



CODE OF PRACTICE HYDROGEN SELENIDE H_2Se

AIGA 096/16

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PREFACE

As part of a program of harmonization of industry standards, the Asia Industrial Gases Association has issued AIGA 096, *Hydrogen Selenide*, jointly produced by members of the International Harmonization Council and originally published by the Japan Industrial and Medical Gases Association (JIMGA) as JIMGA-T-S/85/12 *Hydrogen Selenide*.

This publication is intended as an international harmonized standard for the worldwide use and application of all members of the Asia Industrial Gases Association (AIGA), Compressed Gas Association (CGA), European Industrial Gases Association (EIGA), and Japan Industrial and Medical Gases Association (JIMGA). Each association's technical content is identical, except for regional regulatory requirements and minor changes in formatting and spelling.

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1 Introduction

Hydrogen selenide is a highly toxic, flammable, colorless gas with a disagreeable penetrating odor at room temperature and atmospheric pressure [1]. It is shipped as a liquefied compressed gas under its own vapor pressure of 0.950 MPa (138 psi) at 20 °C (68 °F) [2]. It is also supplied in a gaseous state, diluted with other gases under pressure.

The use of hydrogen selenide has constantly been growing and this usage is expected to continue throughout the world. The issue of the safe handling of hydrogen selenide is a very important and relevant topic to the compressed gas industry as well as the user community of this electronic specialty gas.

Hydrogen selenide is used to prepare metallic selenides and organoselenium compounds. It is used in doping gas mixtures for the preparation of semiconductor materials containing a controlled amount of a significant impurity [3]. It is also used to manufacture photovoltaic cells such as copper-indium selenide/sulfide (CIS) or copper-indium-gallium-selenide (CIGS) as in thin-film deposition of multiple junction photovoltaic cells.

Hydrogen selenide can be safely handled if equipment is properly designed, maintained, and employees are trained. As a minimum, all personnel should have access to a hydrogen selenide safety data sheet (SDS) and training in the use of the SDS and other reference material.

NOTE—In this publication, hydrogen selenide is understood to be in the gaseous phase unless otherwise stated.

2 Scope and purpose

2.1 Scope

This publication is intended for the suppliers, distributors, and users of hydrogen selenide and its handling equipment. The publication includes guidance for design of equipment, cylinders and valve usage, handling controls, and safety. Guidelines on the operational steps associated with the use of hydrogen selenide and hydrogen selenide mixtures as well as fire protection, gas detection, ventilation, and related safeguards are also included. The manufacture, purification, and analysis of hydrogen selenide are beyond the scope of this publication, although the general guidance given is also relevant to these processes.

2.2 Purpose

This publication was written to address the high toxicity and flammability of hydrogen selenide where the consequences of improper handling of hydrogen selenide could cause injury, death, and/or facility damage. This publication will provide a description of the potential hazards involved in handling hydrogen selenide and the guidelines to be taken to minimize risk potential.

3 Definitions

For the purpose of this publication, the following definitions apply.

3.1 Publication terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May

Indicates that the procedure is optional.

3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

3.2 Technical definitions**3.2.1 Absolute pressure**

Based on a zero reference point, the perfect vacuum. Measured from this reference, the standard atmospheric pressure at sea level is 101.325 kPa, abs (14.696 psia); however, local atmospheric pressure can deviate from this standard value because of weather conditions and the elevation above or below sea level.

3.2.2 Apparatus

Accessory equipment such as valves, pressure relief devices (PRDs), regulators, and non-return valves (check valves) used with compressed gas.

3.2.3 ADR/RID

European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR) and Rail (RID).

3.2.4 Containers

Vessels of various shapes, sizes, and materials of construction such as cylinders, portable tanks, or stationary tanks, of designs meeting the specifications of the American Society of Mechanical Engineers (ASME), Transport Canada (TC), U.S. Department of Transportation (DOT), European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR), Japanese Industrial Standard (JIS), or national authorities and are filled with compressed gases.

3.2.5 Corrosive

Gas that in contact with materials or living tissue can cause damage or destruction.

3.2.6 Critical temperature

Temperature above which a pure gas cannot be liquefied, regardless of the degree of compression.

3.2.7 Cryogenic liquid

Refrigerated liquefied gas having a boiling point lower than $-90\text{ }^{\circ}\text{C}$ at 0.101 MPa, abs ($-130\text{ }^{\circ}\text{F}$ at 14.696 psia).

3.2.8 Cylinder

Transportable pressure receptacle having a water capacity that does not exceed 150 liters that can be filled with a gas under pressure.

NOTE—For pure hydrogen selenide or hydrogen selenide mixtures that are classified as highly toxic, some countries prohibit the use of cylinders larger than 57 L.

3.2.9 Filling ratio

Ratio of the mass of liquefied gas introduced in a container to the mass of water at $15\text{ }^{\circ}\text{C}$ ($59\text{ }^{\circ}\text{F}$) that would fill the same container fitted ready for use.

NOTE—Also known as fill density, filling factor, maximum fill degree, or maximum fill pressure.

3.2.10 Flammable gas

When either a mixture of 13% or less (by volume) with air is ignitable at 0.101 MPa, abs (14.696 psia) or has a flammable range with air of at least 12% regardless of the lower limit. These limits shall be determined at 0.101 MPa, abs (14.696 psia) pressure and at a temperature of $20\text{ }^{\circ}\text{C}$ ($68\text{ }^{\circ}\text{F}$).

3.2.11 Gas

Gas or gas under pressure as defined in United Nations (UN) *Recommendations on the Transport of Dangerous Goods, Model Regulations* and in *Globally Harmonized System of Classification and Labelling of Chemicals* (GHS) [4, 5].

A gas is a substance that (a) At 50 °C has a vapor pressure greater than 300 kPa; or (b) Is completely gaseous at 20 °C at a standard pressure of 101.3 kPa.

3.2.12 Gas supplier

Business that produces, fills, and/or distributes compressed gases and compressed gas containers.

3.2.13 Handling

Moving, connecting, or disconnecting a gas container under normal conditions.

3.2.14 Hazard

Any condition that could potentially cause injury to personnel or property.

3.2.15 Highly toxic

Gases that have an LC₅₀ in air less than or equal to 200 ppm for a 1 hour exposure. National regulations may have additional classifications.

NOTE—In this publication, ppm means parts per million by volume.

3.2.16 Hot zone

Area immediately around the chemical spill and the surrounding region that may be in serious danger from physical hazards such as fire, explosion, or chemical exposure. Generally, only firefighters and emergency response team who are members of a specialized hazardous material (HAZMAT) team will enter the hot zone.

3.2.17 Inert gas

Gas that is not toxic, doesn't support human breathing, and reacts scarcely or not at all with other substances.

3.2.18 LC₅₀

Concentration of a substance in air, exposure to which for a specified length of time is expected to cause the death of 50% of the entire defined experimental animal population.

NOTE—Usually measured as ppm or mg/m³.

3.2.19 Lower flammability limit (LFL)

Lower limit of flammability (point at which a flame just starts to propagate) of a gas or vapor at ordinary ambient temperatures and pressures expressed in percent of the gas or vapor in air by volume. The LFL will vary with temperature and pressure.

NOTE—Also referred to as lower explosive limit (LEL).

3.2.20 National standards, guidelines, regulations

Technical standards set by the regulatory authorities of the country in which the equipment/facility is used, with respect to design, construction, testing, and use. Where available and applicable, these standards shall be followed.

3.2.21 Oxidizer

Gas or gas mixture that is able, at atmospheric pressure, to support the combustion more than a reference oxidizer consisting of 23.5% oxygen in nitrogen (for example, gaseous oxygen, nitrous oxide, or fluorine).

