

Rapport

Sulfurylfluoride – filtersystemen

Auteur : 2E
Datum : 9 april 2021
Kenmerk : SF/210409/FS/JU

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Convenant ILENIT

Inleiding

Sulfurylfluoride (SF) met registraties in Nederland onder de merknamen ProFume en Vikane als Gewasbeschermingsmiddel, respectievelijk Biocide is ruim 10 jaar toegelaten op de Nederlandse markt. Vooral de toepassing als gewasbeschermingsmiddel om boomstammen te begassen voorafgaand aan export heeft een grote vlucht genomen. Niet alleen in Nederland maar ook in vooral België en Duitsland.

SF is een toxisch gas met een relatief snelle werking, waardoor boomstammen binnen het logistieke traject, direct voorafgaand aan de export worden begast conform export-eisen. Boomstammen zijn wegens hun aard onderworpen aan zogenaamde fytosanitaire eisen welke zijn opgesteld door het importerende land, in het geval van boomstammen is dat voor meer dan 95% China.

In Nederland is de NVWA verantwoordelijk voor de uitgifte van fytosanitaire certificaten conform de importeisen van China. Het behandelen van boomstammen voorafgaand aan de export is vastgelegd in het document "Export planten, groenten, fruit, plantaardige producten/landeisen China/Diverse producten". Hierin is vastgelegd dat SF een geëigend middel is om toe te passen. Andere door China geaccepteerde toepassingen zijn praktisch niet mogelijk of zelfs verboden in de EU.

Een groot nadeel van SF is echter het Global Warming Potential (GWP) van SF. Het GWP van SF heeft de factor 4.780 ten opzichte van koolstofdioxide (CO₂). Door toename van het aantal SF-behandelingen draagt Fumico ongewild bij aan de opwarming van de aarde. Daarom onderzoeken we al geruime tijd alternatieven voor SF alsmede de mogelijkheden SF professioneel af te vangen. Dit rapport gaat in op filter-/afvangsystemen voor SF, de technieken en de (on)mogelijkheden. Ook komt nog kort hergebruik van SF aan de orde.

Hergebruik SF

Het hergebruiken van SF is in de praktijk niet mogelijk. Testen wijzen uit dat het "overpompen" van SF van de ene container in de andere container praktisch niet lukt. Dat komt omdat het gas volledig is verspreid door de container en gepenetreerd is in de lading. Bovendien wordt ook veel gas verloren tijdens het overbrengen. Dit levert in de praktijk helemaal niets op.

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Filtersystemen voor SF

SF is een anorganisch gas waarvoor geen actief koolfilter voor beschikbaar is. Hierdoor is Fumico op zoek gegaan naar een andersoortig systeem. Hierbij zijn wij terechtgekomen bij de industriële rookgasreiniging.

Chemisorb S van Trevi is een filtersysteem gebaseerd op een reactie tussen SF en natrium-/calciumoxide in korrelvorm. Het filter wordt m.b.v. slangen aangesloten op de containers, waarbij het gas via een ventilator door het absorptiefilter gaat en daarin wordt opgenomen.

Chemisorb S gaat een reactie aan met sulfurylfluoride waarna het gas wordt opgenomen in het filter. De adsorbentia bestaat uit een onschuldig residu dat, volgens de leverancier, als normaal bedrijfsafval kan worden afgevoerd.

Het grote nadeel van Chemisorb S is dat het ook een reactie aangaat met kooldioxide uit de omgevingslucht. Tijdens het ontgassings-/absorptieproces zal zowel sulfurylfluoride als kooldioxide worden opgenomen in het filter, waardoor verzadiging van het filter snel optreedt. Chemisorb S verandert van kleur tijdens het absorptieproces. Zodra de verkleuring volledig is, zal de absorptie stoppen en zal sulfurylfluoride niet meer worden opgenomen. Chemisorb S bestaat uit natrium-/calciumoxide in korrelvorm. Het reactieproduct is natrium-/calciumfosfaat. Voor 1 kg SF is 10 kg Chemisorb S nodig (verhouding 1:10).

Praktijktesten filtersysteem SF

In de periode december 2020 – januari 2021 heeft Fumico meerdere testen uitgevoerd met het Chemisorb filtersysteem. Op zich werkt het filtersysteem goed. We zien echter inderdaad een zeer snelle verzadiging van het filter. Hieronder zien we foto's van het filter en Chemisorb S:



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Het filter bestaat uit een gesloten vat waarop een in- en uitlaat is bevestigd. De inlaatzijde is via een slang verbonden met de container en de uitlaatzijde is verbonden met een ventilator met een debiet van 200 m³/h. We hebben 20" containers gebruikt met een inhoud van 33 m³. Dit betekent dat de container per uur 6x gespoeld wordt. De schone lucht wordt aangezogen via de ventilatieroosters in de container.

Wij hebben 2 kg SF in de container ingebracht. De containers waren leeg en leverde na gasevenwichtstelling (equilibrium) een concentratie op van 60 g/m³ (14.000 ppm). Het equilibrium bereikten we ca. 15 minuten na einde ingassing. Direct aansluitend zijn we gestart met de ontgassing. Deze test hebben we in zijn geheel nog een keer herhaald om te bezien of de resultaten gelijk zijn als de 1^e test.

Resultaten filtersysteem SF

Het filtersysteem op zich werkt goed. Direct aan de uitlaatzijde blijven de concentraties zeer laag rond 3-5 ppm. De STEL-waarde van SF (10 ppm) wordt niet overschreden bij de start van de ontgassing. Bij de 2^e test zien we concentraties wel wat oplopen vanaf het begin met waarden van 10-40 ppm verder oplopend tot waarden boven het meetbereik (> 100 ppm).

In totaal hebben we 8 kg SF gebruikt over 4 containers verdeeld over 2 dagen. We zien dat verzadiging van het filter geleidelijk begint op te treden bij de 2^e serie containers. Theoretisch is 80 kg Chemisorb S nodig om 8 kg SF te adsorberen. In de praktijk zien we dat het filter met 200 kg Chemisorb S na adsorptie van 4 kg SF geleidelijk begint "door te slaan" en langzaam steeds grotere hoeveelheden SF doorlaat. Dit betekent in de praktijk dat het filter tevens grote hoeveelheden CO₂ adsorbeert. Uit onze metingen blijkt dat 200 kg Chemisorb 6-8 kg SF kan adsorberen. Tijdens het adsorberen van SF is tevens ca. 125 kg CO₂ geadsorbeerd.



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Kosten filtertechniek

De toepassing van Chemisorb S als filtermateriaal zorgen voor 15% meerkosten per container. Dit zijn enkel de kosten voor de filterkorrels inclusief aan- en afvoer en verwerking hiervan. Niet inbegrepen hierin zijn de kosten voor materialen: ventilatoren, koppelingen, slangen, aansluitingen voor elektriciteit etc. Ook is er meer arbeid nodig om al deze filters aan te sluiten. De meerkosten hiervan bedragen minimaal 10% per container, waardoor de totale kosten met een filtersysteem zeker met 25% zullen toenemen.

De beoogde milieuwinst met het filtersysteem is er ook niet. De Chemisorb S moet worden aan- en afgevoerd en verwerkt en ook is er elektriciteit nodig om de ventilatoren te laten draaien.

Conclusies Chemisorb S

In de praktijk is Chemisorb S niet het juiste middel om SF mee af te vangen. De kosten voor aankoop, aan- en afvoer en verwerking zijn zeer hoog. Bovendien zal iedere container separaat moeten worden aangesloten op een container: ook dit is praktisch onhaalbaar.

