

Chlorosilane Emergency Response Guidelines

2nd edition

Joseph Aleksa James Blum Jeffrey Gray Timothy Gregory William Maki Michael D. Snyder Michael C. Strong



Joseph Aleksa, James Blum, Jeffrey Gray, Timothy Gregory, William Maki, Michael D. Snyder, and Michael C. Strong

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Foreword

THIS PUBLICATION, *Manual on Chlorosilane Emergency Response Guidelines*, was sponsored by Committee(s) F20, F20.11 on Hazardous Substances and Oil Spill Response. This is Manual 33-2nd in ASTM's manual series. The editors, all members of the Operating and Safety Committee of the Silicones Environmental, Health and Safety Center (SEHSC), a sector group of the American Chemistry Council (ACC), were the following: Joseph Aleksa, Process Safety Management Leader, Momentive Performance Materials, 3500 South State Route 2, Friendly, WV 26146; James Blum, Product Stewardship Manager, Bluestar, 2 Tower Center Blvd., Suite 1601, East Brunswick, NJ 08816; Jeffrey Gray, Dow Corning Safety Business Partner, Core and Polysilicon Operations, Dow Corning Corporation, 2200 West Salzburg Road, Midland, MI 48611; Timothy Gregory, EHS Engineer, Shin-Etsu, 1150 Damar Dr., Akron, OH 44305; William Maki, Manufacturing Consultant, Dow Corning Corporation, 2200 West Salzburg Road, Midland, MI 48611; Michael D. Snyder, Corporate Safety, Industrial Hygiene and Loss Prevention, Dow Corning Corporation, 2200 West Salzburg Road, Midland, MI 48611; and Michael C. Strong, Senior Regulatory Affairs Specialist, Wacker Silicones Corporation, 3301 Sutton Road, Adrian, MI 49211-9397.

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Chapter 1 | Introduction

THIS GUIDE, WHICH HAS BEEN DIVIDED into twelve chapters, has been put together by the Operating Safety Committee of the Silicones Environmental, Health, and Safety Council (SEHSC). The purpose of this document is to provide persons who handle or use chlorosilanes with information on how to safely handle chlorosilanes and respond to fires, leaks, and spills involving chlorosilanes. The techniques described in this guide have been assembled to be used by trained and knowledgeable emergency response teams.

The Operating Safety Committee of SEHSC has divided chlorosilanes into four distinct classes (see Chapter 2, "Initial Emergency Response Guides"). These four classes define the various hazards of the materials and provide the emergency responder with some general information concerning the unique hazards of chlorosilanes. The SEHSC guidelines are organized in the same manner as the 2012 Emergency Response Guidebook (ERG) pages for maximum familiarity to emergency responders. The ERG contains guidance for similar classes of materials in Guides 139, 155, 156, and 157. Guides 139, 155, and 156 contain some notes on fire response actions specific to chlorosilanes, but they do not fully cover all of the unique hazards specific to chlorosilanes. These four classes are

- 1. SEHSC-001 (ERG Guide 139): Any chlorosilane containing a SiH bond
- 2. SEHSC-002 (ERG Guide 155): Flammable chlorosilanes not containing SiH bonds
- 3. SEHSC-003 (ERG Guide 156): Combustible chlorosilanes not containing SiH bonds
- 4. SEHSC-004 (ERG Guide 157): Silicon tetrachloride

All chlorosilanes will burn with the exception of Class SEHSC-004. Class SEHSC-001 chlorosilanes may be either flammable or combustible and may release hydrogen under certain conditions. SEHSC-001 chemicals will react with:

- Water and base to release hydrogen
- Water and acid to release hydrogen
- Water and the chlorosilane may ignite
- Water to form hydrolysis byproducts that may ignite upon contact with water or mechanical impact
- Water to release corrosive/toxic hydrogen chloride (HCl) vapors

Many of the techniques described in these guidelines will cause hydrogen to be released from SEHSC-001 chemicals. Care should be taken to provide adequate ventilation and to prevent these materials from entering a sewer system. Note that flowing chlorosilanes are susceptible to static buildup and ignition because of their low electrical conductivity.

The primary objective of a response to a chlorosilane spill or fire is to limit the chlorosilane/HCl vapor release. Fighting the fire should

be considered secondary to this primary objective. Chlorosilanes all react with moisture in the air to form HCl. The primary objective will be met by minimizing the amount of water contacting the chlorosilane liquid.

Chlorosilane fires are not easily extinguished by conventional fire-fighting techniques. Chapter 4 describes the use of foam in fighting a chlorosilane fire and reducing the amount of vapor release. This guide also recognizes that the acid created by water coming in contact with chlorosilane is an environmental and a responder's safety concern.

In the course of responding to a fire involving chlorosilanes, if wind patterns are expected to remain stable and calm (i.e., little or no wind as determined by observation of a vertical smoke plume from the fire), then it may be preferable to let the fire burn rather than attempt to extinguish it. Rising hot air currents will carry the HCl vapor cloud to higher elevations, where the cloud will disperse and reduce the risk of overexposure to personnel at ground level. Because this method depends on stable and calm conditions, atmospheric conditions must be closely monitored. If conditions change, then another means of mitigating the emergency as suggested in this guide should be considered.

As stated previously, this document has been developed to provide procedures that can be used to safely handle a chlorosilane fire or spill. Generally accepted emergency response procedures for which most emergency response teams have been trained (e.g., container patching techniques and relief valve field repair) are not included in this guide. Please refer to the ASTM Guide for Containment by Emergency Response Personnel of Hazardous Material Spills (F1127) for these procedures. Emergency responders should also refer to ASTM Manual 10-A Guide to the Safe Handling of Hazardous Materials Accidents and the ASTM Guide for Using Aqueous Foams to Control the Vapor Hazard from Immiscible Volatile Liquids (F1129). Note also that the personal protective equipment (PPE) normally used with HCl exposures does not necessarily protect a responder from chlorosilanes (see Chapter 10, "Personal Protective Equipment Requirements"). Note also that all flashpoints identified in this guide are based on Occupational Safety and Health Administration (OSHA), not U.S. Department of Transportation (DOT), definitions.

Because a chlorosilane spill or fire can occur under many different circumstances, it is not possible to assemble a plan that is applicable in every situation. Nevertheless, Chapter 3 contains a decision tree that should assist emergency response teams in determining the correct course of action and finding the section of the guide that provides guidance on how to perform the appropriate task. Updates to this manual will be made by the Operating Safety Committee of SEHSC.

Chapter 2 | Initial Emergency Response Guides

A. GUIDE SEHSC-001 (Any Chlorosilane Containing a SiH Bond)

1. POTENTIAL HAZARDS

a. FIRE OR EXPLOSIONS

- Flammable; may self-ignite in air.
- May re-ignite itself after fire is extinguished.
- Releases dense, irritating, and corrosive fumes.
- Violent reaction with water, releasing flammable (hydrogen) and corrosive vapor.
- Runoff may create fire or explosion hazard in sewer/ confined space.
- When the fire is above ground or inside of a container, consider letting the fire burn until expert assistance is obtained.

b. HEALTH HAZARDS

- Contact with moisture in air forms a corrosive vapor.
- Causes severe burns if swallowed or inhaled.
- Contact causes burns to skin and eyes.
- Fire or spill produces irritating and corrosive vapors.
- Runoff from fire or spill control may cause pollution.

2. EMERGENCY ACTIONS

- Keep unnecessary people away; isolate hazard area and deny entry.
- Stay upwind; keep out of low areas.
- Positive pressure self-contained breathing apparatus (SCBA) and structural firefighter protective clothing may provide limited protection.
- In case of fire, isolate for 0.5 mile in all directions if tank, tank car, or cargo tank is involved.
- In case of spill, isolate according to Table of Initial Isolation and Protective Action Distances for Hydrogen Chloride, ID #1050. (From *Emergency Response Guidebook* [ERG].)
- CALL CHEMTREC AT 1-800-424-9300 FOR EMERGENCY ASSISTANCE.
- If water pollution occurs, then notify the appropriate authorities.

a. FIRE

- These materials will react violently with water; do not apply water directly to burning material.
- Fires are difficult to extinguish using conventional methods.
- Do not put extinguishing medium inside container.

(i) Small Fires

- Use CO₂ or medium-expansion alcohol compatible aqueous film-forming foam (AFFF).
- Expect to use large quantities of extinguishing medium compared with similar sized hydrocarbon fires.

(ii) Large Fires

- Use AFFF alcohol-resistant medium-expansion foam. Repeated applications may be required for fire extinguishment.
- Liquid may re-ignite if foam blanket is not maintained.
- Initial applications of foam will release significant amounts of flammable and corrosive vapors and could trap them under the blanket.
- Water spray may be used downwind to knock down corrosive vapor cloud.
- Apply cooling water to sides of containers that are exposed to flames until fire is out, provided the water does not come in contact with the tank contents. Stay away from ends of tanks.

b. SPILL OR LEAK

- Do not touch or walk through spilled material; stop leak if it can be done without risk.
- Fully encapsulating, vapor-protective clothing should be worn if working in the vapor cloud.
- Consider the use of flash protection where appropriate.
- Eliminate ignition sources: no flares, smoking, or flames in hazard area.

(i) Small Spills

- Absorb spill with dry absorbent materials or cover with medium-expansion foam.
- Do not allow any of these materials to enter container.

(ii) Large Spills

- Dike to contain spill.
- Cover with any medium-expansion AFFF.
- Do not allow any of these materials to enter container.
- Applications of foam will release significant amounts of flammable and corrosive vapors and could trap them under the blanket.
- Water spray or fog may be used downwind to knock down corrosive vapor cloud.
- Do not apply water directly to spilled material.
- Clean up only under supervision of an expert.

- Move victim to fresh air and call emergency medical care. If not breathing, then give artificial respiration. If breathing is difficult, then give oxygen.
- In case of contact with material, immediately flush skin and eyes with running water for at least 15 min.
- Speed in removing material from skin and eyes is of extreme importance.
- Remove and isolate contaminated clothing and shoes at the site.

B. GUIDE SEHSC-002 (Flammable Chlorosilanes Not Containing SiH Bonds)¹

1. POTENTIAL HAZARDS

a. FIRE OR EXPLOSIONS

- Flammable, may be ignited by heat, sparks, or open flame.
- Releases dense, irritating, and corrosive fumes.
- Violent reaction with water, releasing irritating and corrosive vapor.
- Runoff may create fire or explosion hazard in sewer/ confined space.

b. HEALTH HAZARDS

- Contact with moisture in air forms a corrosive vapor.
- Causes severe burns if swallowed or inhaled.
- Contact causes burns to skin and eyes.
- Fire or spill produces irritating and corrosive vapors.
- Runoff from fire or spill control may cause pollution.

2. EMERGENCY ACTIONS

- Keep unnecessary people away; isolate hazard area and deny entry.
- Stay upwind; keep out of low areas.
- Positive pressure self-contained breathing apparatus (SCBA) and structural firefighter protective clothing may provide limited protection.
- In case of fire, isolate for 0.5 mile in all directions if tank, tank car, or cargo tank is involved.
- In case of spill, isolate according to Table of Initial Isolation and Protective Action Distances for Hydrogen Chloride, ID #1050. (From *Emergency Response Guidebook* [ERG].)
- CALL CHEMTREC AT 1-800-424-9300 FOR EMERGENCY ASSISTANCE.
- If water pollution occurs, then notify the appropriate authorities.

a. FIRE

- These materials will react violently with water; do not apply water directly to burning material.
- Fires are difficult to extinguish using conventional methods.
- Do not put extinguishing medium inside container.
- When fire is above ground or inside of a container, consider letting fire burn until expert assistance is obtained.