3.2.22 Pressure

Force per unit of area exerted by a gas to its surroundings. The term megapascal (MPa) will be the standard term for pressures used in this publication. 1 MPa = 1000 kPa = 20,885.4 psf = 145 psi = 10 bar.

3.2.23 Pressure relief device

Pressure and/or temperature activated device that may be used to prevent the pressure from rising above a predetermined maximum and thereby prevent equipment or container failure due to overpressurization.

3.2.24 Safety data sheet (SDS)

Written or printed information concerning a hazardous material (properties, precautions, etc.) following national regulations.

3.2.25 Test pressure

Pressure at which the pressure receptacle is hydraulically or pneumatically tested and is the pressure which shall not be exceeded under any foreseeable normal operating conditions (for example, during filling).

3.2.26 Toxic gas

Compressed gas that has an LC₅₀ in air of less than or equal to 5000 ppm but greater than 200 ppm for a 1 hour exposure. National regulations may have additional classifications.

3.2.27 Threshold limit value—time-weighted average (TLV®—TWA)

Concentration to which a person may be exposed, 8 hours a day, 40 hours a week, without harm [6].

3.2.28 Upper flammability limit (UFL)

Upper limit of flammability (point at which a flame can still nominally propagate) of a gas or vapor at ordinary ambient temperatures and pressures expressed in percent of the gas or vapor in air by volume. The UFL will vary with temperature and pressure.

NOTE—Also referred to as upper explosive limit (UEL).

3.2.29 Valve outlet caps and plugs

Removable attachments that usually form a gas-tight seal on valve outlets provided by the gas supplier with certain gases.

NOTE—Some caps are designed only for valve thread protection and are not gas-tight.

3.2.30 Valve protection cap

Rigid removable cover provided for container valve protection during handling, transportation, and storage.

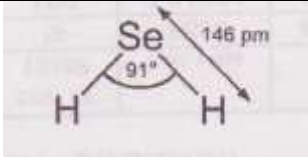
4 Gas properties**4.1 General**

Hydrogen selenide is a hydride gas with the chemical formula H₂Se. It is highly toxic with an established LC₅₀ of 0.3 ppm/8 hours inhalation-guinea pig. In addition to its toxicity, it is also flammable and is capable of forming flammable mixtures when mixed with air. It possesses a disagreeable, unpleasant odor. The odor threshold is less than 0.1 ppm. At higher concentrations, olfactory fatigue can rapidly occur with loss of any awareness of the gaseous odor [7].

Hydrogen selenide is routinely shipped in seamless steel or aluminum alloy cylinders. For safety reasons, cylinders used for pressurized hydrogen selenide will have a test pressure of 4.2 MPa (609 psi). Some national bodies mandate higher test pressures. The vapor pressure of hydrogen selenide is 0.950 MPa (138 psi) at 20 °C (68 °F) [2].

Table 1 shows properties of hydrogen selenide.

Table 1— Properties of hydrogen selenide

Property	SI Units	U.S. Units	Reference
Synonyms	Selenium hydride; hydrogen selenide, anhydrous; hydroselenic acid, anhydrous; dihydrogen selenide; selenium dihydride; selane		[1]
Chemical formula	H ₂ Se		
CAS number	7783-07-5		
UN number	UN 2202		
Physical state	Gas		
Color	Colorless		[3]
Odor	Disagreeable, unpleasant. Similar to decayed horseradish or garlic		[3, 8, 1]
Molecular weight	80.976		[9]
Boiling point	−41 °C	−42 °F	[9]
Freezing point	−64 °C	−83 °F	[9]
Decomposition temperature	160 °C	320 °F	[3]
Critical temperature	138 °C	280.4 °F	[3]
Critical pressure	9017 kPa, abs	1308 psia	[2]
Critical volume	112.24 cm ³ /mol		[3]
Critical density	675.7 kg/m ³	42.18 lb/ft ³	[2]
Critical compressibility factor	0.274		[3]
Density of the liquid at −41 °C (−42 °F)	2004 kg/m ³	125.1 lb/ft ³	[2]
Density of the gas (1 atm) at 20.0 °C (−68 °F)	3.348 kg/m ³	0.209 lb/ft ³	[2]
Relative density of gas at 21.1 °C (70 °F) at 101.325 kPa (air=1)	2.796		
Vapor pressure at 20 °C (68 °F)	0.950 MPa	138 psi	[2]
Solubility in water, vol gas/vol water at 0 °C (32 °F) and 1 atm	2.05 vol/vol		[2]
pH	Acidic		[1]
Volatility	Not applicable		
Odor threshold (varies with impurities)	0.1 ppm		[1]
Lower flammability limit (LFL)	4.0%		[9, 10]
Upper flammability limit (UFL)	67.5%		[2]
Molecular shape	Bent		
Standard enthalpy of formation at 25 °C, Δ _f H ⁰ gas	+29.7 kJ/mol		[3]
Structure: H ₂ Se adopts a “bent” structure with a H-Se-H bond angle of 91°. Consistent with this structure, three IR-active vibrational bands are observed: 2358, 2345, and 1034 cm ^{−1} .			

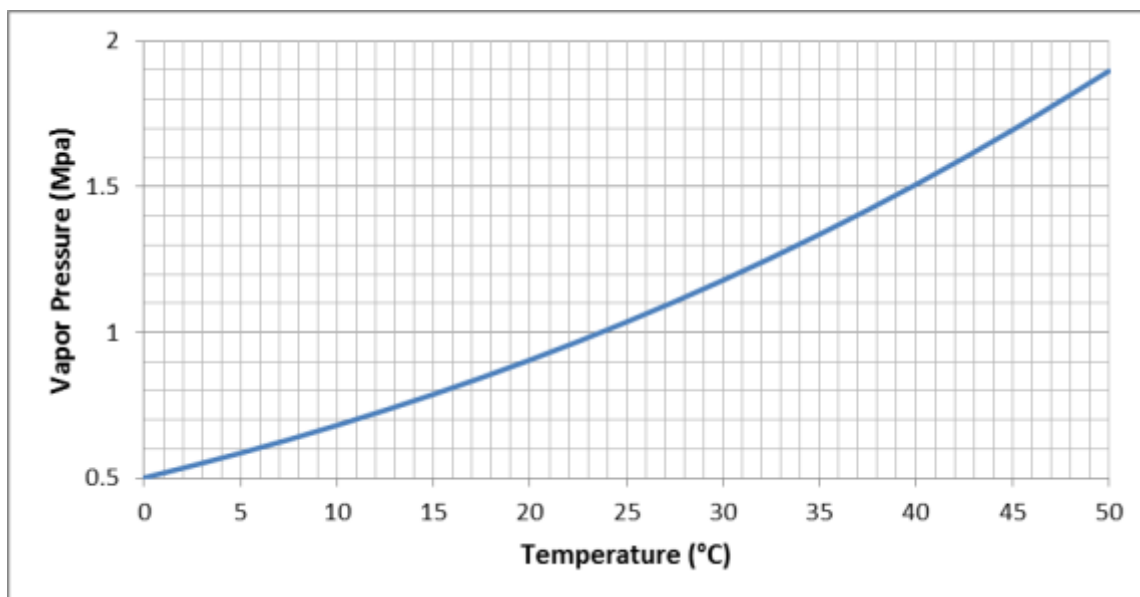


Figure 1—Hydrogen selenide vapor pressure versus temperature (SI units) [9]