Andere technieken

Al geruime tijd verricht in de Verenigde Staten de USDA onder leiding van ^{2E} onderzoeken naar het afvangen / filteren / neutraliseren van SF. Enige ervaringen zijn op 25/1/21 gedeeld met begassingsbedrijven in de EU, maar deze onderzoeken staan nog in de kinderschoenen. Voorlopig is er nog geen commercieel systeem op de markt om SF op een praktische manier te neutraliseren na begassing.

Als bijlage bij dit rapport is een presentatie van de USDA van januari 2021 bijgevoegd.

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Convenant II en IT

Bijlage:

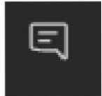
Presentatie Douglas Products, USDA, Filtersystemen SF

Filter technology for Sulfuryl fluoride

Industry information session Jan 25th 2021

Welcome!

We'll start at 4PM

- Please mute yourself
- Questions in chat 
- Presentation will be available



Your speakers today



2E

Research Chemist
**U.S. Department
of Agriculture** 



2E

Global Business Leader

2E

@douglasproducts.com



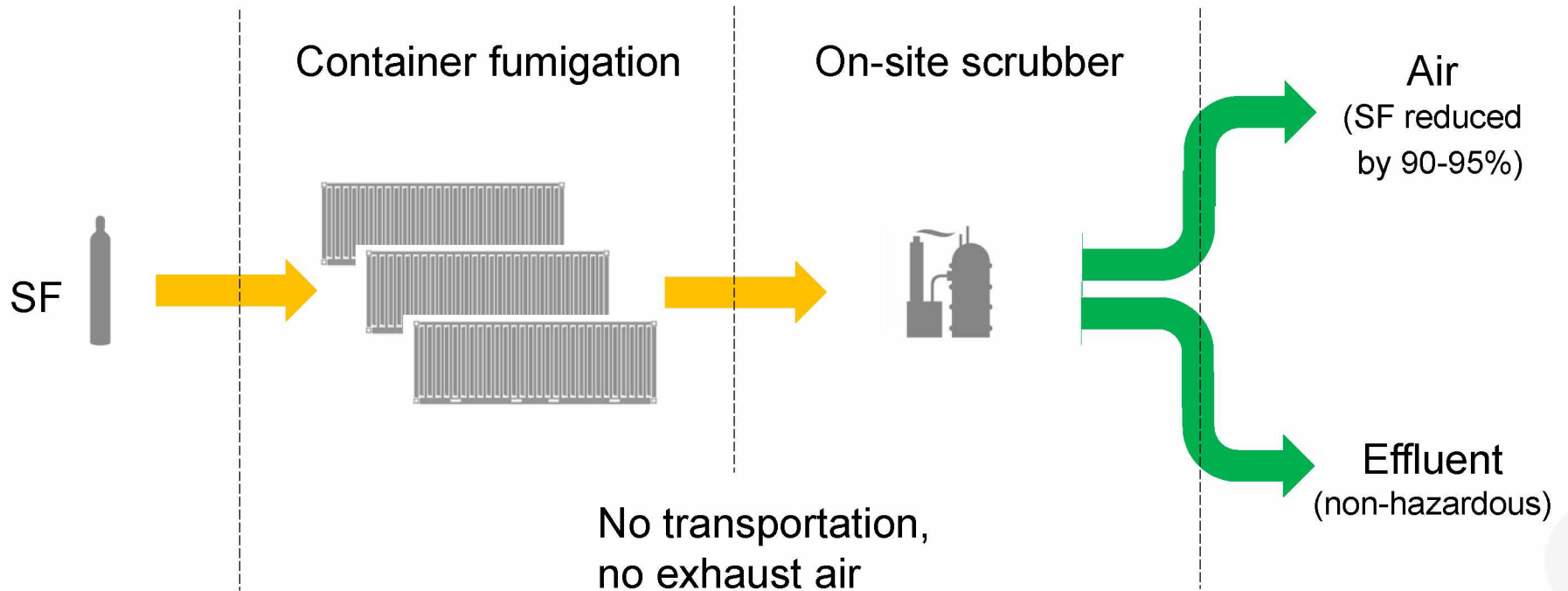
2E

EU Business Development

2E

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Background & goal

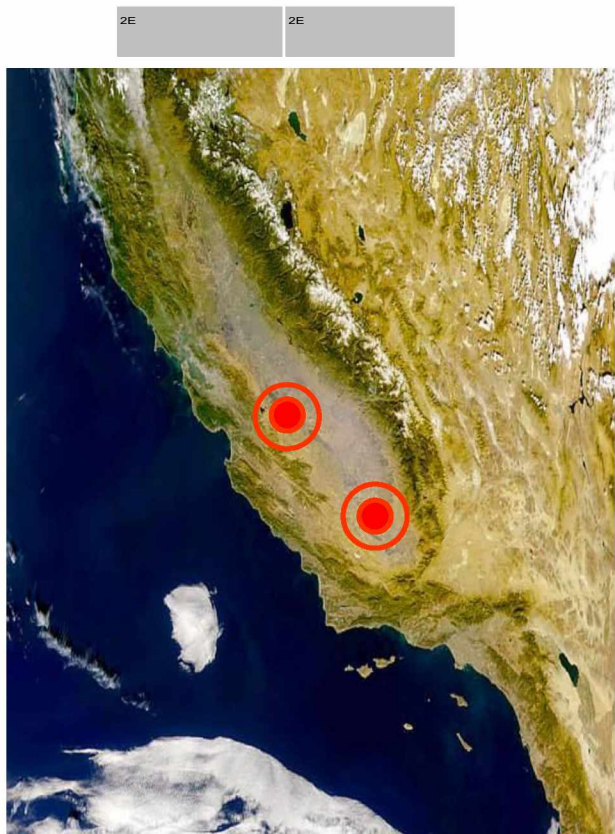


Timeline (to date)



"2020 sulfuryl fluoride project"

Crop Protection & Quality Unit



<http://fresno.ars.usda.gov>

<http://agchem.ucdavis.edu/>

UCDAVIS UNIVERSITY OF CALIFORNIA

Assigned

BROAD (TRADE):