(i) Small Fires

• Use dry chemical, CO₂, or medium-expansion aqueous film-forming foam (AFFF).

¹*Flammable liquid*—defined as a liquid with a flash point of less than 100°F (37.7°C).

• Expect to use large quantities of extinguishing medium.

(ii) Large Fires

- Use AFFF alcohol-resistant medium-expansion foam. Repeated applications may be required for fire extinguishment.
- Initial applications of foam will release significant amounts of corrosive vapors.
- Water spray or fog may be used downwind to knock down corrosive vapor cloud.
- Apply cooling water to sides of containers that are exposed to flames until fire is out, provided the water does not come in contact with the tank contents. Stay away from ends of tanks.

b. SPILL OR LEAK

- Do not touch or walk through spilled material; stop leak if it can be done without risk.
- Fully encapsulating, vapor-protective clothing should be worn if working in the vapor cloud with no fire. It may provide little or no thermal protection.
- Consider the use of flash protection where appropriate.
- Eliminate ignition sources: no flares, smoking, or flames in hazard area.

(i) Small Spills

- Absorb spill with dry absorbent materials or cover with medium-expansion foam.
- Do not allow any of these materials to enter container.

(ii) Large Spills

- Dike to contain spill.
- Use AFFF alcohol-resistant medium-expansion foam.
- Do not allow any of these materials to enter container.
- Applications of foam will release significant amounts of corrosive vapors.
- Water spray or fog may be used downwind to knock down corrosive vapor cloud.
- Do not apply water directly to spilled material.
- Clean up only under supervision of an expert.

- Move victim to fresh air and call emergency medical care. If not breathing, then give artificial respiration. If breathing is difficult, then give oxygen.
- In case of contact with material, immediately flush skin and eyes with running water for at least 15 min.
- Speed in removing material from skin and eyes is of extreme importance.
- Remove and isolate contaminated clothing and shoes at the site.

C. GUIDE SEHSC-003 (Combustible Chlorosilanes Not Containing SiH Bonds)²

1. POTENTIAL HAZARDS

a. FIRE OR EXPLOSIONS

- Combustible.
- Releases dense, irritating, and corrosive fumes containing hydrogen chloride gas.
- Violent reaction with water releases irritating and corrosive gas.

b. HEALTH HAZARDS

- Contact with moisture in air forms a corrosive vapor.
- Causes severe burns if swallowed or inhaled.
- Contact causes burns to skin and eyes.
- Fire or spill produces irritating and corrosive gases.
- Runoff from fire or spill control may cause pollution.

2. EMERGENCY ACTIONS

- Keep unnecessary people away; isolate hazard area and deny entry.
- Stay upwind; keep out of low areas.
- Positive pressure self-contained breathing apparatus (SCBA) and structural firefighter protective clothing may provide limited protection.
- In case of fire, isolate for 0.5 mile in all directions if tank, tank car, or cargo tank is involved.
- In case of spill, isolate according to Table of Initial Isolation and Protective Action Distances for Hydrogen Chloride, ID #1050. (From *Emergency Response Guidebook* [ERG].)
- CALL CHEMTREC AT 1-800-424-9300 FOR EMERGENCY ASSISTANCE.
- If water pollution occurs, then notify the appropriate authorities.
- a. FIRE
 - These materials will react violently with water; do not apply water directly to burning material.
 - Do not put extinguishing medium inside container.

(i) Small Fires

• Use dry chemical, CO₂, low or medium-expansion aqueous film-forming foam (AFFF).

²Combustible liquid—defined as a liquid with a flash point of 100°F (37.7°C) or higher.

(ii) Large Fires

- Use AFFF alcohol-resistant medium-expansion foam. Repeated applications may be required for fire extinguishment.
- Initial applications of foam will release significant amounts of corrosive vapors.
- Water spray or fog may be used downwind to knock down corrosive vapor cloud.
- Apply cooling water to sides of containers that are exposed to flames until fire is out, provided the water does not come in contact with the tank contents. Stay away from ends of tanks.

b. SPILL OR LEAK

- Do not touch or walk through spilled material; stop leak if it can be done without risk.
- Fully encapsulating, vapor-protective clothing should be worn if working in the vapor cloud with no fire. It may provide little or no thermal protection.

(i) Small Spills

- Absorb spill with dry absorbent materials or cover with medium-expansion foam.
- Do not allow any of these materials to enter container.

(ii) Large Spills

- Use AFFF alcohol-resistant medium-expansion foam.
- Do not allow any of these materials to enter container.
- Applications of foam will release significant amounts of corrosive vapors.
- Water spray or fog may be used downwind to knock down corrosive vapor cloud.
- Do not apply water directly to spilled material.
- Clean up only under supervision of an expert.

- Move victim to fresh air and call emergency medical care. If not breathing, then give artificial respiration. If breathing is difficult, then give oxygen.
- In case of contact with material, immediately flush skin and eyes with running water for at least 15 min.
- Speed in removing material from skin and eyes is of extreme importance.
- Remove and isolate contaminated clothing and shoes at the site.

D. GUIDE SEHSC-004 (Silicon Tetrachloride)

1. POTENTIAL HAZARDS

a. FIRE OR EXPLOSIONS

- Noncombustible.
- Violent reaction with water releasing corrosive gas.

b. HEALTH HAZARDS

- Contact with moisture in air forms a corrosive vapor.
- Causes severe burns if swallowed or repeatedly inhaled.
- Contact causes burns to skin and eyes.
- Spill produces irritating and corrosive gases.
- Runoff from spill control may cause pollution.

2. EMERGENCY ACTIONS

- Keep unnecessary people away; isolate hazard area and deny entry.
- Stay upwind; keep out of low areas.
- Positive pressure self-contained breathing apparatus (SCBA) and structural firefighter protective clothing may provide limited protection.
- In case of spill, isolate according to Table of Initial Isolation and Protective Action Distances for Hydrogen Chloride, ID #1050. (From *Emergency Response Guidebook* [ERG].)
- CALL CHEMTREC AT 1-800-424-9300 FOR EMERGENCY ASSISTANCE.
- If water pollution occurs, then notify the appropriate authorities.

a. FIRE

• Noncombustible.

b. SPILL OR LEAK

• Do not touch or walk through spilled material; stop leak if it can be done without risk.

• Fully encapsulating, vapor-protective clothing should be worn if working in the vapor cloud with no fire. It may provide little or no thermal protection.

(i) Small Spills

- Absorb spill with dry absorbent materials or cover with medium-expansion foam.
- Do not allow any of these materials to enter container.

(ii) Large Spills

- Dike to contain.
- Use aqueous film-forming foam (AFFF) alcohol-resistant medium-expansion foam
- Do not allow any of these materials to enter container.
- Initial application of foam will release significant amounts of corrosive vapors.
- Water spray may be used downwind to knock down corrosive vapor cloud.
- Do not apply water directly to spilled material.
- Clean up only under supervision of an expert.
- Initial applications of foam will release significant amounts of corrosive vapors.

- Move victim to fresh air and call emergency medical care. If not breathing, then give artificial respiration. If breathing is difficult, then give oxygen.
- In case of contact with material, immediately flush skin and eyes with running water for at least 15 min.
- Speed in removing material from skin and eyes is of extreme importance.
- Remove and isolate contaminated clothing and shoes at the site.

E. REFERENCE GUIDE FOR SELECTED CHLOROSILANES

UN/ DOT#	Name	SEHSC Response Guide	ERG	Flash	Point	Vapor Pressure	NFF	PA 704	4 Cod	es	CAS#
				°F	°C	@68°F/ 18°C	н	F	I	SP	
1724	Allytrichlorosilane	SEHSC002	155	88	31.1	13	3	3	1	₩2	107-37-9
1728	Amyltrichlorosilane	SEHSC003	155	135	57.2	-1	3	2	1	₩2	107-72-2
1747	Butyltrichlorosilane	SEHSC003	155	130	54.4	8	3	2	1	₩2	7521-8-4
1753	Chlorophenyltrichlorosilane	SEHSC003	155	203	95	<1	3*	1	1	₩2	26571-79-9
	Chloropropyltrichlorosilane (and various isomers)	SEHSC003	155	207	97.2	<1	3*	1	1	W2	2250-06-3 (7787-88-4, 7787-89-5)
2434	Dibenzyldichlorosilane	SEHSC003	155		N/A	<1	3*	1	1	₩2	18414-36-3
1766	Dichlorophenyltrichlorosilane	SEHSC003	155	302	150	<1	3*	1	1	₩2	27137-85-5
2189	Dichlorosilane	SEHSC001	139	-62	-52.2	1230	3	4	2	₩2	4109-96-0
1767	Diethyldichlorosilane	SEHSC002	155	81	27.2	9	3*	3	1	₩2	1719-53-5
	Dimethylchlorosilane	SEHSC001	139	-18	-27.8	380	3	3	2	₩2	1066-35-9
1162	Dimethyldichlorosilane	SEHSC002	155	30	-1.1	113	3	3	1	₩2	75-78-5
	Dimethylvinylchlorosilane	SEHSC002	155	9	-12.8	220	3	3	1	₩2	1719-58-0
1769	Diphenyldichlorosilane	SEHSC003	155	314	156.7	<1	3	1	1	₩2	80-10-4
1771	Dodecyltrichlorosilane	SEHSC003	155	329	165	<1	3*	1	1	₩2	4484-72-4
1183	Ethyldichlorosilane	SEHSC001	139	64	17.8	96	3	3	2	₩2	598-14-1
2435	Ethylphenyldichlorosilane	SEHSC003	155	221	104.1	<1	3*	1	1	₩2	1125-27-5
1196	Ethyltrichlorosilane	SEHSC002	155	80	26.7	34	3	3	1	₩2	115-21-9
1781	Hexadecyltrichlorosilane	SEHSC003	155	309	153.9	<1	3	1	1	₩2	5894-60-0
1784	Hexyltrichlorosilane	SEHSC003	155	185	85	<1	3*	2	1	₩2	928-65-4
	Isobutyltrichlorosilane	SEHSC002	155	99	37.2	9	3*	3	1	₩2	18169-57-8
	Methyl(phenethyl)dichlorosilane	SEHSC003	155	250	121.1	<1	3*	1	1	₩2	772-65-6
1242	Methyldichlorosilane	SEHSC001	139	<-10	-23.3	353	3	3	2	₩	75-54-7
2437	Methylphenyldichlorosilane	SEHSC003	155	180	82.2	<1	3*	2	1	₩2	149-74-6
1250	Methyltrichlorosilane	SEHSC002	155	43	6.1	147	3	3	1	₩2	75-79-6
	Methylvinyldichlorosilane	SEHSC002	155	40	4.4	55	3	3	1	₩2	124-70-9
1799	Nonyltrichlorosilane	SEHSC003	155		N/A	<1	3*	1	1	₩2	5283- 67-0
1800	Octadecyltrichlorosilane	SEHSC003	155	192	88.9	<1	3	2	1	₩2	112-04-9
1801	Octvltrichlorosilane	SEHSC003	139	204	95.6	<1	3*	1	1	₩2	5283-66-9
	Phenyldichlorosilane	SEHSC001	139	118	47.8	<1	3*	2	2	₩2	696-28-6
1804	Phenyltrichlorosilane	SEHSC003	155	177	80.6	<1	3	2	2	₩2	98-13-5
1816	Propyltrichlorosilane	SEHSC002	155	99	37.2	11	3	3	1	₩2	141-57-1
1818	Silicon Tetrachloride	SEHSC004	157	No F	lash Point	194	3	0	0	₩2	10026-04-7
1295	Trichlorosilane	SEHSC001	139	-18	-27.8	500	3	4	2	₩2	10025-78-2
1298	Trimethylchlorosilane	SEHSC002	155	0	-17.8	200	3	3	1	₩2	75-77-4
1305	Vinvltrichlorosilane	SEHSC002	155	59	15	54	3	3	1	₩2	75-94-5
2985	Chlorosilanes Flammable, Corrosive, N.O.S.	SEHSC002	155								
2986	Chlorosilanes Corrosive, Flammable. N.O.S.	SEHSC003	155								
2987	Chlorosilanes Corrosive, N.O.S.	SEHSC004	157								
2988	Chlorosilanes Water Reactive, Flammable, Corrosive, N.O.S	SEHSC001	139								
3361	Chlorosilanes Toxic, Corrosive N.O.S.	SEHSC004	157								
3362	Chlorosilanes Toxic, Corrosive, Flammable N.O.S.	SEHSC002	155								