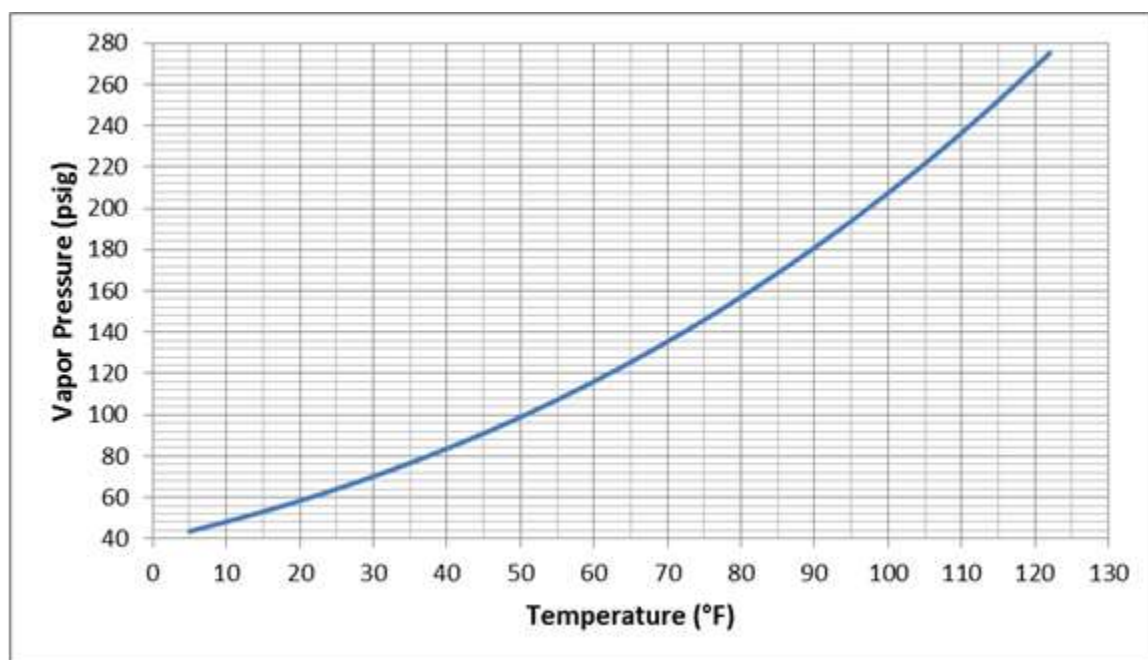


Figure 2—Hydrogen selenide vapor pressure versus temperature (US units) [9]

4.2 Physical properties

Hydrogen selenide is a weak acid. It is less thermally stable than hydrogen sulfide. It decomposes to elemental selenium at about 160 °C (320 °F). If ignited, it burns to give off selenium dioxide and water [3, 8]. Hydrogen selenide will react violently with nitric acid [11].

It is best to avoid sources of ignition, sparks, and flames because of the flammable properties of hydrogen selenide. The concern for explosions shall be recognized. Hydrogen selenide poses a severe fire hazard and a moderate explosion risk.

A flammable mixture of hydrogen selenide in air requires an ignition source to ignite; it is not pyrophoric. The autoignition temperature of hydrogen selenide is not defined.

4.3 Chemical properties

Hydrogen selenide is incompatible with oxidizing materials, members of the halogen family, acids, other combustible materials, and will react slowly with water. Hydrogen selenide is a strong reducing agent and reacts vigorously with oxidizers such as potassium permanganate, sodium hypochlorite, oxygen, ozone, chlorine, fluorine, and nitric oxide. Hydrogen selenide can react with the alkali metal family. Hydrogen selenide, like other hydrides, is not known to polymerize.

4.4 Health properties

Refer to 5.2.

4.5 Flammability properties

Refer to 5.1.

4.6 Environmental properties

If hydrogen selenide enters the environment through an accidental release, it can contaminate land, water, and air with potentially disastrous results. Many countries have strict regulations and measures to be taken should a release occur. The users of hydrogen selenide should review the regulations that apply.

- Selenium compounds including hydrogen selenide are considered hazardous air pollutants (HAPs) in certain jurisdictions. These pollutants are known or suspected to cause liver disorders, respiratory disorders, other serious health effects, and adverse environmental effects. There is no information that hydrogen selenide will cause cancer [8, 12];
- Hydrogen selenide users should employ a variety of tools to prevent direct pollutant discharges into waterways, municipal wastewater treatment facilities, or allow polluted runoff;
- Emergency response programs are established and at times mandated to eliminate any danger to the public and the environment posed by hazardous substance releases. To help fulfill this mission, local governments may require that the person or organization responsible for hydrogen selenide use notify the government when the amount onsite reaches a predetermined limit;
- If a release or spill of hydrogen selenide occurs, the government may require additional notifications be made. These requirements vary by governments;
- Guidance documents should be obtained from the local government agency to offer direction in following regulations and control emissions. Legal action may be undertaken to pursue those who do not fully comply with the requirements of environmental legislation; and
- Risks to human health and the environment will vary considerably depending upon the type and extent of exposure. Hydrogen selenide users are strongly encouraged to characterize risk on the basis of locally measured or predicted exposure scenarios.

National agencies such as the United States Environmental Protection Agency (EPA) establish drinking water standards and have determined that selenium is a health concern at certain high levels of exposure. Pure selenium is also an essential nutrient at low levels of exposure. This inorganic chemical is found naturally in food and soils. EPA has set the drinking water standard for selenium at 0.05 ppm to protect against the risk of adverse health effects. Drinking water that meets EPA's standard is associated with little to no risk and is considered safe with respect to selenium [13]. In Japan, there is a limit of 0.01mg/l for hydrogen selenide and selenium compounds.

Risk assessment values or other media quality standards may be used in countries to evaluate the health risks posed by exposures to toxic chemicals. These values are typically specified as concentration limits that shall not be exceeded to avoid health risk. These published values can be compared directly to information about the concentration of a chemical in the environment to identify potential health hazards. If a chemical concentration exceeds a relevant media quality standard, action to reduce environmental contamination or exposure is warranted.

5 Gas hazards

5.1 Fire and explosion hazards [11, 14, 15, 16]

Hydrogen selenide is flammable and presents a severe fire hazard. The vapors are heavier than air. Vapors can ignite at ignition sources downstream and flash back to the leaking source. Vapor and air mixtures are explosive. Containers can rupture or explode if exposed to heat. The low vapor pressure of hydrogen selenide generally prevents long streams of burning gas. However, as the container temperature/pressure increases, the burning hydrogen selenide can be several meters long and can shift quickly with the slightest breeze. By-products of hydrogen selenide combustion are selenium and/or selenium oxide (both solids) and water. Selenium can be absorbed by the skin. Therefore, personnel shall wear appropriate personal protective equipment (PPE) and self-contained breathing apparatus (SCBA) when fighting hydrogen selenide fires. Only trained personnel should respond to hydrogen selenide fires. As in the case of a fire of any flammable gas, the flow should be stopped if it is safe and practical to do that. Normally, this can be accomplished by shutting off the cylinder valve.

NOTE—If no ignition occurs or the flame has been extinguished and flow cannot be stopped, it is possible that the mixture can be reignited from a separate ignition source causing further damage or explosion.

In order for a hydrogen selenide ignition to occur, three conditions need to occur simultaneously:

- concentration of hydrogen selenide shall be within its flammable limits;
- presence of sufficient air or an alternate oxidizing source; and
- source of ignition shall exist.

Hydrogen selenide shall not be used near open flames, sources of heat, adjacent to oxidizers, or non-electrically classified electrical systems. Transportation, storage, and use of hydrogen selenide should be in well ventilated areas.