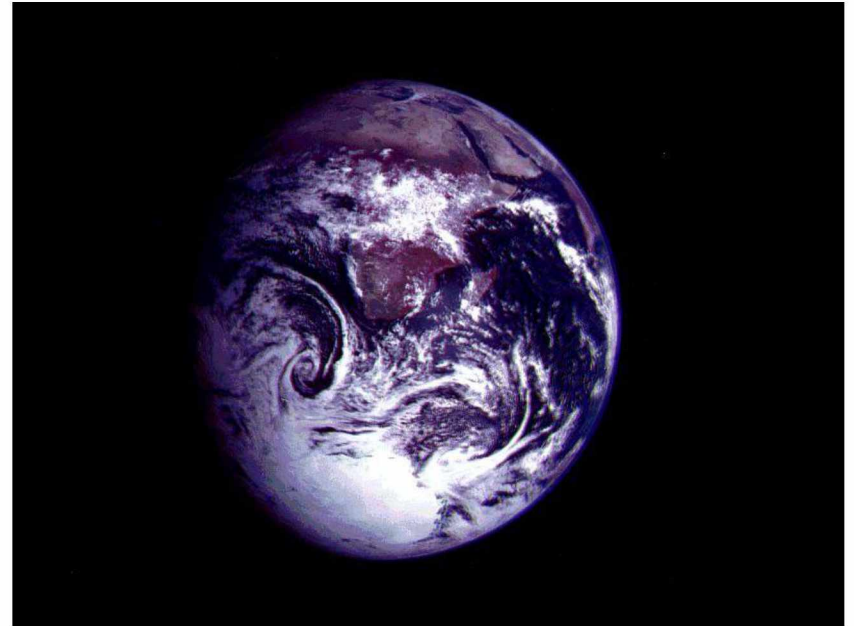
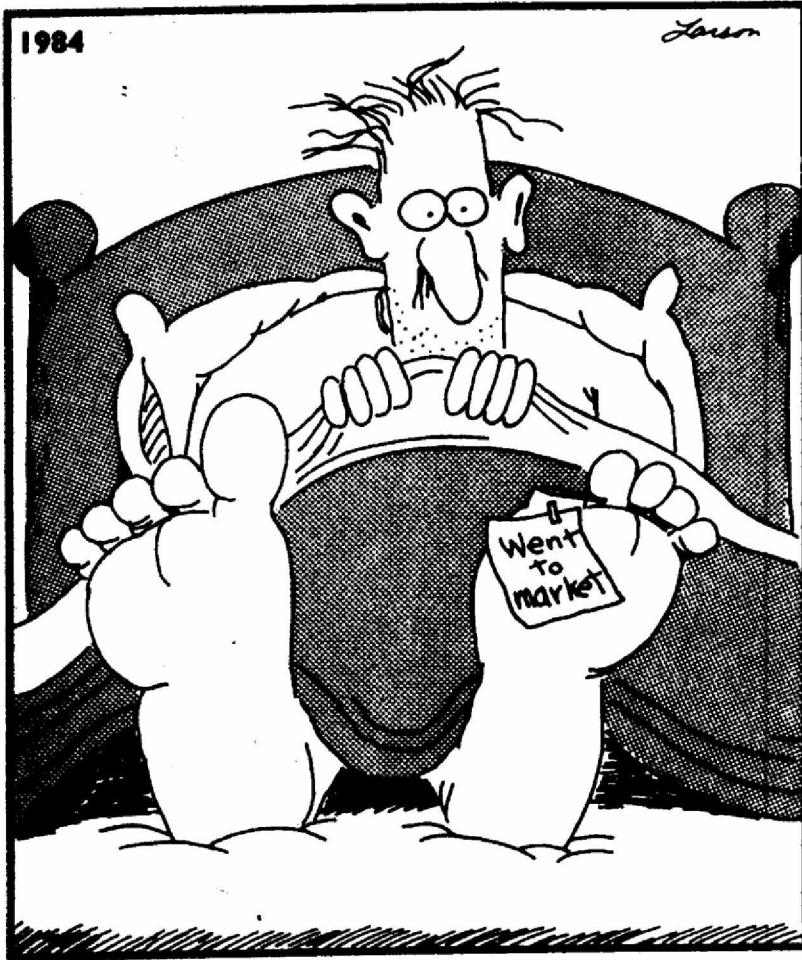
- enhance the production, distribution, quality, and safety of United States-grown horticultural commodities
- promote and retain access of the horticultural commodities to domestic and foreign markets
- protect the United States and trading partners from the agricultural, ecological, and economic threat posed by horticultural pests.

SPECIFIC:

- 1) methyl bromide (MB) and alternative fumigants in postharvest applications
- 2) novel technologies to reduce and eliminate atmospheric emissions used in postharvest fumigation
- 3) agrochemical use strategies and novel technologies to ensure compliance with regulations

30,000 ft view – what do we want to do?

(Proactively) Address Consumer & Regulatory Demands.....



....for the Global Ag. Market

Foreign Agricultural Service (FAS)

FAS works to improve foreign market access for U.S. products.

Operates programs designed to build new markets and improve the competitive position of U.S. agriculture in the global marketplace.



Technical Assistance for Specialty Crops (TASC) program provides funding to U.S. organizations for projects that address sanitary, phytosanitary and technical barriers that prohibit or threaten the export of U.S. specialty crops.

Agreements: # 2010-19 & # 2014-15

Project Title: "Retaining export and food security of U.S. specialty crops: **low-emission methyl bromide fumigations** for quarantine and pre-shipment (QPS) uses"

- AMOUNT: \$2,500,000 USD

TASC –emission control team

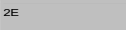
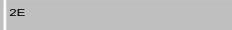
Principle Investigator:   **USDA-Agriculture Research Service, San Joaquin Valley Agricultural Science Center and University of California at Davis**

-internationally recognized expert in phytosanitary treatments and their regulation.

Co-Principal Investigators

 **IV, Safe Food Alliance (DFA of California)**

-internationally recognized expert in residue analyses.

  **Connecticut Agricultural Experiment Station and Yale University**

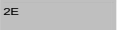
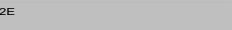
-internationally recognized expert on physicochemical aspects of sorption, including: sorption reversibility, conditions favoring desorption, screening of new sorbents, and destroying sorbed substances.

  **Stanford University**

- internationally recognized expert in the reductive properties of carbon solids and contributes understanding toward the sorbent-mediated destruction of fumigants.

 **University of California at Berkeley**

-Recommended by the USDA Office of the Chief economist, is the one of the world's preeminent agricultural economists.

  **Consultant**

- A recently retired Professor at the University of California at Davis, Department of Agricultural Engineering with > 30 years experience as the principal advisor to the California specialty crop industry regarding postharvest handling and marketing.

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Selected pubs : MB scrubbing project