NFPA 704 (2012) - H = Health Effects Hazard Rating

ERG -

F = Flammability Hazard Rating

I = Instability (formerly Reactivity) Hazard Rating

SP = Special Notation \forall do not use water.

Hazard Ratings are from 0-4 with 0 = Low Hazard to 4 = High Hazard

* Indicates an estimated hazard rating; no listing given per NFPA 325, 49, 491

Also see Table 1—Initial Isolation and Protective Action Distances

Note: Data provided are based on readily available information concerning the properties of the indicated substances. Consult manufacturer's Material Safety Data Sheet (SDS) and other vendor information to confirm information applicable to the specific product(s) of interest.

Chapter 3 | Emergency Response Decision Trees

CHAPTER 3 CONTAINS A SERIES of emergency response decision trees summarizing operational procedures that have been successfully used to manage chlorosilane emergency events. The decision tree starts on p. 8 and presents an overview of general scenarios involving (1) a chlorosilane spill or leak with fire and (2) a chlorosilane spill or leak without fire. Each general scenario in the tree is further subdivided into specific, detailed scenarios.

Once the specific scenario is identified, there are additional decision trees (pp. 9-14) that are referenced for additional

detailed information and tailored to additional details of each event. The decision trees on pp. 9–14 link specific information from the chapters in the *Manual on Chlorosilane Emergency Response Guidelines* to provide guidance and information for management of each scenario.

The decision trees can be used either as a pre-planning tool to determine the types of equipment and procedures necessary to properly respond to a chlorosilane emergency or as an action guide during an actual emergency event.

















Chapter 4 | Foam Applications

A. PURPOSE

THE PURPOSE OF THIS CHAPTER is to provide general guidelines for the use of low expansion, medium expansion, and compressed air foam (CAFS) Class B alcohol-resistant aqueous film-forming foam (AR-AFFF) applications for fire and vapor suppression in response to liquid spills and liquid spill fires involving chlorosilanes. This chapter provides suggestions and guidelines for development and use of portable foam delivery systems. In addition, the hazards associated with using water-only applications on chlorosilane spills and fires are highlighted.

B. PHILOSOPHY

The intent of the procedure described below is to provide the best practice guidelines on how to safely and efficiently extinguish a chlorosilane spill fire and suppress chlorosilane and hydrogen chloride vapors using foam applications. In large- and smallscale tests, results have indicated that this is best accomplished by using Class B medium-expansion AR-AFFF systems to extinguish a fire and to minimize the overall amount of hydrogen chloride and chlorosilane vapor released from a spill. The use of mediumexpansion or CAFS foams provides a stable foam blanket that has significantly longer drain down times than lower aspirated foam streams. With all chlorosilane spills, it is not possible to provide total control of hydrogen chloride emissions using foam applications because it is impossible to prevent some of the water in the foam application from reacting with the chlorosilane to generate hydrogen chloride.

C. SPILL CONTROL AND VAPOR SUPPRESSION

Chlorosilanes react rapidly with water, forming hydrogen chloride and a siloxane. As outlined in the initial emergency response guides for spills, it is critical to perform diking and containment of the material. This will not only prevent or minimize the environmental impact, but it will also stop the spilled chlorosilane from reaching a water source and reacting to form additional hydrogen chloride hazards. If water spray is being used downwind to hydrolyze chlorosilane or hydrogen chloride vapors, then it is critical that the water runoff does not run back to the chlorosilane spill. When foam is first applied, the water contained in the foam will react with the chlorosilane liquid and evolve a dense, white cloud that is a mixture of hydrogen chloride vapor, small droplets of hydrochloric acid, and the reaction product formed when some of the chlorosilane that is stripped from the liquid reacts with moisture in the air. This mixture of white vapor is called *hydrogen chloride vapor* in this manual.



Depending on the chlorosilane species, the siloxane formed may be either a solid or liquid. Chemical names containing the term *trichlorosilane* or *silicon tetrachloride* form solids with water. Most other chlorosilanes when reacted with water form lighter than water siloxanes (silicone oils) that may be flammable. Those chlorosilanes that are included in Guide SEHSC-001 may react, further liberating hydrogen gas. The siloxane may gel, forming a solid that is difficult to neutralize and stabilize to prevent further hydrogen gas from forming.

When the foam is first applied, the hydrogen chloride vapor cloud will initially increase significantly. Once a solid or oil barrier is formed above the spill, it and the foam will reduce the evaporation rate and minimize evaporation caused by convection from the wind. In all cases, during foaming, the hydrogen chloride is initially absorbed in the water until the water in the foam becomes saturated with acid. Thereafter, hydrogen chloride vapor is released. Consequently, a periodic reapplication of the foam will be necessary.



Because all chlorosilanes are water reactive, a Class B mediumexpansion AR-AFFF is recommended. In the context of this guide, *medium expansion* means that the ratio of air-to-water foam concentrate is between approximately 30:1 and 70:1. These types of foam demonstrate two important criteria necessary for control with water-reactive chemicals:

- 1. The amount of water in the foam is reduced.
- 2. With the correct foam system, water drainage from the foam is slow, with 25 % of the water draining from the foam between 15 and 25 min after application.

Low-expansion foams contain too much water and, more importantly, drain too rapidly, causing rapid hydrolysis, release of hydrogen chloride, and a visible white cloud. Using low-expansion foam or water is expected to result in the maximum release of hydrogen chloride. The two exceptions in which water can be used are described in Chapter 6, "Hydrolysis of Chlorosilanes" and Chapter 8, "Small Fire and Spill Handling Procedures."

D. FIRE CONTROL

Application of only water to a chlorosilane fire is generally ineffective. If water alone is used, then the fire will become more pronounced, and the fire will continue until all of the fuel is consumed. However, AR-AFFF foams have been demonstrated to be effective for extinguishing chlorosilane fires. Because all chlorosilanes are water reactive, medium expansion or CAFS-generated foam is preferred because it uses the least amount of water to extinguish the fire.

For chlorosilanes that have a hydrogen attached to silicon (SEHSC-001), only a medium-expansion AR-AFFF is recommended. Trichlorosilane test fires have been extinguished most effectively using medium-expansion AF-AFFF applications. When foams such as lowor medium-expansion AFFFs have been applied to a trichlorosilane test fire, they were found to be ineffective and in most tests the fire burned more violently and would continue until the fuel was consumed.

For chlorosilanes in Guides SEHSC-002 and 003, in which the fire is hotter, medium-expansion foam should be tried first. If a mediumexpansion foam is not effective, only then should a low-expansion foam be considered for use.

E. FOAM SYSTEMS

The foam system is critical for mitigation of chlorosilanes. The foam system requires matching the foam concentrate with the foam eductor (line proportioning system), the foam nozzle, the pressure drop across the eductor, and the pressure at the foam nozzle to make a foam of the right expansion with slow water drainage and the correct dilution of the foam concentrate. Use only a foam system recommended by the foam manufacturer.

Portable Foam Units

These self-contained units come in various forms. A common unit that uses a premixed foam solution delivers a foam blanket using a pre-pressurized extinguisher through an expansion nozzle. These systems can provide various expansion foams based on interchangeable nozzles.

Also available are units that have a foam concentrate reservoir with a built-in eductor that can be set to the ratio of foam or wetting agents being used. The unit relies on a fresh water supply at low volume (8-10 gpm) and typical pressures of 30–50 psi. Units are typically easy to use and provide good foam coverage with minimal training or experience necessary.

The in-line foam eductor coupled with an appropriate foam expansion nozzle on a fire stream hand line is a common system. Foam is educted through a pick-up system from a concentrate source. The in-line mixing with the fire stream is then expanded through a foam nozzle, often allowing for a range of foam expansions.



Fire Apparatus Foam Systems

Truck-mounted foam units typically carry foam concentrate and have either a water tank or rely on water supply at the incident scene. There are two basic types of systems available today.

The standard system consists of a built-in foam proportioning unit that mixes foam with the water supplied to the various discharges on the truck. This line then relies on the nozzle at the end of the fire stream to provide the expansion of the foam. By adjusting the foam concentration and nozzle configurations, various foam expansion rates can be achieved as desired.

A compressed air foam system consists of a typical directinjection foam proportioning system that uses compressed air injection to generate consistent foam at the apparatus. The expanded foam is then delivered through the apparatus discharge lines. The air compressor provides additional energy, which, gallon for gallon, propels compressed air foam farther than aspirated or standard water nozzles. These systems deliver consistent foam with typically longer drain down times similar to those produced by medium-expansion appliances.

Foam Application Guidance

These are some guiding principles for foam application for consideration when using any of the above foam systems.

- See Chapter 10, "Personal Protective Equipment Requirements," for information on what must be worn during this operation.
- To minimize the initial water reaction, ensure good foam quality and expansion before application to the fire or spill. Divert the flow from the fire or spill until the foam quality at the nozzle has become consistent.
- Foam blankets should be applied gently without plunging and agitating the spill or fire fuel. Roll the foam onto the fire or spill by banking or deflecting the foam flow. If necessary, lob (rain down) the foam to cover only open areas that are missed.
- Chlorosilanes tend to break down the foam, and foam barriers may need to be reapplied frequently to secure the spill/fuel.
- It is important to realize that live, unreacted chlorosilane pools may be present under the foam barrier, and the hazards associated must be mitigated. See Chapter 6, "Hydrolysis of Chlorosilanes," for stabilizing the remaining chlorosilanes.

Chapter 5 | Transfer Procedures

A. BULK CONTAINERS (Cargo Tanks, Intermodal Containers, Tank Cars, Fixed Tanks)

1. Purpose

The purpose of this procedure is to provide general guidelines for the safe field transfer of chlorosilanes from a damaged or disabled bulk container to another container.