If the flow of hydrogen selenide cannot be stopped, let it burn until the fire stops naturally, keeping adjacent cylinders and equipment cool. If a hydrogen selenide fire is extinguished and the flow of hydrogen selenide is not stopped, a hazardous combustible mixture can continue to form. It is possible that the mixture can be ignited, explode, cause more damage, and restart the fire. Measures shall be taken to protect persons from cylinder rupture in the case of cylinder failure or piping failure.

Although a hydrogen selenide fire shall not be extinguished until the flow of hydrogen selenide is stopped, water sprays, etc., should be used to extinguish any secondary fire and to prevent the spread of fires. The hydrogen selenide containing equipment may be kept cool by water sprays to decrease the rate of hydrogen selenide release or to prevent further damage. This is best done at a distance. Water used in firefighting could become contaminated so there should be measures in place to contain and possibly treat such contaminated water.

Remote-controlled water spray equipment is preferable to the use of hoses in cooling equipment and to reduce the spread of fire. When the use of hoses is necessary, operating personnel should remain behind protective structures, upwind of the fire, and wear PPE and SCBA.

Firefighting or other emergency personnel should communicate and cooperate with personnel who are familiar with the physical and toxic properties of hydrogen selenide. They should also communicate and cooperate with personnel who are familiar with materials in the area of the emergency. Unexpected conditions can require special actions.

If a cylinder of hydrogen selenide or supply piping system ruptures so that quantities of hydrogen selenide are released and ignited, hazardous conditions can exist:

- Flame effects—The major concern is that the generated flames can impinge on surrounding valves and piping thus weakening these structures with the possibility of failure taking place. Fire balls or jet fires can be present (depending on source pressure). Wind velocity and direction can change the shape of the flame to an elliptical shape and push it further downwind of the release;
- Radiation effect—The major concern is that radiation effects from the fire can result in the excessive heating of adjacent equipment and process lines; and
- Reaction by-products—Selenium and selenium oxide can form as a result of the fire and deposit as a dust over the affected facility and be carried downwind of the fire. Such forms of selenium are toxic by inhalation, ingestion, and absorption.

A thorough process hazard analysis (PHA) with identified safeguards shall be in place to minimize the risk of a potential incident if the operating personnel should err in procedures or the equipment fails.

5.2 Toxicology

5.2.1 Hydrogen selenide exposure [17]

Hydrogen selenide has a disagreeable, unpleasant odor that smells like decayed horseradish or garlic. There have been reports of hydrogen selenide exposure for a long time, but its acute toxicities to humans are not well established. Naturally occurring selenium is toxic at high concentrations but is also a nutritionally essential element.

The primary route of exposure is inhalation. Hydrogen selenide is a highly toxic systemic poison. The primary symptom is moderate irritation of the eyes and mucous membranes. Acute exposures can result in chemical bronchitis and delayed pulmonary edema. Hydrogen selenide is metabolized to the relatively nontoxic dimethyl selenide. The excretion of this compound results in a garlic odor to the breath, sweat, and urine [7]. See Table 2.

Table 2—Regulatory exposure limits for hydrogen selenide

Chemical :HYDROGEN SELENIDE			
CAS Number :	7783-07-5		
Conversion Factor :	1 ppm = 3.31 mg/m ³ [4]		
	Value	Units	Reference
Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) Time Weighted Average (TWA)	0.05 0.2	ppm mg/m ³	[41]
National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) TWA	0.05 0.2	ppm mg/m ³	[8]
NIOSH Immediately Dangerous to Life or Health (IDLH)	1.0	ppm	[8]
NOTES			
1. OSHA limits are the legal exposure limits allowed by United States law and are enforceable.			
2. <u>NIOSH limits are recommended values and are not enforceable by law.</u>			
3. <u>In Europe, the SDS of the supplier shall be consulted to find the applicable regulatory exposure limits in the different European countries where determined.</u>			

In this publication, some reports are shown for reference as follows.

Data on the potential carcinogenicity of selenium and various selenium compounds in humans are inadequate. The only selenium compound that has been shown to be carcinogenic in animals is selenium sulfide, which resulted in an increase in liver tumors in rats and mice and lung tumors in female mice from oral exposure [12]. Epidemiological studies have evaluated selenium in blood and cancer death rates in areas of high versus low naturally-occurring selenium. However, these studies have limited value because they do not assess specific selenium compounds or correlate exposure with cancer risk [17]. See Table 3.

Selenium has been detected in blood, urine, hair, and nails of exposed individuals [18, 19, 20, 21, 22, 23]. Various estimates of selenium intake for the U.S. populations have been reported [24, 25, 26, 27, 28, 29]. The largest numbers of exposed workers were heavy equipment mechanics, painters, mechanics, and special trade contractors [30].

Preliminary data from another workplace study indicate that workplace exposure decreased from 1976 to 1984 [31]. Continued monitoring of data is necessary to understand and evaluate human exposures to selenium in both occupational and nonoccupational settings.

Table 3—Regulatory exposure limits for selenium

Chemical : SELENIUM (as a by-product of hydrogen selenide combustion)			
CAS Number :	7782-49-2		
	Value	Unit	Reference
OSHA PEL TLV-TWA	0.2	mg/m ³	[41]
NIOSH REL	0.2	mg/m ³	[8]
NIOSH IDLH	1.0	ppm	[8]
NOTES 1. OSHA limits are the legal exposure limits allowed by United States law and are enforceable. 2. <u>NIOSH limits are recommended values and are not enforceable by law.</u> 3. The exposure levels apply to other selenium compounds except selenium hexafluoride. 4. <u>In Asia, the SDS of the supplier shall be consulted to find the applicable regulatory exposure limits in the different Asian countries where determined.</u>			

Minimum risk levels (MRLs) are stated as follows:

- **Inhalation MRLs**—No MRLs were derived for inhalation exposure to selenium because of insufficient quantitative data concerning both human and animal exposures. Data on the health effects of inhaled selenium in humans are available from studies of occupationally exposed workers [32, 33, 34, 35, 36]. These studies suggest that the respiratory system is the most sensitive end point for inhaled selenium dust, but they do not provide quantitative measurements of exposure levels and are frequently confounded by concurrent exposures to other chemicals. Laboratory animal studies support the respiratory system as the main target of selenium inhalation toxicity but the available data are for acute exposures to high concentrations of selenium that also produced serious health effects, including death [38, 39]; and
- **Oral MRLs**—No MRLs were derived for acute or intermediate oral exposure to selenium because of insufficient information regarding adverse health effect levels in humans and experimental animals. For acute exposure, no quantitative data are available from studies of humans. Some acute oral animal studies identify lowest observed adverse effect levels (LOAELs) for organ weight changes, behavioral changes, and reduced body weight but these occur at doses similar to those producing serious LOAELs for paralysis and developmental effects in other mammalian studies.

NOTE—Hydrogen selenide exposure routes are by inhalation, skin, and/or eye contact. After burning hydrogen selenide, selenium oxide is generally absorbed by the skin.

Symptoms can be delayed up to several days and can include [17, 12]:

- irritation of the eyes, nose, throat, and/or mouth;
- coughing, sneezing, chest tightness;
- metallic taste;
- lassitude (weakness, exhaustion);
- dizziness;
- garlic odor of breath, perspiration, and/or urine;
- pulmonary edema;
- numbness, coldness, tingling of hands and feet;
- nausea;
- vomiting, abdominal cramping;
- diarrhea; and
- chills and tremors.

Dudley and Miller reported that 12.5% of the guinea pigs that had been exposed for 2 hours at 1.8 ppm (0.006 mg/l) died within 30 days of the exposure [37]. A 4 hour exposure at 1.8 ppm was lethal to 18.8% of the guinea pigs exposed, and a 4 hour exposure at 2.1 ppm was lethal to 25% of the animals exposed [17]. See Table 4.