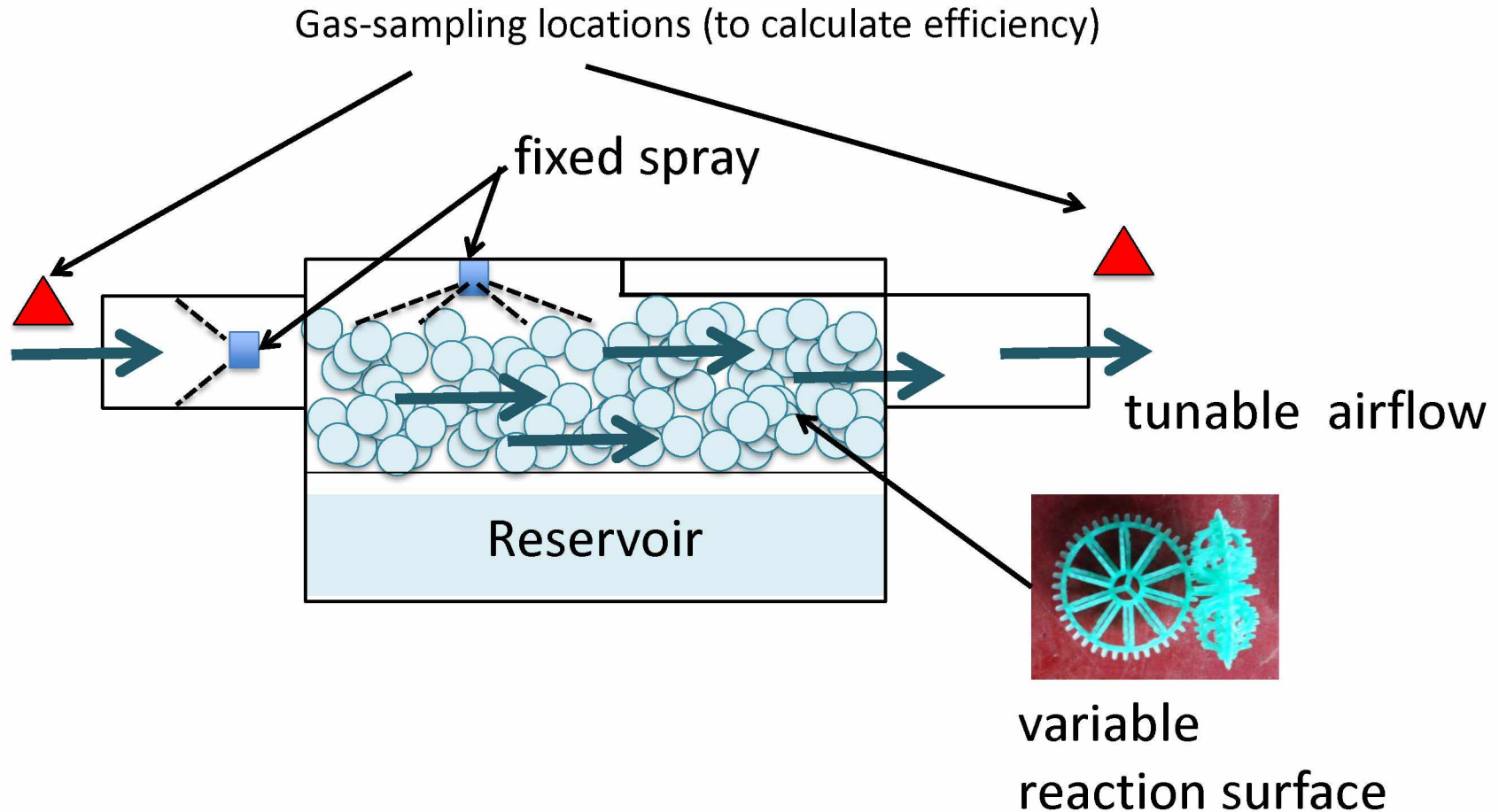
- C. Chen; J. J. Pignatello “**Catalytic oxidation** for elimination of methyl bromide fumigation emissions using cerium catalysts” *J. App. Cat. B* 2013 (142-143), 785-794.
- Y. Yang; Y. Li, S.S. Walse, W.A. Mitch “Destruction of Methyl Bromide Sorbed to Activated Carbon by **Thiosulfate and Electrolysis**” *Environ. Sci. Technol.* 2015, 49, 4515–4521
- Hall, W.A., Bellamy, D.E., and Walse, S.S. **Activated carbons from end-products of tree fruit and tree nut** production as sorbents for removing methyl bromide in ventilation effluent from postharvest chamber fumigations. *J. Agric. Food Chem.*, 2015, 63 (12), pp 3094–3103
- Waterfield, Gina Moon. “**Trade Effects of the Methyl Bromide Phaseout.**” Chapter 3 in “Essays in Environmental Economics” *PhD Dissertation at UC Berkeley* (2015): 72-97.
- Y. Li, J. Kemper, G. Datuin, A. Akey, W.A. Mitch, R. Luthy “Reductive dehalogenation of disinfection byproducts by an **activated carbon-based electrode system**” *Water Research* 98 (2016) 354e362
- Y. Li, Y. Cui, S.S. Walse , and W.A. Mitch, Development of an **Activated Carbon-Based Electrode** for the Capture and Rapid Electrolytic Reductive Debromination of Methyl Bromide from Post-Harvest Fumigations submitted *Environ. Sci. Technol.*
- Hsieh, H.-S.; Pignatello, J. J., **Activated Carbon Mediated Alkaline Hydrolysis** of Alkyl Bromides. *App. Cat. B* <http://dx.doi.org/10.1016/j.apcatb.2017.04.010>
- Hsieh, H.-S.; Pignatello, J. J., **Modified carbons** for enhanced nucleophilic substitution reactions of adsorbed methyl bromide. *App. Cat. B* 233 (2018) 281–288.

Conclusions - costs

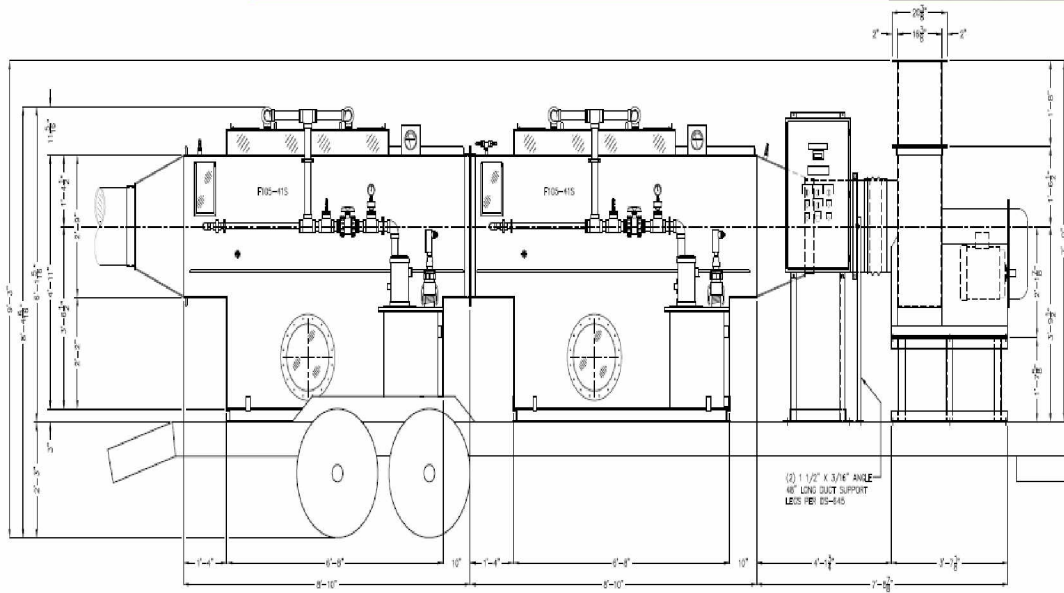
- activated carbon
 - moderate capital (transportation)
 - moderate reuse, residual
- catalytic oxidation and/or combustion
 - high capital
 - low reuse, residual
- liquid-air scrubber
 - low capital
 - moderate reuse, residual (disposal)
 - nucleophile
 - phase-transfer catalysts (not as relevant for SF)

TECHNOLOGY/COSTS ARE SCENARIO DEPENDENT

Horizontal Scrubber: equipment



Horizontal Scrubber: sources



HEE-Dual
 A CECO Environmental Brand

Terms and Delivery

Price Items A: F105-112S Custom Scrubber Mounted on Trailer, Transitions, NH80 Fan, Interconnecting Ducting, and Exhaust Stack	\$115,258.....USD
Price Items B: - OPTIONAL - OE Factory Certified Installation Services – One(1) Day On-Site	\$ 6,362.....USD
TOTAL OFFER	\$121,620.....USD

Liquid-air Scrubber: chemistry

Table 13.3 Relative Nucleophilicities of Some Important Environmental Nucleophiles: *n*-Values Determined from the Reaction with Methyl Bromide or *n*-Hexyl Bromide in Water (Eq. 13-3, *s* = 1)

Nucleophile	$n_{\text{Nu}, \text{CH}_3\text{Br}}^a$
ClO_4^-	<0
H_2O	0
NO_3^-	1.0
F^-	2.0
SO_4^{2-}	2.5
CH_3COO^-	2.7
Cl^-	3.0
HCO_3^- , HPO_4^{2-}	3.8
Br^-	3.9
OH^-	4.2
I^-	5.0
CN^- , HS^-	5.1
$\text{S}_2\text{O}_3^{2-}$	6.1 ^b
S_4^{2-}	6.8 ^b
S_4^{2-}	7.2 ^b

^a Data from Hine (1962). ^b Data from Haag and Mill (1988a).

**0-0-25-17
KTS Solution**

Conc to compete with water

Nucleophile M conc.