2. Philosophy

In the event that an emergency involving a chlorosilane bulk container occurs, all necessary resources, supplies, and equipment must be brought together at the scene to result in a safe transfer that has minimal effect on human health and the environment.

There are two procedures for performing these transfers—the closed-loop transfer and the vented transfer. The closed-loop transfer is preferred because it minimizes emissions to the atmosphere and cleanup.

3. Receiving Container

- The receiving container must have a capacity equal to or greater than the damaged container or it must have a means to measure the amount transferred.
- The receiving container must be clean, dry, and have been purged with nitrogen.
- The receiving container must be Department of Transportation (DOT) approved for the product.
- The receiving container and piping systems must have compatible materials of construction.
- The receiving container initially should be vented to as low a pressure as possible.

4. Transfer Equipment

- A stainless or carbon steel nitrogen-driven diaphragm pump with Teflon[®] or Viton[®] diaphragms, gaskets, and balls should be used. This pump can be driven by an air compressor, but, because of the flammability of the product, nitrogen is preferred to prevent inadvertent introduction of oxygen into the system. NOTE: Polyethylene pumps, hoses, or gaskets should *not* be used because they are incompatible materials of construction and could melt in a fire.
- A braided stainless steel flex hose with a stainless steel or Teflon[®] lining should be used if possible.
- Piping connections should be of stainless or carbon steel construction and be equipped with blowdown connections and drains.

- Portable containers must be chocked.
- All connections must be Teflon[®] taped.
- All hoses, fittings, pumps, and connections must be pressure tested with nitrogen and purged free of air.
- Hoses must also be checked for electrical continuity. All containers must be grounded and bonded.
- Consider means to ensure complete transfer of the material.

5. Closed-Loop Transfer Procedure (See Fig. 5.1)

- See Chapter 10, "Personal Protective Equipment Requirements," for information on what must be worn during this operation.
- Equalize the containers by opening the vent valves.
- Position an individual at each container and at the pump. Slowly open the liquid valve on the damaged container to allow the hose to fill with liquid. Check for leakage.
- Open the liquid fill valve on the receiving container.
- Slowly open the nitrogen supply to the pump and start transfer.
- Continuously monitor hoses, fittings, and the pump during transfer for leaks.
- After transfer is complete, purge and clear lines of all chlorosilane liquid and vapors.
- Disconnect all hoses, fittings, and connections.

6. Vented Transfer Procedure (See Fig. 5.2)

- See Chapter 10, "Personal Protective Equipment Requirements," for information on what must be worn during this operation.
- Set up purge, scrub, and vent equipment as described in Chapter 5E and connect to the receiving bulk container vent.
- Open vent valve on receiving bulk container to the scrubber.
- Position an individual at each container. Open liquid valves on the receiving container and slowly open the liquid valve on the damaged container. Check for leakage.
- Transfer as much as possible using gravity. If necessary, then pressurize the damaged container with nitrogen to transfer the remaining liquid (a pump as described in Chapter 5A.4 could also be used for this transfer). Before pressurization, evaluation of the damaged container should be done to determine its capability to sustain the desired pressure for transfer.
- Continuously monitor hoses and fittings for leaks.
- After transfer is complete, purge and clear all lines of all liquid and heavy vapors.
- Disconnect all hoses, fittings, and connections.



- ⋈ Valve
- L Liquid (via dip tube)
- V Vapor

Note: 1. Liquid line may be off bottom of container

2. Damaged container may have a pneumatic, mechanical, or hydraulic actuated valve and/or excess flow valve on at least the liquid lines

FIG. 5.1 Closed-loop transfer.

B. DRUM TRANSFER

1. Purpose

The purpose of this section is to provide general guidelines for the safe field transfer of chlorosilanes from one drum to another drum.

2. Philosophy

In the event that an emergency involving a chlorosilane drum occurs, all necessary resources, supplies, and equipment must be brought together at the scene to result in a safe transfer that has minimum effect on human health and the environment.

To minimize the risk of exposure to chlorosilanes, the preferred method of handling a damaged drum is to patch the leak and overpack the drum. If this cannot be done, then there are three procedures for performing transfers: gravity transfer, pump closed-loop, and pump vent transfer. The gravity transfer and the pump closed-loop transfer are preferred because they minimize emissions to the atmosphere and cleanup.

3. Transfer Equipment (Applicable for All Drum Transfers)

- Standard 55-gal (208-L) drums are equipped with a 2-in. (5.1-cm) bung and 3/4-in. (1.9-cm) bung in the drum head. Chlorosilane drums are of a heavier construction than normal drums but are not considered pressure containers (e.g., DOT 5B).
- The receiving drum must be clean, dry, and purged with nitrogen before the transfer.
- All associated piping must be clean, dry, and compatible with the material to be transferred. A braided stainless steel flex hose with a stainless steel or Teflon[®] lining should be used if possible. The fittings must also be compatible.
- Ground and bond both containers.
- Check electrical continuity on all hoses and connections.



- Note: 1. Liquid line may be off bottom of container
 - 2. Damaged container may have a pneumatic, mechanical, or hydraulic actuated valve and/or excess flow valve on at least the liquid lines
 - 3. Transfer can be done with a pump instead of nitrogen pressure transfer as in Figure 5.1

FIG. 5.2 Vented transfer.

4. Gravity Transfer Procedure (See Fig. 5.3)

- See Chapter 10, "Personal Protective Equipment Requirements," for information on what must be worn during this operation.
- Elevate the damaged drum above the receiving drum. After making sure the valves are closed, lay the damaged drum on its side as indicated in **Fig. 5.3**. NOTE: Be sure this drum is chocked to prevent it from rolling.
- With the receiving drum in the upright position, attach the piping to the 2-in. (5.1-cm) and 3/4-in. (1.9-cm) bungs. Insert dip tube into 3/4-in. bung. NOTE: Use Teflon[®] tape on all threaded fittings.
- Connect the necessary piping to the bungs on the receiving drum.
- After ensuring that both drums are secure, connect the balance of the piping to both drums.
- Begin the transfer by opening the liquid valves on both drums.
- After the flow has started, open the vapor valves on both drums.
- After the transfer is complete, tilt the damaged drum to ensure the drum and hoses are empty.

- Close all valves on the drums and hoses.
- Remove hoses and valves. Use caution: They may contain liquid. If so, then drain into a clean, empty bucket (see Chapter 5E, "Purge, Scrub, and Vent Procedure," for precautions and neutralization procedures).
- Remove fittings and reinstall the drum bungs.
- Reinstall the valves and fittings on the ends of the hoses and secure them for shipment.
- The damaged empty drum should be overpacked and both drums should be labeled and returned to the shipper.
- As an alternative, vent the receiving drum using the vent procedure in Chapter 5E.

5. Pump Closed-Loop Transfer Procedure (See Fig. 5.4)

- See Chapter 10, "Personal Protective Equipment Requirements," for information on what must be worn during this operation.
- Carefully remove the 3/4-in. (1.9-cm) bungs from each drum and install a valve in each bung hole.
- Connect a hose between the two 3/4-in. (1.9-cm) valves.



Note: 1. Use 3/4" Bung Hole for Liquid Transfer 2. Use Dip Tube in Receiving Drum

FIG. 5.3 Gravity transfer.

- Insert a dip tube into the 2-in. (5.1-cm) bung of the damaged drum. Connect the dip tube to the suction side of pump. Any manually operated or explosion-proof electrical or nitrogenoperated pump may be used. The pump, hose, and fittings must have compatible materials of construction. Consider secondary containment around pump to contain leakage.
- Connect the pump discharge to the 2-in. (5.1-cm) bung on the receiving drum. The receiving drum must be of the same material of construction with the same pressure rating and capacity as the damaged drum. The pump discharge should have a bleed valve.
- Equalize the two drums by opening the valves between the two drums.
- Transfer the material from the damaged drum to the receiving drum.
- After transfer is complete, connect a small hose or tubing to the transfer hose's atmospheric valve to a water bucket to scrub any vapors that may come from the drums and hoses during venting. Visually observe the water level in bucket to be sure water does not backflow into the hose from the bucket while venting.
- Carefully vent the pressure from the hose at the pump discharge.
- Remove the hoses, pumps, and valves. Use caution; they may contain liquid. If so, drain into a clean, empty bucket. (See Chapter 5E, "Purge, Scrub, and Vent Procedure," for precautions and neutralization procedures.)

- Purge the hoses with nitrogen to remove vapors and any liquid present. Purge to a bucket of water.
- Reinstall the bungs in the drums.
- Label the receiving drum and return it to the shipper.
- Overpack the damaged drum, label the overpack, and return to the shipper.

6. Pump Vent Transfer Procedure (See Fig. 5.5)

- See Chapter 10, "Personal Protective Equipment Requirements," for information on what must be worn during this operation.
- Remove the 3/4-in. (1.9-cm) bung from both drums and install valves.
- Connect a regulated nitrogen supply to the valve on the damaged drum to keep a slight positive purge on it during the transfer. The purge rate should not increase the pressure on the drum by more than 1 psig. Purge off gas to scrubber as per procedure in Chapter 5E, "Purge, Scrub, and Vent Procedure."
- Insert a dip tube into the 2-in. (5.1-cm) bung of the damaged drum. Connect the dip tube to the suction side of a nitrogendriven carbon or stainless steel diaphragm pump. Consider secondary containment around pump to prevent leakage.
- Connect the pump discharge to the 2-in. (5.1-cm) bung on the receiving drum. The receiving drum must be of the



FIG. 5.4 Pumped closed-loop transfer.

same material of construction with the same pressure rating and capacity as the damaged drum. The pump discharge should have a bleed valve.

- Vent the receiving drum to a scrubber as per procedures in Chapter 5D, "Liquid Nitrogen Purging Procedure."
- Open the receiving drum's valve to the scrub vent equipment.
- Turn a slight nitrogen purge into the damaged drum at not more than 1 psig to displace the liquid being removed.
- Transfer the material from the damaged drum to the receiving drum. NOTE: A manually operated or explosion-proof electrical or nitrogen-operated pump may be used.
- After transfer is complete, connect a small hose or tubing to the transfer hose's atmospheric valve to a water bucket to scrub any vapors that may come from the drums and hoses during venting. Visually observe water level in the bucket to be sure water does not backflow into the hose from the bucket while venting.
- Carefully vent the pressure from the hose at the pump discharge.
- Remove the hoses, pumps, and valves. Use caution; they may contain liquid. If so, then drain it into a clean, empty bucket or to the vent scrubber. See Chapter 5E, "Scrub, Vent, and Neutralization Procedure."
- Purge the hoses with nitrogen to remove vapors and any liquid present. See Chapter 5E, "Purge, Scrub, and Vent Procedures."
- Reinstall the bungs in the drums.
- Label the receiving drum and return it to the shipper.

• Overpack the damaged drum, label the overpack, and return to the shipper.

C. TRANSFERRING CHLOROSILANES FROM CONTAINERS (CYLINDERS)

1. Purpose

The purpose of this procedure is to provide general guidelines for the safe transfer of chlorosilanes from one cylinder to another container (cylinder) or larger container suitable for the material.