Table 4—Lethal concentration data

Species	LC ₅₀ (ppm)	LC _{Lo} (ppm)	Time	Adjusted 0.5-hr LC	Derived value	Reference
Guinea pig	—	0.3	8 hr	0.75 ppm	0.08 ppm	[37]
Guinea pig	LC ₁₉ :1.8	—	4 hr	3.6 ppm	0.36 ppm	[37]
Guinea pig	LC ₂₅ :2.1	—	4 hr	4.2 ppm	0.42 ppm	[37]
Guinea pig	LC ₁₃ :1.8	—	2 hr	2.9 ppm	0.29 ppm	[37]
Rat	—	5.9	1 hr	7.4 ppm	0.74 ppm	[39]

Although very toxic, it is noted that no fatalities have been reported, possibly because hydrogen selenide is easily oxidized to red selenium on the surface of mucous membranes of the nose and throat [40]. Concentrations of 1.5 ppm have been found to be intolerable due to eye and nasal irritation [37].

NOTE—Combustion products resulting from the exposure of hydrogen selenide to a flame are toxic.

5.2.2 Medical treatment for hydrogen selenide exposure

There is no antidote for hydrogen selenide poisoning. Treatment is symptomatic and consists of measures to support respiratory, vascular, and renal function. Selenium can be measured in the blood, urine, and fingernails or toenails of exposed individuals [12]. The hemolytic edema affect to exposure can result in precipitation of free hemoglobin in kidney tubules with resultant acute tubular necrosis. Mannitol, alkaline diuresis, and hydration should be used to prevent hemoglobin precipitation and preserve renal function [7].

Victims exposed only to hydrogen selenide gas do not pose serious risks of secondary contamination to personnel outside the hot zone and do not need decontamination.

5.2.3 Leak or release of hydrogen selenide

In view of the toxic nature of hydrogen selenide, in the case of a leak, all personnel shall be immediately evacuated from the affected areas. Only trained emergency response personnel wearing appropriate PPE and equipped with SCBA shall enter the area [12].

In the event of the release of hydrogen selenide from a cylinder, personnel in the immediate area of the release will likely be at risk. As in the case of the release of any toxic gas, first responders shall station themselves upwind of the release point.

Because of the high toxicity of the material, any release of the product, whether accidental or intentional will likely require the filing of a report with governing agencies.

6 Gas handling equipment

The equipment used to handle hydrogen selenide shall be designed, constructed, and tested in accordance with the regulatory requirements of the country in which the equipment is operated. The equipment shall be designed to withstand the maximum pressure and temperature at which it is to be operated. A PHA shall be performed and documented on all hydrogen selenide systems. As hydrogen selenide is a highly toxic and flammable gas, consideration should be given to the following issues when designing systems to handle hydrogen selenide:

- materials of construction;
- compatibility of sealing compounds;
- system pressures and overpressure protection;
- pressure gauges;
- valve types and filter types;
- tubing;
- purification materials;
- system leak tests and purge;
- system temperature control;
- use of electrical control and use of electrically classified equipment;
- monitoring system;
- abatement system;
- system vents; and
- regulators.

6.1 Materials of construction

The selection of metals and non-metals shall be made taking into account the compatibility guide listed in [Table 5](#). It is important that all gas control equipment be compatible with the gas being passed through it. The use of

a device that is not compatible with the service gas can damage the unit and cause a leak that could result in property damage and/or personal injury. If a material is not listed and is required to be used in hydrogen selenide service and is thought to be compatible it should be first tested to confirm suitability prior to use under defined temperature, pressure, and flow conditions.

Table 5 contains a material compatibility guide that is prepared for use with dry hydrogen selenide at normal operating temperature of 21.1 °C (70 °F). Information may vary if different operating conditions exist.

Table 5—Material compatibility guide

Materials of construction																		
Metals									Non-metals									
Carbon steel	303 SS	304 SS	316 SS	Monel®	Aluminum	Brass	Hastelloy®	Copper	Nylon	Pyrex®	Quartz	Glass	Kel-F®	Teflon®	Buna-N	Kalrez®	Neoprene	Viton®
S	S	S	S	S	S	S	S	?	S	S	S	S	S	S	?	?	?	S
S=Satisfactory U=Unsatisfactory ?=Unknown or limited data																		

6.2 Compatibility of sealing compounds

Consideration should be given to the compatibility of lubricants, seals, greases, and sealing compounds, which come in contact with hydrogen selenide under normal or upset conditions. Refer to vendor supplied data as well.

6.3 System pressures and overpressure protection

System pressures are low due to the low vapor pressure of hydrogen selenide which is 0.950 MPa (138 psi) at 20 °C (68 °F) [2]. Design should address conditions where system pressure can be subjected to subatmospheric conditions and draw in air or other gas stream contamination that is used in the system. Due to the hazardous nature of hydrogen selenide, a conservative engineering and design approach shall be applied to the system design as applicable whether for pure hydrogen selenide or hydrogen selenide mixtures.

Gaseous mixtures of hydrogen selenide are routinely packaged at pressures at or below the rated cylinder working pressure. Gas panels typically use a gas regulator to reduce the cylinder pressure to the operating condition.

Care is needed to ensure that all components in the system are rated for these pressures.

Where system design pressures can be exceeded due to any component failure or operator error, overpressure protection shall be provided. Overpressure protection may involve safety relief devices and/or instrumented systems depending on local code requirements.

Piping system safety relief valve outlets shall link to a properly designed abatement system (see Section 11).

6.4 Pressure gauges

Pressure gauges are used to monitor the pressure within the hydrogen selenide system. Analog and digital pressure gauges may be used as necessary. However, the pressure gauge dead volume should be considered along with ease of inert gas purge. Gauges shall be placed so they are easily monitored by the operator. Since

hydrogen selenide is flammable, the use of digital pressure gauges (operated by electricity) should be at low voltage intrinsically safe (via low voltage or electrical barriers) to avoid ignition source potential.

6.5 Valve types and filter types

Metal diaphragm valves and bellows valves provide a better leak-tightness as compared to packed valves. The use of non-metal material for diaphragms or bellows is not recommended due to permeation potential of hydrogen selenide through the non-metal. Ball valves, butterfly valves, gate valves, needle valves, or packed valves are not recommended for use in hydrogen selenide service due to a higher leak potential either through or around the valve seat, seals, or the valve body.

Mesh filters made of stainless steel work well as do those made of polytetrafluoroethylene (PTFE). Sintered metal filters are also recommended.

The use of restrictive flow orifices (RFOs) has been a routine practice since the mid-1980s. For example, the restrictor has a small diameter of 0.152 mm (0.006 in), 0.254 mm (0.010 in), and 0.3 mm (0.012 in), and is of stainless steel materials of construction. While early designs had a filter element capable of capturing particles that were greater than two microns, these filters are not currently part of RFOs in service today. The RFO threads into the valve outlet. In the event of a shearing of a process line or a valve being accidentally opened, the RFO significantly reduces the amount of gas that would be released and that would need to be environmentally treated. Some jurisdictions and insurance companies require the use of RFOs.

Also during the 1980s, air actuated valves began to be used. They allowed for remote opening and closing of the cylinder valve, and afforded an extra measure of safety both at filling as well as at the point of use.

6.6 Tubing

Some national bodies or insurance companies require the use of coaxial tubing when the tubing is outside of an exhausted enclosure. Welded or metal face seal connections are the preferred connection methods due to their leak integrity.

6.7 Purification materials

Hydrogen selenide is offered at high purity by the supplier. Typical purity offered is 99.99+%. Purification materials can be as basic as molecular sieves to remove water and other impurities and more sophisticated materials may be used to also remove moisture and specific impurities such as sulfur, germanium, etc.