NO_3^-	6
F^-	0.6
SO_4^{2-}	0.2
Cl^-	0.06
HCO_3^- , HPO_3^{2-}	0.009
Br^-	0.007
OH^-	0.004
I^-	0.0006
CN^-	0.0004
HS^-	0.0004
$\text{S}_2\text{O}_3^{2-}$	0.00004
S_4^{2-}	0.000004

x 100
x 1000



LIME-SULFUR SOLUTION

ACTIVE INGREDIENT:	By Weight
Calcium Polysulfide	29.0%
OTHER INGREDIENTS	71.0%
TOTAL	100.0%

DENSITY—
Baume at 60°F 31°
Lbs. Per Gallon at 68°F 10.6

Contains Calcium and Sulfur expressed as Gypsum - 3.0 lbs. per gallon. Other combined Sulfur 1.9 lbs. per gallon.

EPA Reg. No. 66196-2

EPA Est. No. 66196-CA-1

Guaranteed Analysis
Soluble Potash (K₂O).....25.0%
Sulfur (S).....17.0%

Derived From: Potassium Hydroxide.

Lbs. of K₂O/Gal.....3.05

Density = 12.2 lbs. per gallon @ 68° F.

Information regarding the contents and levels of metals in this product is available on the internet at <http://www.asfco.org/metals.htm>

APPLICATION INSTRUCTIONS:

Deep-Placed:

Deep place 1-3 gal/acre KTS 0-0-25+17S at planting time 3-4" to side and 3" deep with nitrogen (may need additional water) or other N-P-K analysis.

Side-Dress:

Side-dress 1-5 gal/acre KTS 0-0-25+17S 6-8" to side with nitrogen* or other N-P-K analysis.

Irrigation:

In irrigation, use 1-3 gallons of KTS 0-0-25+17S with 28% nitrogen.*

* Mix 1 gallon of KTS 0-0-25+17S with 9 or 10 gallons of 28% nitrogen with no additional water needed. If more concentrated mixes are required, water should be added.

This applies to deep-placed, side-dressed, and irrigation practices.

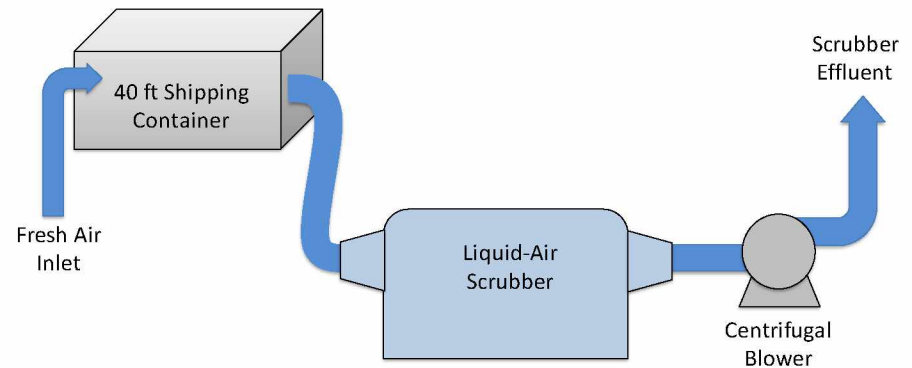
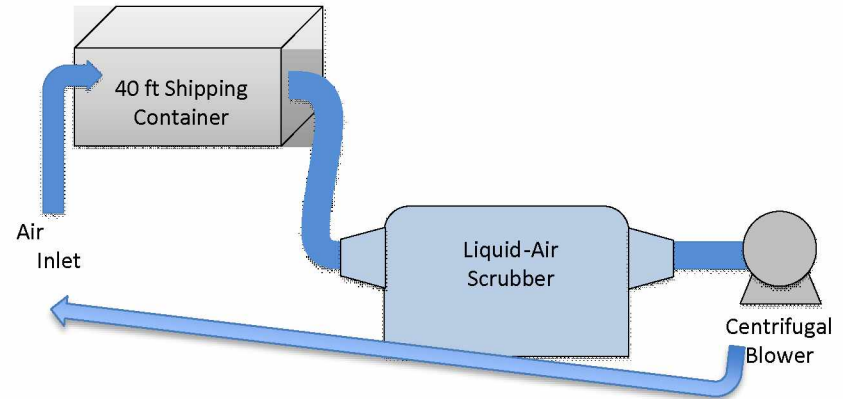
KTS 0-0-25+17S should NOT be applied in-furrow.

KTS 0-0-25+17S can be blended with other N-P-K products for foliar application, but should NOT be applied by itself and use caution. Please consult with your distributor or agronomist for specific recommendations.

Application Restrictions: Do not apply to sensitive crops. Do not apply to sensitive crops.

Liquid-air scrubber: scenarios

- Non-food
 - Recirculation is an option
 - not a large focus, so far
- Food products
 - Recirculation was not an option
 - Major focus



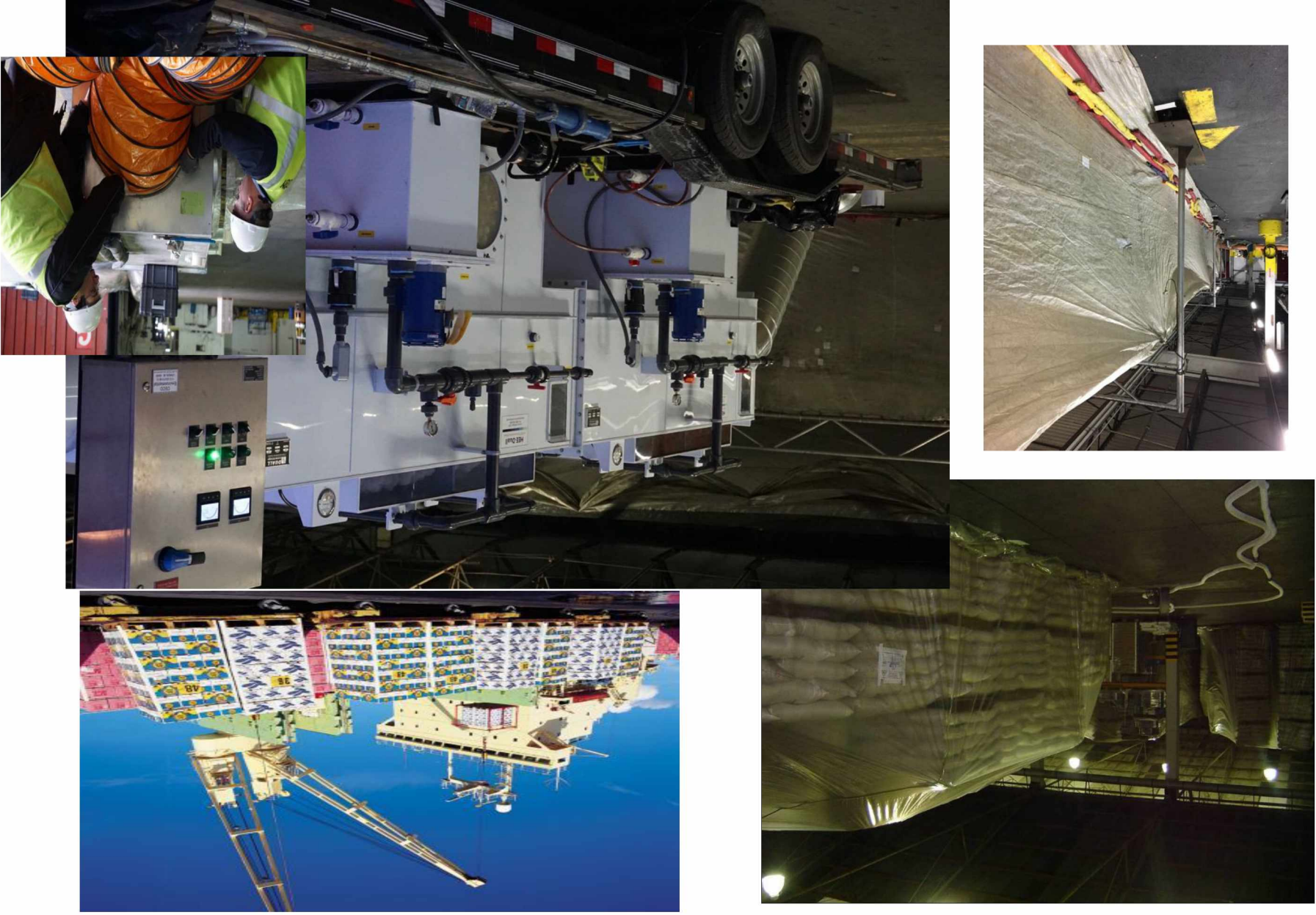
Scale, time, operations and logistics critical