The emergency response guidelines make reference to transferring chlorosilanes to and from DOT Spec 51 and 4BW containers (cylinders). However, there are several other types of containers, including DOT and ISO specification portable tanks, which can be used for chlorosilane shipments. These containers are of varying sizes, valve configurations, and capacities that must be taken into account when performing transfer operations.

2. Philosophy

To minimize the risk of exposure to chlorosilane, the preferred procedure is to plug and patch the cylinder before starting a transfer. When a cylinder is damaged in transit, the chlorosilane must be transferred to another container. This transfer must be to another container of equal or larger size. The receiving container must be



FIG. 5.5 Pumped vented transfer.

suitable for chlorosilanes such as a DOT Spec 51, a 4BW cylinder, or a MC331 trailer. These procedures will minimize the effect on human health and the environment.

There are two procedures for performing these transfers (i.e., the closed-loop transfer [see **Fig. 5.6**] and the vented transfer [see **Fig. 5.7**]). The closed-loop transfer is preferred because it minimizes emissions to the atmosphere and cleanup.

3. Cylinder Descriptions

- Cylinders are equipped with valves on the liquid and vapor line.
- The dip tube extends on the liquid line to within 3/4-in. (1.9-cm) of the bottom of the cylinder.
- Cylinders will have a relief device that will vary based on its design.
- Generally, the middle port is the liquid line and the other port is the vapor line.

4. Receiving Container

• The receiving container must have an equal or greater capacity than the damaged container or it must have a means to measure the amount transferred.

- The receiving container must be clean, dry, and have been purged with nitrogen.
- The receiving container must be DOT approved for that product (as applicable).
- The receiving container and piping must have compatible materials of construction.
- The receiving container should be vented to as low of a pressure as possible.

5. Transfer Equipment

- A stainless steel or carbon steel nitrogen-driven diaphragm pump with Teflon[®] or Viton[®] diaphragms, gaskets, and balls should be used. This pump can be driven by an air compressor, but because of the flammability of product, nitrogen is preferred. Consider diking around the pump. NOTE: polyethylene pumps, hoses, or gaskets should *not* be used because they are incompatible materials and may melt in a fire.
- A braided stainless steel flex hose with a stainless steel or Teflon[®] lining should be used if possible.
- Piping connections should be of stainless or carbon steel construction and be equipped with blowdown connections and drains.



- V Vapor
- L Liquid (via dip tube)

FIG. 5.6 Closed-loop cylinder transfer.

- Portable containers must be chocked or strapped to prevent rolling and/or tipping.
- All connections must be Teflon® taped.
- All hoses, fittings, pumps, and connections must be compatible, pressure tested with nitrogen, and purged free of air before starting transfer.
- Consider means to ensure complete transfer of the material.
- Hoses must also be checked for electrical continuity. All containers must be grounded and bonded.

6. Closed-Loop Transfer Procedure (See Fig. 5.6)

- See Chapter 10, "Personal Protective Equipment Requirements," for information on what must be worn during this operation.
- Equalize the containers by opening the vent valves.
- Position an individual at each container and at the pump. Slowly open the liquid valve on the damaged container to allow the hose to fill with liquid. Check for leakage.
- Open the liquid fill valve on the receiving container.
- Slowly open the nitrogen supply to pump and start transfer.
- Continuously monitor hoses, fittings, and pump during transfer for leaks.
- After transfer is complete, purge and clear lines of all chlorosilane liquid and vapor (see Chapter 5E).

- Disconnect all hoses, fittings, and connections.
- Drain any liquid in lines to a clean, empty bucket.
- Label the receiving cylinder and return it to the shipper.

7. Vented Transfer Procedure (See Fig. 5.7)

- See Chapter 10, "Personal Protective Equipment Requirements," for information on what must be worn during this operation.
- Set up purge, scrub, and vent equipment as described in Chapter 5E and connect to the receiving bulk container vent.
- Open vent valve on the receiving container to the scrubber.
- Position an individual at each container. Open the liquid valve on the receiving container and then slowly open the liquid valve on the damaged container. Check for leakage.
- Transfer as much as possible using gravity. If necessary, then pressurize the damaged container with nitrogen to transfer the remaining liquid. Use the least amount of pressure on the damaged container to complete the transfer.
- Continuously monitor hoses and fittings for leaks.
- After transfer is complete, purge and clear all lines of all chlorosilane liquid and vapor (see Chapter 5E, "Purge, Scrub, and Vent Procedure").
- Disconnect all hoses, fittings, and connections.
- Drain any remaining liquid into a clean, empty bucket.



FIG. 5.7 Vented cylinder transfer.

D. LIQUID NITROGEN PURGING PROCEDURE

1. Purpose

The purpose of this procedure is to provide general guidelines concerning a method for cooling and purging liquid chlorosilane in a tank that has or is being exposed to external heating and the hole is too large to patch. Cooling the liquid will allow the material to be pumped.

2. Philosophy

When a chlorosilane fire occurs at a hole in a container, one method of extinguishing the fire is to remove the chlorosilane from the container. Good results can be obtained by cooling the chlorosilane using liquid nitrogen. This will also purge the container. This technique has been used when the container was ruptured with a large hole but still contained liquid chlorosilane.

3. Procedure

See Chapter 10, "Personal Protective Equipment Requirements," for information on what must be worn during this operation.

Pump liquid nitrogen through the liquid line under the chlorosilane liquid in the container. This should be done for a long enough period of time to cool the chlorosilane below its boiling point. This could take a substantial amount of time. Stop the liquid nitrogen. Start the nitrogen gas by purging through the vapor line to keep the atmosphere inert in the container. Follow the bulk container unloading procedures to pump out the chlorosilanes (see Chapter 5E, Purge, Scrub, and Vent Procedure). If pump cavitates, then stop the transfer and resume cooling as above.

E. PURGE, SCRUB, AND VENT PROCEDURE (See Figs. 5.8, 5.9, AND 5.10)

1. Purpose

The purpose of this section is to provide general guidelines concerning methods and procedures to vent containers to minimize the release of chlorosilanes to the atmosphere.

2. Philosophy

This procedure provides a method for removing hydrogen chloride/ chlorosilanes from the gas being vented from containers. Venting

Common Name	Trade Name	Neutralization Capacity Ratio, Ib HCI/Ib Agent
Sodium carbonate	Soda ash	0.69
Sodium bicarbonate	Baking soda	0.43
Calcium hydroxide	Slaked lime or	0.98
	hydrated lime	

TABLE 5.1 Minimum Quantities of Bases Required for Neutralization.

Note: HCl, hydrochloric acid.

is necessary in the event that the pressure in the vessel needs to be reduced to prevent the container from rupturing. If the product is being transferred from a damaged container to a receiving container, then use a venting procedure.

The preferred procedure is to scrub the gas using a basic aqueous solution. This is done for two reasons. First, by having the base added to the water before the venting operation, postneutralization is not necessary, thus avoiding exposure to toxic and/or flammable vapors that would otherwise be produced when the base is added to the acidic water. Furthermore, if either sodium carbonate or sodium bicarbonate is used to neutralize the vessel's contents, foaming can occur from the carbon dioxide gas generated during neutralization. Second, with the bases specified in **Table 5.1**, any unreacted base remaining has a pH less than 12.5, which may render the solution non-RCRA hazardous (RCRA, Resource Conservation and Recovery Act; pH between 2 and 12.5). This material can be more readily transported and disposed of after the incident is over. For SiH-containing materials, hydrogen gas (flammable hazard) may also be released under any circumstances.

Two variations of the procedure are:

- 1. To scrub the hydrogen chloride/chlorosilane with water and either neutralize the water as a post-treatment or ship it directly to a waste disposal facility.
- 2. To vent the hydrogen chloride/chlorosilane through a stack filled with ice. Reaction of the hydrogen chloride/chlorosilane with the ice melts the ice, and the water formed solubilizes and dilutes the hydrogen chloride generated.

With either of the alternative procedures, except where the differences are obvious, the materials, setup, and venting procedures are identical to those described for the preferred method.

3. Materials Required

- a. Water Scrubbing/Neutralizing Equipment Setup
- The scrubbing vessel should be open to the atmosphere. Depending on the amount of gas being scrubbed, the vessel can be an open-top drum, a 300- to 500-gal (1.1 to 1.9-kL) polyethylene water tank that can be obtained at most farm supply stores, a rubber-lined tank, a trailer from a local fire department, or a

vacuum truck from a waste hauler. The scrubber should be placed downwind of other cleanup operations.

- The chlorosilane should be neutralized with an aqueous solution of a weak base. For example, three bases that are commonly available and may be used are sodium bicarbonate (baking soda), sodium carbonate (soda ash), and calcium hydroxide (slaked lime). **Table 5.1** gives an approximate amount of the hydrogen chloride that each base can neutralize. Use more base than what is anticipated.
- Sodium carbonate or sodium bicarbonate can be readily dissolved in water with minimal stirring. **Table 5.2** shows the amount of base that can be dissolved as a function of the water temperature. Sodium carbonate is more soluble and is the preferred base because it will minimize the amount of aqueous solution required to neutralize the acid. It also releases one-half of the amount of carbon dioxide during the neutralization.
- If lime is used, then an agitator is needed to suspend the solids. Lime is practically insoluble in water. The venting rate will need to be slower than with the other bases because lime needs time to dissolve.
- The vent line should extend below the liquid surface as far as possible. Use at least a 1-in. (2.5-cm) diameter dip tube if the chlorosilane contains three or four chloride molecules on silicon because the dip tube will eventually plug with hydrolyzate. Because chlorosilanes readily react with water, they can cause water to backflow into the chlorosilane tank. Chlorosilane vapor reacting with water will create a vacuum that can cause water to be drawn out of the tank to a height of approximately 30 ft (9.1 m). A check valve or a second empty tank of equal volume to the neutralization tank needs to be installed in the vent line to prevent water backflowing into the container. The preferred alternative is to use a sealed tank with an equal or larger volume to the neutralization tank. All screwed fittings should be wrapped with Teflon® tape. See Fig. 5.8, for more detail. The use of a check valve in the vent line in place of an enclosed catch tank is shown in Fig. 5.9.
- Near the receiving container, provide a tee fitting with a valve on one connection and a pressure gauge on the other. Attach the nitrogen line to the valve. If venting a chlorosilane that forms a solid and the headspace is mostly chlorosilane with little nitrogen, then a sufficient supply of nitrogen is needed to keep the dip tube clear of water during the entire venting operation. As a general guide, 40 ft (12.2 m) per second gas velocity in the dip tube will be required to keep liquid out of the dip tube. For example, a 1-in. (2.5-cm) diameter dip tube would require 13 standard cubic feet per minute (scfm) nitrogen flow. The amount of nitrogen may be reduced after flow is established and the dip tube does not show signs of plugging.