System purge shall be done prior to the use or removal of the purifier.

6.8 System leak tests and purge

After system installation or maintenance, the piping systems shall be leak checked and purged prior to commissioning.

Connections that are routinely remade in the process (for example, cylinder pigtail connections) should be leak checked at a pressure higher than maximum usage pressure prior to system purging.

The best purge systems are those that are automated. The number of purge cycles is a function of the inert purge gas pressure available, the use of vacuum, the size of the tubing/piping system to be purged, and the desired final dilution value. Common purge gases are nitrogen and helium. Hydrogen is also used as a purge gas. Typical gas delivery systems shall be purged to a safe level of hydrogen selenide. The use of manual purge control has a higher potential for operator error and requires clear operator instructions if utilized.

6.9 System temperature control

Systems operate at varying temperatures depending on how the hydrogen selenide is being used. Designs should address conditions where system temperature can vary from room temperature. When working with compressed liquids, refer to the vapor pressure versus temperature relationship as shown in Figures 1 and 2.

Some systems can require external heating of the cylinder to maintain flow. In such cases, an engineering review shall be completed to ensure the temperature never exceeds 50 °C (122 °F) and to ensure the cylinder never becomes liquid full.

Some systems can also require heating to maintain constant temperature and/or prevent condensation of hydrogen selenide during use. The preferable method is use of a temperature-controlled environment. Direct heating using of electrical resistance heater on a cylinder has caused accidents and is the least preferred method. Because hydrogen selenide is a flammable gas, electrical resistance heaters, if used, should be classified for use in a flammable environment.

NOTE—Hydrogen selenide starts to decompose at the temperature of 160 °C (320 °F) [3].

6.10 Use of electrical control and use of electrically classified equipment

Since hydrogen selenide is flammable, electrical systems shall meet the requirements of the local regulations covering flammable classifications.

These classifications are for generic volatile flammable liquids or flammable gases that if mixed with air can burn or explode. In such cases, the liquids, vapors, or gases will normally be confined within closed containers or closed systems from which they can escape only in case of accidental rupture or breakdown. It should be noted that ignitable concentrations of gases or vapors of flammable gas, flammable liquid—produced vapor, or combustible liquid—produced vapor mixed with air are normally prevented by having forced mechanical ventilation, which is under negative pressure. This could become hazardous through the failure or abnormal operation of the ventilating equipment.

6.11 Monitoring system

6.11.1 Gas monitoring

Hydrogen selenide is a highly toxic, colorless, and flammable gas with an odor threshold of 0.1 ppm and a disagreeable odor. Very low exposure levels of hydrogen selenide may not produce immediate symptoms. In addition, hydrogen selenide will quickly bring on olfactory fatigue and persons exposed to hazardous levels may be unaware of its presence. A monitoring system shall be used to monitor primary locations such as:

- storage;
- operator areas;
- gas cabinets;
- fume hoods;
- process rooms; and
- abatement system exhaust.

The gas monitoring system shall have a backup source of power.

Life safety control is discussed in greater detail in 7.1.

Detection methods vary as do their sensitivity to hydrogen selenide. It is desirable to have a system capable of networking existing systems from various manufacturers and the ability to accommodate ongoing expansion. Typical detector types suitable for hydrogen selenide include:

- photo-absorption;

- photo-ionization;
- electrochemical;
- colorimetric tape;
- thermal conductivity; and
- catalytic bead.

A gas detection system with a sensing interval not exceeding 5 minutes is recommended and may be required in certain jurisdictions.

6.11.2 Flame and smoke monitoring

Under normal circumstances, most flammable gases should be monitored for concentrations within the flammable range or for detection of flame or smoke. However, the greater hazard with hydrogen selenide is its high toxicity. The toxic concentrations of hydrogen selenide are well below the flammable range and therefore it is recommended that monitoring be done for ppm level exposures.

Hydride fires have occurred without the gas monitoring system detecting a leak due to fire consuming all the hydride. Hydrogen selenide, as a member of the hydride family, is expected to act similarly.

6.12 Abatement system

Refer to Section 11.

6.13 System vents

All vents in the system shall be directed to an abatement system. These include system pressure relief devices (PRDs), vacuum pump exhaust, system vents, and vacuum venturi exhaust.

6.14 Regulators

Refer to 10.2.

7 Process and operation

7.1 Life safety control (gas detection and alarm systems)

Procedures shall be in place to control worker exposure to hydrogen selenide and its by-products. Compliance with these procedures will prevent adverse effects of exposure in the workplace through air exposure or through skin exposure. Specific compliance activity can be prescribed by national regulations. The following items should be considered part of a life safety control program.

7.1.1 Monitoring

- Environmental workplace air/land monitoring—Occupational exposure shall be controlled so that no worker is exposed to concentrations greater than allowed either as gas or solid inorganic compound;
- Monitor calibration/inspection—Routine inspection of monitoring equipment to verify performance and reliability;
- Monitor operation/performance of abatement systems—Routine inspection of abatement equipment to verify performance and reliability; and
- Leak detection devices should be installed to trigger emergency response actions in compliance with national regulations.

7.1.2 Life safety system

- Periodic review of heating, ventilation, and air conditioning (HVAC) air balance through building, fume hoods, gas cabinets, and abatement systems—With time, air flows/exhausts can change and required cap-

ture velocities can be under required levels. Ventilation dampers should be locked in place to prevent the altering of required ventilation between air balances;

- Alarm testing and inspection—Routine testing and inspection of alarm systems to verify performance and reliability;
- Since hydrogen selenide is a flammable gas, firefighting systems shall be considered and should follow national regulations;
- Gas scrubbing or ventilation systems should be installed to handle gas leaks. National regulations may require gas scrubbing or ventilation to handle gas leaks; and
- Gas storage areas should be designed with more than one exit.

7.1.3 Management

- Work clothing management—Daily change outs, a place for contaminated clothing, separate locker room from manufacturing environment;
- Training and recertification in use of PPE. Workers required to wear respiratory protection shall be medically evaluated to confirm worker clearance and fit tested for use;
- Training and emergency response—Training should be conducted on the emergency response to situations that involve the possible release or exposure to hydrogen selenide and its by-products;
- General awareness training—Personnel involved in the manufacturing, processing, maintenance, handling, storage, and/or transportation of hydrogen selenide and its by-products shall be trained on the exposure effects (signs, symptoms, medical treatment) using SDS and other safety information related to the environment and to personnel. Additional training may be required by local jurisdictions, which could include personnel safety, preventive maintenance, and environmental management programs;
- Record keeping programs—A program should be documented explaining what to record, when to record, how often to record, place of record storage, and length of time for records to be stored before disposal;
- Periodic medical surveillance that meets local government requirements shall be made available for all workers. Work history and medical history shall be documented. Some governments can require annual chest X-ray, careful examination of skin for the presence of chronic skin lesions, and/or blood work review;
- Labeling of products/containers—With complete name and applicable hazards as required by regulations;
- Clear, documented work practices/procedures: Control of equipment, process clean-up, waste disposal, and operations control; and
- Emergency action plan—Response and evacuation protocols for site alarms, releases, and abatement of loss of contaminant.

7.2 Operational procedures and personnel

Written operating procedures are required to ensure safe handling and processing of hydrogen selenide. These operating procedures should describe in sufficient detail the information needed on how to perform a specific task. These operating procedures shall exist in any viewable, readily available format and written in clear and simple language. Instructions shall be under version control and the latest versions of the work instructions should be readily available to the operator should questions arise.