- “small” scenarios ($\sim 10 \times 100 \text{ m}^3$ containers per day, chambers, etc.)
- “large” scenarios (~ 100 to $1000 \times 100 \text{ m}^3$ container boats, buildings)

supplier “small” Scenarios



port "large" Scenarios



- Technical Assistance for Specialty Crops (TASC)-USDA Agreement: # 2018-02
- Project Title: “Preserving sulfuryl fluoride for dried fruit exports to the European Union”
 - AMOUNT: \$2,500,000 USD
- Project Goal:
 - Marketing: Long-term retention of USA-grown dried fruit and tree nuts treated with sulfuryl fluoride (SF)



#5 Limit SF emissions following postharvest fumigation

Gas Fumigant

©Trademark of Douglas Products and Packaging Company

If the use of SF is to continue, data must be provided to demonstrate that its concentration in the troposphere is not increasing, or has reached a steady-state. Developing low-emission technologies to limit, or ultimately eliminate, SF emissions to the atmosphere will enable the sulfuryl fluoride levels to reach a lower steady-state concentration, more quickly.

Walse team: short-term, commercial relevance



liquid-air scrubber

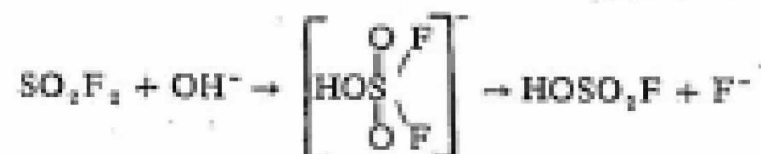
sulfuryl fluoride hydrolysis

Hydrolysis of Sulfuryl Fluoride

GEORGE H. CADY* and SUDHINDRA MISRA

Received August 10, 1973

Sulfuryl fluoride dissolves rapidly in water and may be quickly removed from solution by dynamic vacuum. The solubility of the gas has been measured at 0.0 and 23.3°. Hydrolysis of sulfuryl fluoride is slow in water but rapid in basic solutions, the net reaction being $\text{SO}_2\text{F}_2 + 2\text{OH}^- \rightarrow \text{SO}_3^{2-} + \text{F}^- + \text{H}_2\text{O}$. The rate law may be written as $-\text{d}[\text{SO}_2\text{F}_2]/\text{d}t = [\text{SO}_2\text{F}_2] \cdot (k_w + k[\text{OH}^-])$. At pH values of 7.5 or greater, k_w is negligible when compared to $k[\text{OH}^-]$. Over the temperature range 0–25°, $k = 1.67 \times 10^{12} e^{-13,150/RT}$, when time is in seconds and concentrations are in moles per liter. The reaction is considered to be a nucleophilic displacement of fluorine in which the controlling process is



Sulfuryl fluoride reacts readily in aqueous solution with the nucleophiles NH_3 , $\text{C}_6\text{H}_5\text{O}^-$, and CN^- .

Volumetric Determination of Concentrations of Sulfuryl Fluoride in Air

STANLEY G. HEUSER

Pest Infestation Laboratory, Agricultural Research Council, Slough, Buckinghamshire, England

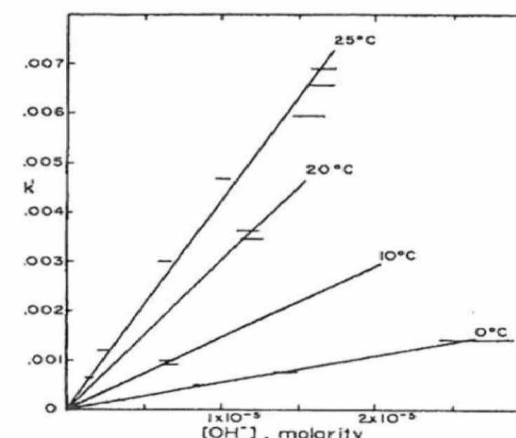
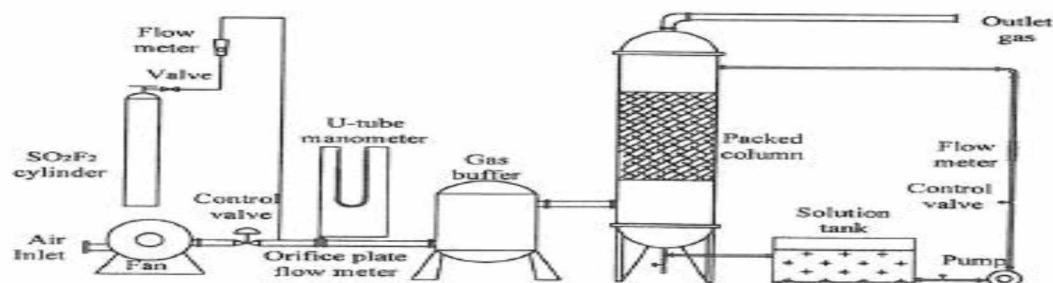


Figure 1. Relationship between the pseudo-first-order rate constant, k' , and the molarity of OH^- at certain temperatures.

sulfuryl fluoride hydrolysis liquid-air scrubbing

ENVIRONMENTAL ENGINEERING SCIENCE
Volume 32, Number 9, 2015
© Mary Ann Liebert, Inc.
DOI: 10.1089/ees.2015.0021



Harmless Treatment of Sulfuryl Fluoride by Chemical Absorption

Yong Nie,^{1,*} Xiaojang Liang,¹ Jianbing Ji,¹ Meizhen Lu,¹ Fengwen Yu,¹ Dayong Gu,²
Qinglong Xie,³ and Min Min³

¹College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, China.

²Shenzhen International Travel Health Care Center, Shenzhen, China.

³Center for Biorefining and Department of Bioproducts and Biosystems Engineering, University of Minnesota, Saint Paul, Minnesota.