TABLE 5.2 Solubility of Common Bases in Water

	32°F (0°C)	68°F (20X)
Sodium carbonate	7.1 lb (3.2 kg)/100 lb (45.4 kg) water	21.5 lb (9.8 kg)/100 lb (45.4 kg) water
Sodium bicarbonate	6.9 lb (3.1 kg)/100 lb (45.4 kg) water	11.1 lb (5.0 kg)/100 lb (45.4 kg) water



• Ground and bond the container and the scrubber (if possible) and check the vent line for electrical continuity and leaks.

b. Ice Tower Scrubbing Equipment Setup

- Wet ice can be used to effectively scrub chlorosilane and hydrogen chloride vapors. The heat generated during the hydrolysis and from the absorption of the hydrogen chloride in the water is controlled by the melting ice. The liquid formed in the bottom of the scrubber is concentrated in hydrochloric acid solution. This solution must be stored in a container made of or lined with polyethylene or polyvinyl chloride (PVC). Concentrated hydrochloric acid will rapidly corrode most metals, including some stainless steels, and generate hydrogen gas.
- The amount of ice needed will depend on the situation. However, it is recommended that 15 lb (5.6 kg) of ice be available for each pound of chlorosilane vented. This ratio of ice is required to keep the solution cool.
- The tower can be constructed from a piece of PVC pipe capped on the bottom and provided with a drain to remove liquid as it is formed per **Fig. 5.10**. *The dip tube used to introduce the vapors to the column should extend down as far as possible into the ice without contacting the liquid in the bottom of the tower.* This is necessary to prevent backflow into the venting tank. The taller the tower, the more effective the scrubber because the ice surface *area is increased.* For situations in which only a small amount of vapors is expected, a plastic or lined drum filled with ice may also be used.
- Venting should be stopped and additional ice added to the tower when fuming becomes apparent.



4. Venting Procedure

- See Chapter 10, "Personal Protective Equipment Requirements," for information on what must be worn during this operation.
- Before venting the container, limit site access only to required personnel.
- Eliminate all ignition sources in the area, including smoking, internal combustion engines, and nonexplosion-proof electrical equipment.
- Purge the line from the container to the scrubber with nitrogen. Double check all connections for leaks. Initially adjust the nitrogen flow rate to keep liquid from accumulating in the dip tube.
- Slowly open the valve from the container to the scrubber and adjust the flow to prevent foaming, fuming, or both from the scrubber. Once flow is established, the nitrogen flow may be reduced if the dip tube does not plug. Do not stop the nitrogen flow entirely because it will help prevent water from being drawn back to the container.
- During the venting operation, periodically:
 - Check the pH of the scrubber water. If the pH becomes acidic (pH < 7), then stop venting the container and either replace the basic solution in the scrubber or add an additional neutralization agent.



Note: Bottom of Dip Tube in Ice Column Must Be Above Liquid Trap Level

P	Pressure Gauge	L	Liquid (via dip tube)
\bowtie	Valve	۷	Vapor
\bowtie	Check Valve		

FIG. 5.10 Purge vent-scrub procedure through ice.

- Monitor the pressure on the vent line. If it builds significantly, then the dip tube is plugging with solids. When this occurs, stop venting the container and purge the line free of chlorosilanes. If necessary, then pull the dip tube and replace it or clean the solids from the pipe before resuming.
- Monitor the site using vapor monitoring equipment (e.g., a colorimetric detector tube for hydrogen chloride) and adjust the venting rate as required.
- Drain any liquid from hoses into a clean, empty bucket.
- When the container is vented down, purge the vent line with nitrogen before dismantling.

Chapter 6 | Hydrolysis of Chlorosilanes

A. PURPOSE

The purpose of this procedure is to provide general guidelines concerning methods for hydrolyzing chlorosilane after the initial mitigation procedure.

B. PHILOSOPHY

Once the chlorosilane has been covered with foam, the unreacted chlorosilane must be managed. The best method to accomplish this is to react the chlorosilane with water to a less hazardous form. This can be accomplished by neutralizing the acid at the same time that the hydrolysis is being accomplished. The first two procedures listed below meet this objective. Where that is not possible, an additional procedure is provided that will eliminate the chlorosilane but will leave an acidic material to be handled. In all cases, the principal objective remains to minimize the release of chlorosilane/hydrogen chloride vapors to the atmosphere. A second objective of this procedure is to reduce the chlorosilane to a less hazardous product that can be more easily handled at the scene of the emergency.

C. PIPELINE REACTOR (See Fig. 6.1)

1. Equipment

- A pipeline reactor can be constructed using a 3-in. by 4-ft (7.6-cm by 1.2-m) section of pipe constructed of carbon steel or fiberglass. A "wye" is installed on the inlet to the pipe. This unit will allow 10 gal/min (37.9 L/min) of chlorosilanes to mix with 95 gal/min (360 L/min) of water.
- The pump discharge should have a nitrogen connection to clear piping after using or to unplug the transfer line if needed. The chlorosilane line into the reactor needs to be reduced via a "pitot tube." The pitot tube must extend into the reactor past the wye. This allows for better mixing and reduces plugging. See **Fig. 6.1**.
- A stainless or carbon steel nitrogen-driven diaphragm pump with Teflon[®] or Viton[®] diaphragms, gaskets, and balls should be used. This pump can be driven by an air compressor, but, because of the flammability of the product, nitrogen is preferred. NOTE: Polyethylene pumps, hoses, or gaskets should *not* be used.
- A braided stainless steel flex hose with a stainless steel or Teflon[®] lining should be used if possible.
- Piping connections should be of stainless or carbon steel construction and be equipped with blowdown connections and drains.
- The water supply can be from a fire truck, hydrant, or a water trailer with a pump. Water flow must be at least 10 times the chlorosilane flow.

- The reactor must be elevated so the discharge is higher than the inlet. This allows the reactor to run liquid full with no air pockets.
- The reactor discharge can empty to an open portable tank, trailer, or diked area. A neutralizing agent should be added to the discharge area. See Chapter 5E, "Purge, Scrub, and Vent Procedure," for recommended neutralizing agents and minimum quantity requirements. See **Fig. 6.2** for layout.

2. Procedure

- See Chapter 10, "Personal Protective Equipment Requirements," for information on what must be worn during this operation.
- Connect the reactor outlet hose to the receiver with no kinks in any hose.
- Connect the portable pump discharge to the reactor.
- Stabilize the pump so it does not move during the operation.
- Connect nitrogen to the pump discharge; begin a nitrogen purge. Keep purge on at all times.
- Connect a 1 1/2-in. (3.8-cm) fire hose to the reactor inlet wye from the water source.
- Insert the sump suction pipe into the spill.
- Turn on the water to the reactor at 95 gal/min (360 L/min).
- Start the pump at low flow.
- Observe the liquid coming out of the reactor discharge; it should change consistency but should not have visible vapors. Increase the pump flow until vapors appear. Reduce the pump flow until vapors disappear.
- Monitor the pressure gauges during the operation. If the differential pressure across the reactor increases significantly, then it may mean that the reactor is plugging. Shut down the pump and try to clear the system with nitrogen.
- The pump suction hose may have to be moved around under the foam blanket to pick up all of the spill. Caution must be taken by the operators. Footing will be bad and probably slippery. NOTE: An extension pipe can be attached to the suction hose to allow ease in moving the suction hose around the spill.
- The system may have to be shut down from time to time to allow the receiver to be emptied. Simply shut down the pump and allow the water to flush out the reactor. Remember to leave the nitrogen purge on the pitot tube to prevent water backing up to the pump.
- When all of the spill has been picked up, remove the suction hose from under the foam, place it in a supply of water, and flush the pump. Blow the system free of chlorosilane with water and nitrogen.



Note: Pipeline Reactor Elevated, Must Be Kept Filled With Water

- Pressure Gauge
- ⋈ Valve
- M Check Valve
 - FIG. 6.1 Continuous water scrubber.



FIG. 6.2 Details of portable pipeline reactor.

D. NEUTRALIZATION IN PLACE PROCEDURE

- See Chapter 10, "Personal Protective Equipment Requirements," for information on what must be worn during this operation.
- Gently agitate foam-covered chlorosilane using a mortar hoe, squeegee or similar long-handled tool. Preferably, nonsparking tools should be used during cleanup operations. This will promote hydrolysis of the reacted chlorosilane. (Approximately 10 lb [4.5 kg] of water is needed for each pound of chlorosilane that is to be neutralized.)
- Concurrently add a dry neutralization agent using a plastic grain shovel. See Chapter 5E, "Purge, Scrub, and Vent Procedure," for type of neutralization agents and amount required. Use a longhandled shovel if possible. If a hydrogen-containing chlorosilane is involved, then be aware that the material could ignite. If this happens, then stop and add more foam to extinguish the fire.
- Depending on the amount of foam used, it may be necessary to add additional water to ensure good dispersion of the neutralization agent as well as complete hydrolysis of the remaining chlorosilane. Water should be added under the foam blanket using a fire hose. Water should be added incrementally (in small quantities) to minimize the hydrogen chloride release.
- Be prepared for some hydrogen chloride vapor emissions during this procedure. Use water fog to knock hydrogen chloride vapors out of the air (see Chapter 7, "Cloud Dispersal Procedures").
- Once hydrolysis and neutralization is complete, one of two situations will exist.
 - 1. If chlorosilane spilled is trifunctional or silicon tetrachloride, then solids will be formed.
 - Prepare a drying bed using two layers (minimum) of heavy (>8 mil) polyethylene sheets. Shovel solids onto the drying bed and allow to dry. For example, a 50-gal (189.3-L) spill requires 25 × 25 ft (7.6 × 7.6 m) of drying area.
 - Collect any liquid draining from the solids and pump into a polyethylene or fiberglass container using an air-driven diaphragm pump. Adjust pH to greater than 2 by using a neutralizing agent. This liquid can then be disposed of as a nonhazardous waste in accordance with local regulations.
 - Turn solids until completely dry (solids must pass wet paint filter test [i]). Then shovel into fiberpaks for disposal as nonhazardous waste according to local regulations. Line fiberpaks with polyethylene liner.
 - If solids are from SEHSC-001, then vent the plastic bag, including any container it is placed in; residual hydrogen may escape from gels even after dry.
- 2. All other chlorosilanes will form a fluid and a water layer. Adjust the pH to greater than 2 but less than 12.5. (The pH should be kept as close to 7 as possible to reduce the corrosive effects on personnel.) Pump liquid to cargo tank and transport to approved facility for final disposal. Depending on the

chlorosilane, the liquid could be either a hazardous or nonhazardous waste. If lime is used as the neutralization agent, then some solids will also be present to handle.

- Test soil for pH. Place all contaminated soil into lined fiberpaks for disposal at an approved disposal site.
- An alternative procedure for disposal is to immobilize neutralized material with absorbent materials meeting ASTM Methods of Testing Sorbent Performance of Absorbents (**F716**) or absorb with absorbent materials meeting ASTM Method of Testing Sorbent Performance of Absorbents (**F726**). Solids must pass wet paint filter test [i]. Dispose of dry solids as described above.