Operators shall be consulted and trained when procedures are changed. All operations involving hydrogen selenide shall be covered by clear language written operating procedures. A risk assessment should be carried out on all operations involving hydrogen selenide.

Components and materials that may be used on hydrogen selenide systems shall be clearly identified, carefully stored, and handled to ensure that they do not become contaminated. It is recommended that cylinder valve outlet connection gaskets are only handled while wearing approved gloves. This will avoid the risk of:

- contamination of the gasket by the natural oils found on the skin; and
- contamination of the operator from residual hydrogen selenide by-products found on the used gasket.

All personnel involved in handling of hydrogen selenide and the operations of hydrogen selenide systems shall be trained. This training shall include the importance of cleanliness and the need for exclusive use of specified materials and components on hydrogen selenide systems.

Personnel who operate gas systems shall have a good understanding of the properties, fire and explosion hazards, and toxicity of hydrogen selenide. They should also be trained to take prescribed action in the event of an emergency. Wherever possible, preventative measures such as gas cabinets, fume hoods, PPE, remote controlled valves, and barrier walls shall be considered to protect operators.

7.3 Ventilation

Ventilation is required for storage areas, gas cabinets, fume hoods, and areas where hydrogen selenide is processed, stored, or handled. Regulations may vary by country and should be verified, but common guidelines are as follows.

7.3.1 Necessity of ventilation for hydrogen selenide

- Do not vent hydrogen selenide to the atmosphere except through a properly designed abatement system; and
- Mechanical ventilation shall be used to exchange air where hydrogen selenide is processed or handled to quickly exhaust any fugitive hydrogen selenide emissions.

7.3.2 Type of ventilation

- Indoor storage and use areas and storage buildings for compressed gases and cryogenic fluids shall be provided with mechanical exhaust ventilation or natural ventilation, where natural ventilation can be shown to be acceptable for the material as stored. In certain jurisdictions, the use of natural ventilation shall be approved by governmental and/or local authorities;
- For indoor storage, forced ventilation is required and should follow national regulations;
- Gas rooms shall be provided with an exhaust ventilation system; and
- Where outdoor storage is allowed, forced ventilation is generally not required.

7.3.3 Consideration for ventilation design

- The gas cabinet or exhausted enclosure shall be provided with an exhaust ventilation system designed to operate at a negative pressure relative to the surrounding areas;
- The velocity at the face of access ports or windows, with the access port or window open, shall be adequate to protect the user from fugitive emissions. In the United Kingdom, a minimum velocity of 1 m/s across the face of the small valve manipulation opening is recommended for normal operating conditions
- The number of air exchanges per hour (inside the gas cabinet or exhausted enclosure) may be regulated by local authorities;

- Mechanical ventilation rate shall be adequate. In the United States, the rate of not less than 0.3 m³/min/m² (1 ft³/min/ft²) of floor area over the area of storage or use is required;
- The exhaust system shall take into account the density of the potential gases released and leak points:
- For gases that are heavier than air, like hydrogen selenide, exhaust should be taken near the floor. Typically within 0.3 m (1 ft), but varies by local authority
- For some hydrogen selenide mixtures (helium, hydrogen) that are lighter than air, the exhaust should be taken near the ceiling. Typically, within 0.3 m (1 ft), but varies by local authority
- The location of both the exhaust and inlet air openings shall be designed to provide air movement across all portions of the floor or room to prevent the accumulation of vapors;
- Exhaust ventilation shall not be recirculated within the room or building
- Ventilation systems shall discharge at the required distance from intakes of air handling systems, air conditioning equipment, and air compressors;
- Storage and use of compressed gases should be located at an adequate distance from air intakes;
- In the United States where powered ventilation is provided, a manual shutoff switch should be provided outside of the room in a position adjacent to the principal access door to the room or in an approved location. The switch shall be the break-glass or equivalent type and shall be labeled as follows: VENTILATION SYSTEM EMERGENCY SHUTOFF;
- Where mechanical ventilation is provided, the system shall be operational as a minimum during the time the building or space is occupied; and
- There shall be an alarm system that will activate in the event of the loss of ventilation.

7.4 Ongoing maintenance and preventive maintenance programs

It is essential that hydrogen selenide handling equipment be maintained.

Attention should be provided to any replacement parts for compatibility with hydrogen selenide and other system products.

Preventive maintenance (PM) is directed at eliminating potential causes of equipment failure before they occur. The manufacturer's equipment manual provides guidelines for PM management of their equipment. It is the responsibility of each user to ensure control exists. Users of hydrogen selenide should have a strong PM program installed and implemented at all sites that process or handle hydrogen selenide.

8 Gas cylinder filling/packaging

8.1 Filling facility consideration

Good practices for filling facilities should follow those as described under Section 9.

8.2 Containers

8.2.1 Cylinders

Hydrogen selenide is routinely packaged in seamless steel cylinders or aluminum alloy cylinders with a minimum test pressure set by a regulatory body. Low pressure welded cylinders may be accepted for this service, with a special approval that has been granted by a regulatory body.

The quantity of hydrogen selenide and its mixtures allowed on-site can be limited by local government regulations. Verify your limits before bringing in cylinders from vendors in other jurisdictions.

Generally, cylinders that are used in high purity electronic hydrogen selenide service have special internal pre-treatment to maintain gas purity. This treatment is provided by the gas supplier.

Containers shall be certified and shall be retested regularly in compliance with national standards. Container retest shall follow national standards or the container manufacturer's country laws and regulations, whichever is more stringent. Containers failing to meet these standards shall be removed from service. If they can be repaired to meet the standards, they may be put back to use; otherwise they shall be scrapped. In some countries, hydrogen selenide cylinders cannot be used in other services.

Prior to fill, ensure that a container has not been damaged. Prefill inspection of containers and correct verification of their pressure rating prior to filling is very important.

8.2.2 Valves and pressure relief devices

It is recommended that diaphragm seal valves be used for hydrogen selenide in that it provides a level of leak tightness that is not normally achievable with a packed valve. The diaphragm valve can be either a diaphragm packless or a tied diaphragm valve. Some jurisdictions such as the United States and Europe mandate the use of the diaphragm valve.

There are different types of valve outlets that are used for hydrogen selenide in Asia, North America, and Europe. It is important that the ancillary equipment used to connect to the cylinder valve be of the same thread configuration as the cylinder valve outlet to ensure a leak-tight connection. Most countries require a gas-tight valve outlet cap on the cylinder valve. The use of adapters to connect cylinder valves to ancillary equipment is not recommended.

There are a variety of different cylinder valve inlets that are in use today for hydrogen selenide as well as all gases. There are also a variety of cylinder neck threads that are used worldwide. The threads on the valve inlet shall match the threads on the container neck. It is very dangerous to match cylinders and valves that have been manufactured to different national standards since the possibility exists that the valve, under pressure, could be ejected from the cylinder.

The use of PRDs for cylinder valves with hydrogen selenide is required for cylinders filled in Japan and Korea. However, in the United States and Europe PRDs are prohibited because of the toxicity of hydrogen selenide. In other countries, PRDs are neither required nor prohibited.

8.2.3 Fill density

Containers shall be filled with hydrogen selenide and mixtures in accordance with authorities having jurisdiction.

The United Nations *P200 Packaging Instruction* currently permits a maximum fill density of 1.60 kg/L for hydrogen selenide packaged in cylinders with a minimum test pressure of 3.1 MPa (31 bar) [4].

8.3 Filling equipment

Many countries regulate the disposal of selenium contaminated wastes. Any equipment in contact with hydrogen selenide should be treated as a hazardous waste when the time comes for disposal. Clean-up procedures and employee protection guidelines should be documented and understood.

