipole-dipole (in polar molecules, or induced dipoles in non-polar molecules) interactions to 'stick' molecules to the sorbent surface.[53] Packed bed materials such as limestone undergo surface reactions to chemically bind the target molecules. Sorbent materials such as zeolites and activated carbon may both chemically react with the gas being processed and provide a porous surface which physically traps gas molecules. The Enervac E736A Gas Cart described in Section 3.1 uses an activated carbon bed and an activated alumina bed, both of which chemically and physically react with SF_6 decomposition byproducts.

Physical adsorption-based separations can either be used to adsorb all of the SF_6 and leave behind impurities, such as in the pressure-swing adsorption method described in Section 3.3 (using zeolite 13X), or the impurities can be selectively removed from the SF_6 by adsorbing or reacting the impurities (using 5A molecular sieves). This method is sufficient for removing small molecule impurities or removing a small amount of SF_6 from a gas mixture that is primarily composed of smaller molecules, but size-based separations are not reported as an effective method of SF_6 decomposition byproduct removal. Weakly binding adsorbents can be used to selectively remove certain decomposition species, such as SO_2 on activated carbon and zeolites, and HF on sodium fluoride (NaF) and alumina.[54, 55, 56, 57] Activated alumina is also an excelling drying agent. Many authors report selective adsorption of SF_6 decomposition byproducts in theoretical studies for the purpose of developing sensing materials, however selective adsorbents of SF_6 decomposition byproducts for purification purposes are not reported.[58, 59, 60]

References 6 and 48 describe an evaluation of limestone/calcium carbonate ($CaCO_3$) as a chemical sorbent for HF. In one case, sodium bicarbonate is described as necessary to supplement the calcium carbonate to adequately capture HF. Limestone may also be used in SO_2 dry scrubber systems.[51] Solid chemisorption methods such as these face difficulty at scale either due to surface passivation of the solid material, as in the case of limestone and HF, or complicated systems to fluidize the solid material to ensure adequate surface area and contact time without unacceptable pressure drop scenarios occurring.[6, 51]

Many of the solid sorbent materials described in this section will undergo other chemical reactions with the decomposition products. Activated carbon is stated to catalytically decompose S_2F_{10}.[5] Zeolite 13X will react with HF to form silicon fluoride. Additionally, tritiated decomposition byproducts may produce tritiated methane while in contact with activated carbon.

Of the SF_6 decomposition byproducts that may be tritiated, T_2O, HTO, and TF could be removed using activated alumina. The most efficient use of this method may be in combination with wet scrubbing methods such as KOH washing. In this case, the majority of decomposition byproducts and tritiated compounds are removed during the KOH treatment, and residual (potentially tritiated) water in the SF_6 is removed by an alumina filter.

3.8 Other Separations

The following sections describe methods of purifying SF_6 which are notable, but unlikely to be efficient or practical for the task of detritiating SF_6.

3.8.1 *Cryogenic Distillation*

Distillation is one of the oldest methods of SF_6 purification. It is a method used at-scale and is capable of producing ultra-pure (99.999%) SF_6. However, it is very energy intensive, requires a significant amount of capital and maintenance operations, and is typically geared to refinement of large quantities of SF_6 that is already of high quality to an ultra-pure state.[33]

3.8.2 Membrane Separation

Membrane-based SF_6 separations are found in limited use in industry and at-scale. This method separates SF_6 from other gasses based on relative rates of permeation through a membrane. Membranes are typically polymeric materials, but nanoporous zeolite-on-alumina membranes and other inorganic membranes have been reported.[33, 61, 62] These materials have not been evaluated for purification of SF_6 from its decomposition byproducts, but for separations from atmospheric gasses such as N_2, O_2, and CO_2. Polymeric materials are easily decomposed during exposure to tritium.

4.0 Tritiated SF_6 Disposition Concept

Of the treatment options discussed in Section 3.0, a KOH-based scrubbing treatment followed by the removal of water from the SF_6 using an activated alumina filtration step presents an option for a relatively simple yet thorough treatment plan. A case-study of a treatment system using this concept follows (Figure 5).