Received January 19, 2015

Accepted in revised form July 20, 2015

Mass transfer and reaction kinetics of sulfuryl fluoride absorption with aqueous sodium hydroxide solutions^{*}

Yong NIE^{†1}, Xiao-jiang LIANG¹, Mei-zhen LU¹, Feng-wen YU¹, Da-yong GU², Min MIN³, Jian-bing JI¹

¹College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China)

²(Shenzhen International Travel Health Care Center, Shenzhen 518033, China)

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Received Feb. 23, 2014; Revision accepted May 8, 2014; Crosschecked June 24, 2014

Nomenclature

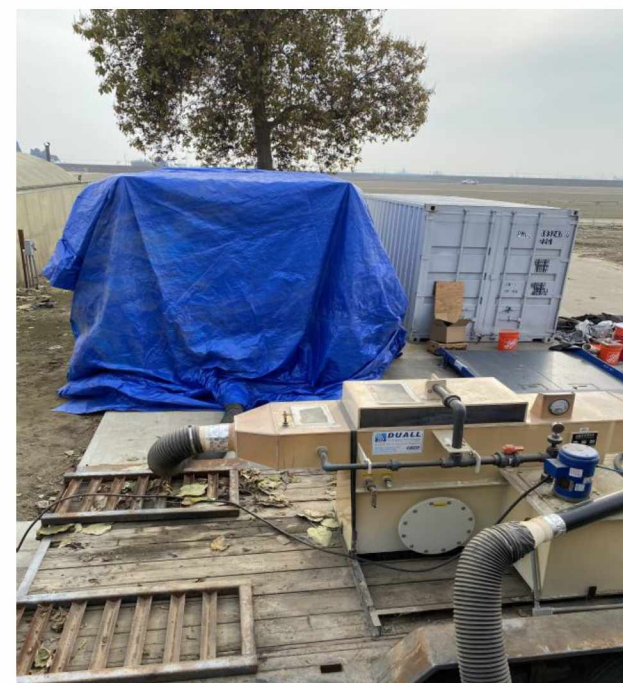
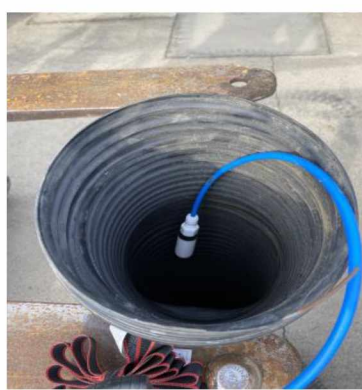
a_i = total surface area per unit packed volume [m^2/m^3]
 a = effective interfacial area per unit packed volume [m^2/m^3]
 C_{NaOH} = molar concentration of sodium hydroxide [mol/L]
 C_{Ain} = volume concentration of SO_2F_2 at the inlet of the packed column [%]
 C_{Aout} = volume concentration of SO_2F_2 at the outlet of the packed column [%]
 D_G = diffusivity of gas phase [m^2/s]
 D_L = diffusivity of liquid phase [m^2/s]
 D_p = diameter of packing [m]
 E = enhancement factor for absorption with chemical reaction, dimensionless
 G = superficial mass velocity of SO_2F_2 [$\text{kg}/\text{m}^2 \cdot \text{s}$]
 g = gravitational constant [m/s^2]
 H = Henry's Law constant [$\text{kmol}/\text{m}^3 \cdot \text{kPa}$]
 K_G = gas-phase overall coefficient [$\text{kmol}/\text{m}^2 \cdot \text{s} \cdot \text{kPa}$]
 k_G = gas-phase mass transfer coefficient [$\text{kmol}/\text{m}^2 \cdot \text{s} \cdot \text{kPa}$]
 k_L = liquid-phase mass transfer coefficient [m/s]
 L = superficial mass velocity of liquid [$\text{kg}/\text{m}^2 \cdot \text{s}$]
 N_A = mass transfer rate of gas [$\text{kmol}/\text{m}^2 \cdot \text{s}$]
 P = total pressure [kPa]
 Q = molar flow rate of gas [kmol/s]
 R = gas constant [$\text{m}^3 \cdot \text{kPa}/\text{kmol} \cdot \text{K}$]
 S = cross-sectional area of column [m^2]
 T = absolute temperature [K]
 y_{Ain} = SO_2F_2 molar fraction at the inlet of the packed column
 y_{Aout} = SO_2F_2 molar fraction at the outlet of the packed column
 Z = height of packing column [m]

Container – Recirculation Results

	Half-life $t^{1/2}$			Scrubbing time*
	UL	LL	95CL	
Nucleophile	(min)	(min)	(min)	(min)
OH	10.1	14.5	61	
S2O3	5.8	9.2	38	

* Estimated time required to reduce SF concentration from 130 g m^{-3} to $< 5 \text{ g m}^{-3}$.

- Nominal SF concentration in chamber = 130 g/m^3 .
- Nucleophile concentration = 2kg in 353kg water (0.14 mol/l)
- Scrubber fluid flow rate = 87 kg/m (23 gpm)
- Scrubber airflow rate = $93 \text{ m}^3/\text{h}$ (55cfm), 24 air changes/h
- SF measured with Spectros sensor and GC -PFPD



Container - Results

Single-Pass Configuration

Commercial scale liquid-air scrubber in Philadelphia- 2020

- 1100L in both reservoirs
- 15 lbs (6,8kgs) of NaOH in each scrubber (~0.1 M)
- 35 lbs/1000 ³ft of SF Gas

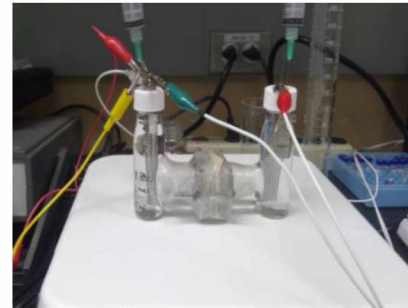
Time (Minutes)	Inlet Conc. (mg/L)	Outlet Conc. (mg/L)	% Reduction
10	31.0	10.0	67.8
21	49.3	4.4	91.0
28	36.3	3.6	90.1
38	26.1	1.9	92.7

Half-life $t^{1/2} = 17.6$ min, a container with 130 g/m³ has a scrub time of ca. 90 min



Future Testing

- Optimize for sulfonyl fluoride
- Necessity of phase-transfer catalyst
- Evaluate scrubber operation parameters: gas flow, fluid flow, reaction surface, etc.
- Electrochemical generation of nucleophiles
- Other cooperators?
- Commercial testing



Summary / next steps

- We have a workable concept, but the optimal nucleophile is still being determined
- Goal for the effluent is to be easily disposed, potential re-use (e.g. in agri industry)
- The technology will need to be transferred and built to meet local requirements (e.g. size & number of containers, turn around time, mobile vs stationary,...)
- Further enhancements of the filter efficiency may require further research and field trials

THANK YOU!

Bijlage:

SDS 6 emisob

Safety Data Sheet



Product name:

Chemisorb S

Safety Data Ref: 23

Initial issue date: 09 March 2012

Revision date: 01 June 2015

Version number: 15

1	IDENTIFICATION OF SUBSTANCE	
1.1	Relevant use	As an absorbent for carbon dioxide and other acidic gases

2	HAZARDS IDENTIFICATION				
2.1	Classification of the substance				
2.1.1	Classification according to Regulation (EC) No 1272/2008 (CLP/GHS) – see section 11		2.1.2	Classification according to EC – see section 11	
	Skin irrit. 2	H315		Xi	R36/38
	Eye irrit. 2	H319			
2.1.3	Labelling in accordance with EC Directives 67/548/EEC and 1999/45/EC (CHIP 4)				
2.2	Labelling elements				
2.2.2	Labelling in accordance with EC Regulation No 1272/2008 (CLP/GHS)				
	Pictogram		Signal word	WARNING	
	Hazard statements				
	H315	Causes skin irritation			
	H319	Causes serious eye irritation			
	Precautionary statements				
	P280	Wear protective gloves / protective clothing / eye protection / face protection			
	P314	Get medical advice / attention if you feel unwell			
	P302/352	If on skin: wash with plenty of soap and water			
	P305/351/338	If in eyes: rinse cautiously with water for several minutes. Remove contact lenses, if present, and easy to do. Continue rinsing.			
	P332/313	If skin irritation occurs: get medical advice / attention			
2.2	Other hazards				
	None known				