E. HYDROLYSIS-IN-PLACE PROCEDURE

- See Chapter 10, "Personal Protective Equipment Requirements," for information on what must be worn during this operation.
- The reaction of chlorosilane with water is exothermic and will give off hydrogen chloride gas. Hydrogen chloride evolution will cool the reaction. The foam blanket must be maintained to scrub out the hydrogen chloride gas to prevent release to the atmosphere. The rate of water addition must be controlled so that the foam blanket will completely scrub the hydrogen chloride gas.
- It is possible to react the chlorosilanes with water under the foam blanket. This has the advantage of leaving the foam in place to "scrub" hydrogen chloride vapors. The disadvantage is that the resultant silicone gel or oil is acidic and must be neutralized.
- Prepare a 1 1/2-in. (3.8-cm) fire hose with a spray nozzle. The hose should be long enough to reach all parts of the spill area without running through the spill (a "navy cellar" pipe or nozzle will also work very well).
- Position the fire nozzle under the foam blanket and adjust so that it is in the spray position but will not break the foam blanket.
- As the water reacts with the chlorosilanes, hydrogen chloride gas will be given off. If it escapes the foam blanket, then a dense white cloud will be seen. One or both of the following actions should be taken whenever this cloud is seen:
 - a. Apply more foam as needed to prevent the release.
 - b. Adjust the rate of water addition to prevent breakthrough from the foam blanket.
- As the reaction progresses, move the nozzle to different places in the containment area. This is necessary to complete the hydrolysis.
- Once the reaction is complete, as evidenced by no more hydrogen chloride gas evolving, it will be safe to allow the foam blanket to disperse.

NOTE: There may be pockets of unreacted chlorosilanes that will be noted as the foam blanket disperses. Where this is noted, reapply foam and water as above to complete the hydrolysis.

• Once the hydrolysis is complete and the foam is dispersed, go to the neutralization in place procedure (see Chapter 6D) because the resultant solids (gel) or liquid will be acidic.

Chapter 7 | Plume and Vapor Cloud Mitigation Procedures

A. PURPOSE

The purpose of this chapter is to provide general guidelines to mitigate the downwind effects of a plume of hydrogen chloride and chlorosilane by scrubbing as much of the vapor from the air as possible. This procedure can be used for any downwind plume whether visible or not.

B. PHILOSOPHY

By scrubbing some of the hydrogen chloride and chlorosilane out of the air, downwind exposure can be minimized. This technique should reduce the amount of hydrogen chloride and chlorosilane downwind. Three key concerns should be considered. The responders may be in the cloud because of shifting wind conditions. If so, then complete personal protective equipment will be needed to avoid acid burns. Second, the water in contact with the hydrogen chloride and chlorosilane will form hydrochloric acid. This dilute acid may cause damage to whatever it comes in contact with. An effort should be made to collect, analyze, and if necessary, neutralize this acid. See Chapter 6D, "Neutralization in Place Procedure," for suggestions on how to perform the neutralization. Third, the water runoff from scrubbing the plume needs to be prevented from entering the spill containment area holding the chlorosilane. Water entering the spill containment area may generate additional hazardous vapors and may make emergency response more difficult.

C. PROCEDURE

See Chapter 10, "Personal Protective Equipment Requirements," for information on what must be worn during this operation. Set up a monitor nozzle(s) (or if not available, a 2-1/2 in. [6.4-cm] nozzle) downwind of the actual release. See **Fig. 7.1**, Primary and Secondary Nozzle Location, as an example of monitor nozzle locations. The nozzles should be set up so that the water from these nozzles does

Cloud Dispersal Procedures



FIG. 7.1 Primary and secondary nozzle location.

not come in contact with the spilled chlorosilane (or fire if one has occurred). A decision on how many nozzles to use will be based on the incident itself, the size of the plume, the wind, what is around the incident in the way of buildings, etc.

Set the nozzles to spray as much as possible directly into the vapor cloud. The water spray should be aimed into the wind and therefore into the vapor cloud. This will provide the best mixing and will put the maximum number of water particles in contact with the vapor cloud. Putting the water in perpendicular to the vapor cloud will have some effect, but it is not as effective as the recommended procedure.

When applying the water, three things are happening:

- 1. Hydrolysis of any airborne chlorosilane to hydrogen chloride.
- 2. Dispersion of hydrogen chloride with introduction of air.

3. Some scrubbing of hydrogen chloride from the air by the water.

The use of water spray from a monitor nozzle will make the cloud look more opaque but will make downwind concentrations of hydrogen chloride less than in an unmitigated condition.

Chapter 8 | Small Fire and Spill Handling Procedures

A. PURPOSE

The purpose of this chapter is to provide general guidelines for handling spills or fires of 5 gal (19 L) or less.

B. PHILOSOPHY

The number of incidents in this category will probably exceed the number of all other incidents. The smaller size of the incident typically will result in a smaller environmental concern. However, in a situation in which the incident occurs inside of a building, the close proximity of the hazard to personnel may have a more immediate effect than a large outdoor spill, where people may have more time to leave the affected area. Therefore, two separate procedures are recommended for small spills and fires.

The use of water on spills and fires involving most chlorosilane materials is usually not recommended. However, in some cases, it does prove useful because one is able to react the chlorosilane quicker with increased exposure to moisture and thus reduce the amount of response time and personnel exposure. The principle is based on reacting the chlorosilane faster than if it were allowed to free burn and react naturally, thus removing the fuel leg of the fire/ reaction tetrahedron. The basis is a faster reaction time plus an ability to control the situation and add a dilution and cooling factor to the process. (Chlorosilanes generally react very slowly and do not dissipate very readily on their own when allowed to react with moisture in the ambient atmosphere.) Because of this fact, by reacting the material in a small spill and fire and mitigating it quickly, one reduces the risk to emergency responders and the general public of a prolonged exposure.

The use of a compatible absorbent pad or material meeting ASTM F716 should also be considered for these small spills. The contaminated absorbent can then be placed in a vapor-resistant bag to minimize vaporization of the chlorosilane and limit contact with moisture in the atmosphere. The contaminated pad can then be removed to

a safe location for hydrolysis of the chlorosilane before ultimate disposal of the waste.

The preferred method of extinguishing a chlorosilane fire is to use an alcohol-resistant aqueous film-forming foam (AR-AFFF) extinguisher. Depending on the size and containment of the fire, use either a portable alcohol-resistant AR-AFFF extinguisher or hose. If either of these options is not available, then water may be used following the guidelines in Section C.

C. PROCEDURE

See Chapter 10, "Personal Protective Equipment Requirements," for information on what must be worn during this operation. Caution should be taken when applying water to a small spill or fire involving chlorosilane materials. The initial reaction vapor cloud and fire can be quite impressive; therefore, responders should be prepared for an initial escalation of activity from the spill-fire-water reaction. Copious amounts of water should be applied if this mitigation technique is selected; therefore, an adequate water supply should be on hand before beginning operations. In general, for this technique, a stream from a 1-1/2-in. (3.8-cm) fire hose flowing between 95 (360 L/min) and 125 gal/min (473 L/min) will be the tool of choice for applying the water. An adjustable fog nozzle is recommended because of the ability to begin applying water from a distance using the straight stream and then adjusting to a fog or power cone pattern for cloud dispersal and better water surface area contact.

Responders should be positioned well upwind of the spill or fire. Water should be applied if possible by bouncing it off of a nearby object and the stream periodically raised off of the spill to knock down the resulting vapor cloud. Containment should be provided to catch as much runoff as possible because it will be acidic. After the reaction process is complete, the contained runoff material may need to be neutralized depending on the results of pH tests and whether the chlorosilane forms an oil or solid. Also consider using downwind water spray on the evolved hydrogen chloride vapor to reduce concentrations.

Chapter 9 | Fire Impingement/Radiant Heat on Other Vessels

A. PURPOSE

The purpose of this chapter is to provide general guidance that will help in determining when it is necessary to either move or apply cooling water to adjacent vessels that are being directly impinged or radiantly exposed to the heat of a chlorosilane fire.

B. PHILOSOPHY

In general, the heat of combustion and radiant heat exposure from a chlorosilane fire are much less than from an organic chemical fire having the same heat of vaporization and boiling point. The silica generated in the fire reduces the amount of radiant transmission of much of the energy. The less the organic content of the specific chlorosilane involved, the lower the radiant energy. For example, trichlorosilane fires have a very low heat of combustion and resulting radiant energy component, and it is possible to walk up to the edge of the fire without feeling significant amounts of heat. The heat release from burning chlorosilanes is typically less than the heat release from burning hydrocarbon fires. Because of the lower radiant energy emitted from a chlorosilane fire, particularly when the material has very low organic content (e.g., trichlorosilane or methyltrichlorosilane), it may not be as necessary to spray adjacent vessels as quickly as would be necessary with a traditional organic fire to prevent them from experiencing the effects of fire exposure (e.g., structural damage, boiling, or polymerizing of tank contents).

C. PROCEDURE

Some general steps should be considered in determining the need for water spray on adjacent vessels exposed to a chlorosilane fire. These steps include:

- See Chapter 10, "Personal Protective Equipment Requirements," for information on what must be worn during this operation.
- Review the safety data sheet (SDS) for the chemical in the affected tank to determine its boiling point, polymerization potential, and any safety concerns with temperature-induced processes.
- If it is possible to safely measure the pressure or temperature on the adjacent vessel, then do so before deciding to spray the vessel with water. If the temperature or pressure is not increasing, then spraying with water may not be required.
- If the vessel can be moved safely from the area, then consider moving the vessel before applying water spray.
- Avoid as much as possible getting water into a damaged chlorosilane container or exposing spilled chlorosilane materials to the water spray-off or runoff.
- If the vessel must be sprayed with water, and time permits, then dike the area to prevent the water runoff from draining into or exposing the chlorosilane spill.
- To be effective, cooling water for tank or vessel protection must be applied at all points of the flame impingement and on the entire vapor space area of the tank/vessel.
- Withdraw any resources used for manual water spray tank cooling in the event of a rising sound from any venting safety devices or visible discoloration of tanks.

Chapter 10 | Personal Protective Equipment Requirements

A. PURPOSE

The purpose of this chapter is to provide general guidelines for the selection of personal protective equipment (PPE) required in chlorosilane fire or spill situations.

B. PHILOSOPHY

A response to chlorosilane emergencies usually involves the use of PPE. The PPE should be selected based on the flammability and permeability of the PPE material involved. NOTE: Permeation study reference sources can be found in Chapter 12.

C. PROCEDURE

1. Nonflammable Situations

Nonflammable situations are those involving silicon tetrachloride, which will not burn, or involving other chlorosilanes in which the ambient temperature is more than 20°F (11°C) below the flash point of the involved chlorosilane, for which the spilled material has not already ignited and there are no open flames or other potential ignition sources present.

PPE should be used based on an assessment of the hazards and risks for the particular situations, including the expected or measured concentration of chlorosilanes. During the initial incident response, when the concentration of chlorosilane vapors and the hydrolysis byproduct hydrogen chloride (HCl) have not been determined, Level A protection should be worn. There are too many variables involved in any incident to be able to predict specific PPE requirements in advance. PPE determinations are made by Incident Command personnel on the basis of their on-scene professional evaluation and knowledge of the incident.

Colorimetric tubes can be used to measure HCl concentrations, or readings from a portable flame ionization detector (FID) can be used to give an approximation of the total chlorosilane vapor concentration. Release modelling software may also be useful in predicting downwind plume distances and estimated vapor concentrations.

HCl, the primary byproduct of chlorosilane hydrolysis, has an immediately dangerous to life or health (IDLH) value of 50 ppm and American Industrial Hygiene Association (AIHA) Emergency Response Planning Guidelines (ERPG) limits of ERPG-1 = 3 ppm, ERPG-2 = 20 ppm, and ERPG-3 = 150 ppm. Other relevant exposure limits can be found in the National Institute for Occupational Safety and Health (NIOSH) *Pocket Guide to Chemical Hazards*, the American

Conference of Governmental Industrial Hygienists (ACGIH) *TLV Booklet*, The AIHA ERPG Guidelines, and the Occupational Alliance for Risk Science (OARS) Workplace Environmental Exposure Levels (WEEL) listing. The online CAMEO Database of Hazardous Materials may also be used: http://cameochemicals.noaa.gov/.