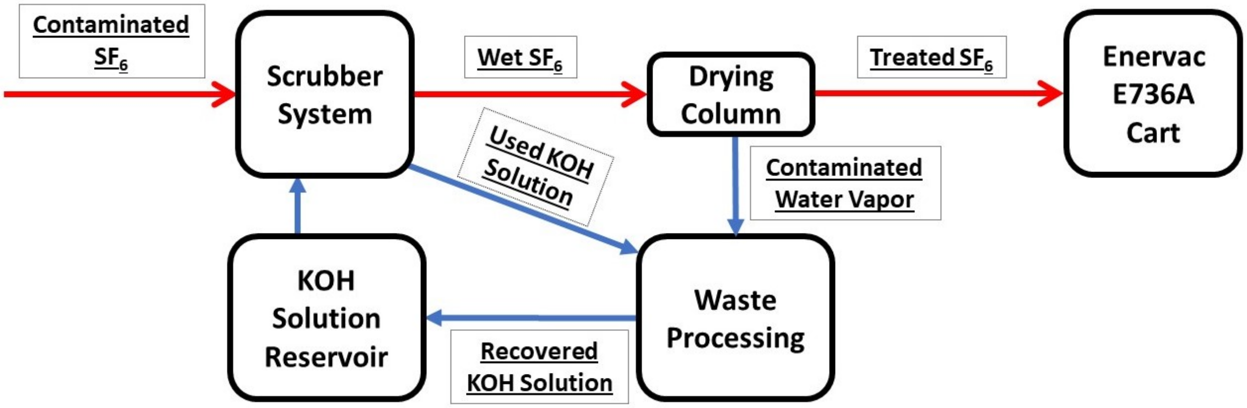

Figure 5: Tritiated SF_6 disposition concept. Contaminated SF_6 is treated with a KOH solution to remove the majority of impurities as discussed in Section 3.6. Scrubbed SF_6 contains a significant fraction of water, which may be tritiated. This SF_6 can then be dried over activated alumina as discussed in Section 3.7. Scrubbed and dried SF_6 is then returned to the routine treatment schedule.

Contaminated SF_6, containing SF_6 decomposition byproducts as described in Section 2.0, and tritium in the form of T_2, HT, and tritiated isotopologues of SF_6 decomposition byproducts is processed using a KOH solution. For small amounts of impurities, the KOH solution may be introduced to the SF_6 by way of a simple bubble column (Scrubber System, Figure 5). At minimum, the pH of the caustic solution used for scrubbing should be maintained over pH 7, preferably as high as can be reasonably achieved. For many SF_6 decomposition byproducts, the rates of solubility, absorption, hydrolysis, and/or acid/base reactions that take place are accelerated as the pH increases. Under pH 7, an undesirable acid/base equilibrium develops for SF_4, SO_2, and H_2S (Table 4). Based on the relative concentrations of SF_6 decomposition byproducts shown in Table 3 and the reaction mechanisms presented in Table 4, approximately 2 moles of KOH will be needed to treat the decomposition byproducts per each mole of decomposition byproducts produced. A pH 12 solution of KOH will contain 10 mmol KOH per liter of water, and therefore may be expected to treat approximately 5 mmol of decomposition byproducts per liter of KOH solution. The magnitude of decomposition byproducts to be removed by this treatment will require laboratory investigation or analytical inspection of the used SF_6 under normal operating conditions to determine.

Treatment of the used KOH solution may follow existing waste processing used for actinide waste, or it may be recycled into the KOH solution reservoir if the pH of the solution is still suitable (Waste Processing loop, Figure 5). The potassium salts produced during treatment are very soluble, however may begin to accumulate as solid residue either due to increasing concentration over time, or in areas where high amounts of evaporation occurs.

Post-KOH scrubbing, treated SF_6 is expected to contain any CF_4, S_2F_{10}, HT or T_2 gas, and water vapor (which may be tritiated). It is passed to an activated alumina column for drying, where water isotopologues are removed from the gas stream (Drying Column, Figure 5). The water removed from the SF_6 gas stream may be desorbed after treating the SF_6, and the water can be passed to a liquid radiological waste treatment process stream. The size of the column and amount of alumina needed may be determined after knowing the water sorption capacity of the alumina and the moisture content of the SF_6 after KOH treatment. Bench-scale laboratory testing can be used determine these quantities. The SF_6 is then passed to the Enervac E736A cart for routine processing.

5.0 Conclusion

Liquefaction, hydrates, dissolution and caustic scrubbing-based approaches all have potential to remove tritium from SF_6 and its decomposition byproducts by sequestering the tritium in water, which may then be treated by water detritiation methods as described by Corona and others.[34, 63, 64, 65] These methods require a drying step for the SF_6 after treatment, such as drying over alumina. Separation of T_2 from SF_6 and its decomposition byproducts in the gas phase before other purification steps are taken is impractical due to the complex nature of SF_6 breakdown, the wide array of breakdown products, and the uncertainty with regards to the actual byproducts in the system. Bench- and pilot-scale testing to determine the degree of SF_6 byproduct generation and the efficiency of detritiation treatment methods is needed to make a recommendation on the best suited treatment method for this application.

6.0 Acknowledgements

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