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3	COMPOSITION / INFORMATION ON INGREDIENTS				
	Chemical characterisation	Solid bases plus additives – see section 16 The CHIP/CLP classification required in this section are related to that of the product supplied. To comply with the legislation the classification of the relevant ingredients of the products, as if they were present at 100%, must be outlined. Where ingredients are present in the product at very low concentrations the level of risk to the user is reduced, hence the reason that the classification for the individual components and the product are different			
	Chemical name	CAS-No	EINECS/ELINCS	Classification	Concentration
	Sodium Hydroxide	1310-73-2	215-185-5	CHIP: C: R35 CLP : Skin Corr. 1A H314	<4%
	Calcium Hydroxide	1305-62-0	215-137-3	CHIP: Xi: R38, 41 CLP : Skin Irrit. 2 H315 Eye Damage 1 H318 WEL assigned	>75%

4	FIRST AID MEASURES	
4.1	Description of measures	
	Inhalation	Remove casualty to fresh air and provide warmth and rest
	Skin contact	Clean areas of skin affected immediately with soap and plenty of water. If necessary, seek medical advice
	Eye contact	Immediately wash out eye thoroughly with plenty of water until irritation subsides; consult an eye specialist/ophthalmologist
	Ingestion	Unlikely route of exposure. But if product is swallowed, do not induce vomiting. Drink plenty of water and, if necessary, seek medical advice
4.2	Most important effects / symptoms	None known
4.3	Immediately / special treatment	Treatment as described above

5	FIRE FIGHTING MEASURES	
5.1	Extinguishing media	To suit local surroundings (e.g. chemical powder, carbon dioxide, dry sand, water)
5.2	Special hazards	None known
5.3	Advice for fire fighters	Self-contained breathing apparatus may be required

6	ACCIDENTAL RELEASE MEASURES	
6.1	Personal precautions	Adhere to personal protective measures
6.2	Environmental precautions	Do not allow to get into waste water or waterways; if this occurs, inform the relevant water authority at once
6.3	Methods and materials for cleaning up	In the event of spillage, take up mechanically (e.g. sweep or vacuum up) into tightly closed containers. Adhere to personal protective measures. Flush any remainder with plenty of water. Label container and dispose of as prescribed

6.4	Reference to other sections	See section 8 for personal protective equipment
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7	HANDLING AND STORAGE	
7.1	Precautions for safe handling	Handle in accordance with good hygiene and safety practice. Avoid the raising and deposition of dust
7.2	Conditions for safe storage	Ensure adequate ventilation of the storage area. Keep containers tightly closed, cool (0-35°C) and dry, avoiding direct sunlight
7.3	Specific end use(s)	As an absorbing agent

8	EXPOSURE CONTROLS / PERSONAL PROTECTION				
8.1	Workplace Exposure Limits (WELs) have been assigned by the HSE (EH40/2005)				
	STEL (15 min)	ppm	2	mg/m ³	Data for sodium hydorxide
	LTEL (8 hour TWA)	ppm	5	mg/m ³	Data for calcium hydroxide
8.2	Exposure controls				
	Engineering controls	Provide adequate ventilation (e.g. local exhaust ventilation)			
	Personal protection	Observe normal standards for handling chemicals Wash hands before breaks and after work Avoid inhalation of dust if raised Wear personal protective equipment appropriate to the task (see below)			
	Eye protection	Safety goggles if risk of eye contamination			
	Skin protection	Suitable gloves (consider your own risk assessment; e.g. breakthrough times, rates of diffusion and degradation, tasks undertaken)			
	Respiratory protection	Approved dust mask or respirator (e.g. EN 149:2001 FFP3) for dust if ventilation is insufficient			
	Other protection	Protective overalls			

9	PHYSICAL AND CHEMICAL PROPERTIES			
9.1	Basic physical and chemical properties			
	Physical form	Solid	Colour	White or coloured
	Odour	Odourless	pH	12-14
	Boiling pt/range	Not determined	Melting pt/range	Not determined
	Flash point	Not applicable	Relative density	~ 0.9 g/cm ³
	Water solubility	Slight	Odour treshold	Not applicable
	Evaporation rate	Not applicable	Flammebility	Not applicable
	Explosion limits	Not applicable	Vapour pressure	Not applicable
	Vapour density	Not applicable	Partition coeff. LogPoct / water	Not applicable
	Auto-ignition temperature	Not applicable	Viscosity	Not applicable
	Explosive properties	Not determined	Oxidising properties	Not determined
	Decomposition temperature	Not determined		

9.2	Other Information	None known
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10	STABILITY AND REACTIVITY	
10.1	Reactivity	Heat is generated if exposed to acids
10.2	Chemical stability	Stable under normal conditions of handling
10.3	Hazardous reactions	Hazardous polymerization will not occur
10.4	Conditions to avoid	Contact with air – formation of calcium and sodium carbonate
10.5	Incompatible material	Chloroform, trichloroethylene
10.6	Hazardous decomposition products	None

11	TOXICOLOGICAL INFORMATION			
11.1	Information on toxicological effects			
	Acute toxicity	LD (lo) rabbit (oral)	500 mg/kg	Data for sodium hydorxide
		LD ₅₀ rat (oral)	> 7 000 mg/kg	Data for calcium hydroxide
	Dermal compatibility	No data available		
	Mucous membrane	No data available		
	Further information	Although using the 'conventional method' under CHIP or 'specific concentration' limits under CLP, the product classification would be 'corrosive', using EU official <u>in vitro</u> tests on the whole product, it was found to be irritating to eyes and skin, not corrosive		

12	ECOLOGICAL INFORMATION				
12.1	Toxicity	LC ₅₀	Aquatic organisms	mg/l	No data available
12.2	Degradability	Not determined	12.3	Bioaccumulative potential	Not determined
12.4	Mobility in soil	Not determined	12.5	PBT/vPvB assessment	Not applicable
12.6	Other adverse effects	WGK (Water-endagerment class): I			

13	DISPOSAL CONSIDERATIONS	
	Advice on disposal	If possible, recycle to supplier or approved recycling company. If not (e.g. designated as waste), dispose of in accordance with national and local authority regulations, e.g. The Hazardous Waste (England & Wales) Regulations 2005
	Contaminated packaging	Treat empty containers in the same way as the product. If possible wash out thoroughly and recycle

14	TRANSPORT INFORMATION				
14.1	United Nations number (ADR, IMDG, IATA)	Not classified	14.2	Proper shipping name (ADR, IMDG, IATA)	Not classified
14.3	Transport class(es) (ADR, IMDG, IATA)	Not classified	14.4	Packing group (ADR, IMDG, IATA)	Not classified
14.5	Environmental hazards (ADR, IMDG, IATA)	The product should not be marked as a marine pollutant	14.6	Special procedures (ADR, IMDG, IATA)	Not applicable
14.7	Transport in bulk	Not applicable			

15	REGULATORY INFORMATION	
15.1	Safety, health and environmental regulations	The product is classified in accordance with the Chemicals (Hazard Information and Packaging for Supply) Regulations (CHIP 4) and EC Regulation 1272/2008 (CLP). Other regulatory information and provisions are not applicable for this product
15.2	Chemical safety assessment	Not applicable

16	OTHER INFORMATION			
	Further information	The SDS has been revised in accordance with EC Regulation 1272/2008 (CLP)		
		Comply with COSHH Regulations		
	Hazard statements and Risk phrases referred to in sections 2/3			
	H314	Causes severe skin burns and eye damage	H318	Causes serious eye damage
	H315	Causes skin irritation	H319	Causes serious eye irritation
	Sources of data	Other suppliers' safety data sheets, Annex VI of the CLP Regulation (EC) No 1272/2008, EH40 (2011) OECD 431, 2004 Testing of chemicals, in vitro skin corrosion, human skin test model		
	Date of issue	01/06/2015		
	This information is based on our present state of knowledge and is intended to describe our products from the point of view of the safety requirements. It should not be construed as guaranteeing specific problems			