Permeation studies indicate that chlorosilanes behave similar to chlorinated hydrocarbons. Therefore, do not use hydrochloric acid permeation data as the basis for selecting PPE. These tests were conducted in accordance with the ASTM Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases under Conditions of Continuous Contact (**F739**). Gloves tested in these studies that have good resistance to chlorosilanes are Viton[®], 4H[®], and Silver Shield[®]. The types of protective clothing that demonstrated good resistance to chlorosilanes during permeation testing and did not show any significant signs of degradation or deterioration are Tychem 7500[®], CPF IV[®], Responder[®], and Chemrel[®].

Level A equipment, which consists of a totally encapsulating gastight chemical-protective suit, attached protective gloves, protective footwear, and a MSHA/NIOSH-approved self-contained breathing apparatus (SCBA), should be required when entering an environment where exposure to vapors of chlorosilane is possible. Level A should also be worn when changing wind conditions could place a responder in contact with chlorosilane vapors. Chemical-protective clothing should be chosen that is compliant with the National Fire Protection Association (NFPA) 1991 *Standard on Vapor-Protective Suits for Hazardous Chemical Emergencies*, the materials of which have demonstrated permeation resistance testing breakthrough times greater than 1 h against chlorosilanes. NFPA 1991-compliant ensembles with aluminized flash covers or an integrated suit are recommended in the event of a flash fire.

Level B equipment, consisting of a splash-resistant suit, protective gloves, protective footwear, and a MSHA/NIOSH-approved SCBA, should be used when approaching a spill where the wind conditions are steady and the responder will not be exposed to chlorosilane vapor under the expected response conditions. Chemical-protective clothing should be chosen that is compliant with NFPA 1992 *Standard on Liquid Splash-Protective Suits for Hazardous Chemical Emergencies.* An aluminized flash cover or integrated suit is recommended in the event of a flash fire.

Level C equipment, consisting of a splash-resistant suit, protective gloves, protective footwear, and an air-purifying respirator (APR), can be used by small-spill responders who spray water, foam, or both from a distance where there is little or no chance of the responder coming in contact with chlorosilane vapor. Level C equipment should only be used outside of the hot or response zone in an unconfined area with known vapor concentrations. Air-purifying respirators must be NIOSH approved and equipped with combination organic vapor (to remove unreacted chlorosilane vapors) and acid gas (to remove HCl vapors) filters. Chemical-protective clothing should be chosen that is compliant with NFPA 1992 *Standard on Liquid Splash-Protective Suits for Hazardous Chemical Emergencies.*

The International Safety Equipment Association (ISEA) in Arlington, Virginia, and Underwriters Laboratories (UL) in Research Triangle Park, North Carolina, maintain lists of products certified to NFPA standards.

Although Level A equipment will afford the greatest degree of chemical protection, extended operations involving any length of physical activity may create severe exertion and lead to possible heat stress. Responders in chemical-protective clothing must be carefully monitored and clothing levels downgraded whenever possible to permit greater responder comfort and mobility. All emergency response operations must be performed in compliance with the OSHA regulations provided in Title 29 the Code of Federal Regulations, Part 1910.120, *Hazardous Waste Operations and Emergency Response*, or the applicable state or local laws.

2. Potentially Flammable Situation

Potentially flammable situations are those in which the temperature of the chlorosilane is less than 20°F (11°C) below its flash point and in which open flames and potential ignition sources may be present. The combination of flash fire or open flame with chemical exposure represents the greatest hazards to the responder. Traditional chemical-protective clothing provides little, if any, flammable protection. Entry in a potential flammable environment should be

avoided. Level A vapor-protective suits are compliant with the baseline requirements and the optional chemical flash fire performance requirements of NFPA 1991 Standard on Vapor-Protective Suits for Hazardous Chemical Emergencies. These suits are intended for escape only in terms of permitting the safe exit of an emergency responder from a chemical flash fire. These suits should not be used for entry. Alternatively, firefighter turnout clothing, which is compliant with NFPA 1971 Standard on Protective Ensemble for Structural Fire Fighting, may be worn over chemical-protective clothing, but this clothing is typically not designed to integrate with chemical-protective clothing and will seriously impair the wearer's mobility and functionality. Moreover, such clothing systems have not been evaluated for combined chemical and flame exposure. Responders may also consider wearing flame-resistant clothing meeting NFPA 2112 Standard on Flame Resistant Garments for Protection of Industrial Personnel against Flash Fire, under any other protective garb as an additional layer of protection.

Firefighter turnout clothing, compliant with NFPA 1971 Standard on Protective Ensemble for Structural Fire Fighting, in combination with an SCBA compliant with NFPA 1981 Standard on Open-Circuit, Self-Contained Breathing Apparatus, should be worn for fighting structural fires. This clothing will not prevent skin contact with chlorosilane vapors.

WARNING: To help prevent skin irritation or corrosive chemical burns, care should be used to avoid entry into a vapor cloud when wearing only turnout gear. Chlorosilane vapors in contact with moisture, including water spray, rain, groundwater, moist skin, eyes, and mucus membranes, form HCl and are considered extremely acidic ($pH \le 2$).

Chapter 11 | Decontamination of E/R Personnel and Equipment

A. PURPOSE

The purpose of this chapter is to provide general guidelines concerning procedures for decontamination of responders and equipment and for site cleanup.

B. PHILOSOPHY

The primary focus of this procedure is to remove the hazardous substance from employees, equipment, and the spill site to the extent necessary to prevent the occurrence of foreseeable adverse health effects and to reduce the possibility of any on-scene environmental effect. Of secondary importance is the cleaning of equipment at the site to the extent necessary to remove it from the site without causing additional health and environmental concerns during shipping.

C. PROCEDURE

All personnel involved in the decontamination of exposed employees, equipment, and spill sites shall wear appropriate personnel protective equipment as specified in Chapter 10 to minimize the potential for exposure while undertaking the decontamination process.

1. Employee Decontamination

- Chlorosilanes are extremely corrosive to the skin and eyes. Saturated clothing should be removed immediately and the affected area washed thoroughly with water to remove all acidic substances. If eyes come into contact with chlorosilane, then they should immediately be flushed thoroughly with water. A pH < 2 or > 12 may cause severe skin and eye damage. See the material safety data sheet (MSDS) for additional safety concerns.
- Residual vapors in clothing may also be irritating to nose and throat. Contaminated clothing should be sealed in polyethylene bags to prevent contact with moisture in the air that would continue to release hydrogen chloride vapors. If clothing is saturated with chlorosilanes, then it should first be washed with water to react the chlorosilane and remove the hydrogen chloride. The contaminated clothing should be sealed in plastic bags to prevent residual hydrogen chloride vapor release. Contaminated clothing must be disposed of in accordance with federal, state, and local regulations.
- Removal of all clothing that contains chlorosilanes and decontamination of that person needs to be done on-site before

transporting that person to a hospital. In addition, send a copy of the relevant MSDS to the hospital with the person in need of medical attention. Please also refer to the Centers for Disease Control Medical Management Guideline for Hydrogen Chloride.

2. Equipment Decontamination

- Any water used for decontamination could be corrosive; therefore, it should be contained to prevent runoff. See Chapter 5E, "Purge, Scrub and Vent Procedure," for proper handling of this liquid.
- Personal protective equipment should be decontaminated in accordance with manufacturer recommendations. This should include, at a minimum, washing clothing or equipment with soap and water and allowing the items to air dry. Because protective clothing and equipment may not be adequately decontaminated, check with pH paper for acidic residue. If acidic residue is present, then use a sodium bicarbonate solution to neutralize the acidic residue and rewash the clothing and equipment. If, in the judgment of the safety officer or other responsible official, the clothing or equipment is still not adequately decontaminated, then it should be disposed of in accordance with federal, state, and local regulations. Clothing or equipment should not be reused if the performance of the item has been affected or if there is a risk that exposure will occur during the next wearing.
- Any equipment or piping that was in contact with chlorosilanes or hydrogen chloride should be flushed, preferably with a weak basic solution of sodium carbonate or sodium bicarbonate, and allowed to dry. Small parts can be placed in polyethylene bags to be shipped off-site; larger pieces of pipe could be wrapped in polyethylene sheeting before shipping off-site. Water can be used instead of a basic solution; however, some residual acid may still be present, and greater care needs to be taken in sealing parts to prevent exposure to residual hydrogen chloride vapors. Sodium bicarbonate solution is a preferable wash along with a detergenttype wetting agent to cut any oil involved.
- Decontamination of equipment can be easily checked by wipe sampling with pH paper for acid residue.

3. Site Decontamination

• Decontamination of personnel, equipment, and spill sites should follow the guidelines found in Chapter 6, "Hydrolysis of Chlorosilanes."

- Any water that may have contacted the chlorosilane or hydrogen chloride should be checked for pH and the presence of an oily residue. If pH is less than 5, then consider neutralizing it on-site to a pH between 5 and 9. Low pH water may become more acidic with time as the water evaporates. Work with the incident commander and the local environmental personnel to determine the proper disposition of the contaminated water.
- If the water contains any oily residue, then the oil will need to be collected and removed from the site.
- Check the pH of any potentially contaminated soils. If the pH is less than 5, then work with the Incident Commander and the environmental agencies to determine what soils need to be removed.

Chapter 12 | References

ASTM STANDARDS

Manual 10—A Guide to the Safe Handling of Hazardous Materials Accidents.

F716—Standard Test Methods for Sorbent Performance of Absorbents.

F726—Standard Test Methods for Sorbent Performance of Adsorbents.

F739—Standard Test Method for Permeation of Liquids and Gases through Protective Clothing Materials under Conditions of Continuous Contact.

F1127—Standard Guide for Containment of Hazardous Materials Spills by Emergency Response Personnel.

F1129—Standard Guide for Using Aqueous Foams to Control the Vapor Hazard from Immiscible Volatile Liquids.

EMERGENCY RESPONSE GUIDEBOOK

A Guidebook for First Responders during the Initial Phase of a Dangerous Goods /Hazardous Materials Transportation Incident

- U.S. Department of Transportation, Pipeline and Hazardous Materials Safety Administration.
- Transport Canada.
- Secretariat of Transport and Communications, Mexico.
- PHMSA ERG: http://www.phmsa.dot.gov/hazmat/library/erg

EPA PUBLICATIONS

SW-846—Paint Filter Liquids Test Method 9095, as described in "Test Method for Evaluating Solid Wastes, Physical/Chemical Methods."

NFPA STANDARDS

NFPA Standards can be viewed online at: http://www.nfpa.org/ codes-and-standards/free-access 704—Standard System for the Identification of the Hazards of Materials for Emergency Response.

1971—Standard on Protective Ensembles for Structural Fire Fighting and Proximity Fire Fighting.

1981—Standard on Open-Circuit Self-Contained Breathing Apparatus (SCBA) for Emergency Services.

1991—Standard on Vapor Protective Ensembles for Hazardous Materials Emergencies.

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