8.3.1 Manifolds

Manifold components in contact with hydrogen selenide filling shall be designed with compatible materials listed in this publication. When not under hydrogen selenide pressure, manifolds should be backfilled with an inert gas such as helium, nitrogen, argon, and plugged to ensure that any contaminants are excluded from the manifold system. Filling manifolds should be located in well ventilated areas. To reduce the potential quantities of gas released in an accident and reduce waste, small diameter tubing and lengths are preferred. Small diam-

eter tubing is subject to the unavoidable deposit of selenium. These deposits can result in blockage and this possibility should be considered in design and operation of the manifold. The filling manifold should be made using welded fitting and metal face seal fitting. The use of threaded fitting should be avoided.

Refer to 6.8 for system leak tests and purge practices.

8.3.2 Compressors

Since hydrogen selenide is a liquefied gas with a very low vapor pressure, compressors are not normally used for pure gas. Use of compressors risk condensing the compressed gas unexpectedly.

8.3.3 Vacuum pumps

Vacuum pumps in contact with hydrogen selenide are typically either dry pumps or oil sealed pumps. However, oil sealed pumps risk oil contamination by hydrogen selenide and waste management and PPE are required.

Dry pumps are recommended to eliminate the risk of oil contamination. Oil sealed (wet) pumps have the potential for oil backstreaming if backstreaming barriers are not maintained. If backstreaming occurs, hydrogen selenide (and system manifold) contamination will occur and downtime/clean up can be lengthy. Personnel shall exercise care when performing vacuum pump maintenance, especially for oil sealed (wet) pumps where the oil could have absorbed hydrogen selenide. Vacuum pump oil contaminated with hydrogen selenide can off gas hydrogen selenide fumes when exposed to air. Perform all work in a well ventilated area.

9 Storage and handling

The following are good practices for storage and use of hydrogen selenide.

9.1 General guidelines

- All facilities shall have an emergency response plan, which should include the plan for gas releases and emergency evacuation (more information is available in AIGA 004/13, *Handling gas container emergencies*, AIGA 83/13, *Disposal of Gases*, AIGA 018/15, *Safe handling of electronic specialty gases*, and CGA P-1, *Standard for Safe Handling of Compressed Gases in Containers* [42, 43, 44, 45]);
- A SDS shall be available for reference;
- Good housekeeping is essential (for example, keeping combustible material away from container storage or use areas);
- Check for insects or foreign material before removing the valve protection cap;
- Hydrogen selenide cylinder valve outlet caps shall be installed except when being filled or in use;
- Always secure (nested, palletized, or chained) the containers whether during transportation, storage or use;
- Never strike an arc (with welding electrode) on the container;
- Never allow containers to contact electrical circuits;
- Never expose containers to corrosive chemicals or vapors (for example, bleach or seawater); and
- Container valves shall be securely closed, outlet seals tightly installed, and valve protection caps in-place during all storage and handling operation.

9.2 Storage

9.2.1 Segregation

- Full and empty containers should be segregated. Containers with residual gas should be treated as if they were full;
- Group containers according to the gas hazard they pose; and
- Hydrogen selenide shall be stored in well ventilated areas, away from incompatible gases (oxidizers, pyrophoric gases, etc.), open flames, sparks, and sources of heat. Incompatible groups shall be separated by required distances or by fire partition. If the local jurisdiction does not specify the distance, separation of at least 6 meters is recommended.

9.2.2 Storage condition

- Practice First-In-First-Out (FIFO) cylinder management;
- Containers should be stored under dry conditions;
- Containers should be stored on level ground to minimize toppling;
- Store containers to prevent the temperature of the containers from exceeding the national guideline;
- The quantity of hydrogen selenide stored should not exceed the design of the facility and should comply with national regulations;
- Cylinders when stored vertically shall be secured (nested, palletized, or chained) to prevent accidental tip over. Standard compressed gas cylinders are designed to be stored vertically. In these cases, precaution shall be taken to ensure that they are secured from falling;
- Other small cylinders such as lecture bottles are more conveniently stored horizontally. However, some local regulations may require vertical storage for toxic liquefied gases, especially when equipped with PRDs; and
- An energy relief wall or blast roof should be incorporated into the room design if flammable gases are stored in large quantities indoors. This wall or roof is designed to allow dissipation of pressure resulting from an explosion.

9.3 Handling

9.3.1 Essentials

- Personnel handling hydrogen selenide cylinders should receive training;
- Use materials of construction compatible for handling hydrogen selenide. This information can be obtained from the SDS and this publication;
- Always wear PPE when handling gas containers. Steel-capped safety shoes, safety glasses with side shields, and leather gloves are recommended;
- All piping, cabinet, and equipment used to handle hydrogen selenide shall have electrical continuity sources and shall be earthed/grounded.

9.3.2 Precautions

- Remove valve outlet cap or connections slowly and look for signs of leakage before removing completely;

- Always stand at the side of the valve outlet cap or connection when removing the cap or breaking a connection;
- Always open valves slowly and carefully;
- Containers with residual gas should be treated as if they were full; and
- Filling and use of hydrogen selenide shall be done in exhausted enclosures or rooms with the discharge treated to below acceptable levels before emission into the atmosphere.

9.3.3 Checking

9.3.3.1 Container

- Check cleanliness of the valve outlet and pigtails;
- Leak check containers and connection before use; and
- Prior to entry, enclosed spaces containing highly toxic gas including shipping containers should be checked for leaks of the toxic gas in the absence of a maintained stationary detection system.

9.3.3.2 Piping

Always purge piping systems with inert gas:

- before introduction of hydrogen selenide; and
- before disconnection of hydrogen selenide cylinders.

9.3.4 Prohibition and restriction

- Do not use adaptors to connect containers;
- Do not overtighten valves. Follow manufacturer's recommendations;
- Never drag or slide the containers;
- Never lift the container by the valve protection cap;
- Use cylinder trolleys or moving devices to minimize rolling of cylinders
- Never use cylinders as a roller to move equipment;
- The use of portable electronic devices (for example, cellular phones and walkie-talkies) is prohibited unless the devices have been proven to be intrinsically safe;
- Prohibit sources of ignition (for example, cigarette smoking);
- Electrical equipment in the vicinity of hydrogen selenide should be intrinsically safe following zoning guidelines in national regulations. If national regulations are not available, consult International Electro-technical Commission (IEC) or NFPA 70, *National Electrical Code*® (NEC) [46, 15];
- Non-sparking tools are recommended to be used when working around hydrogen selenide and are required by some jurisdictions.

9.4 Security

Hydrogen selenide can be used as a weapon of mass destruction (WMD). Security measures should be implemented to prevent access to hydrogen selenide cylinders by unauthorized personnel. For more details, refer

to AIGA 003/14 *Security Guidelines*, EIGA 907/05 *Security Guidelines*, or CGA P-50, *Site Security Standard* [47, 48, 49].

A sale policy for hydrogen selenide shall be in place. It shall be verified by a thorough review prior to the purchase being approved and the delivery being made that the customer has a valid reason to purchase hydrogen selenide and that the tracking records during shipment of hydrogen selenide shall be issued and kept.

10 Gas supply to point of use

Gas supply systems shall be located in a well ventilated area. Gas cabinets or ventilated enclosures shall be used for hydrogen selenide supply systems. Provision shall be made to deal with emergencies, such as leaks in the supply system.

10.1 Process line control

A purge gas shall be used to purge the hydrogen selenide system during commissioning of the system or prior to maintenance. The purge gas is also used to purge the pigtail prior to and after cylinder change. Precautions shall be taken to ensure that the purge gas supply does not become contaminated with hydrogen selenide. A dedicated purge gas source shared with other compatible gases such as a compressed gas cylinder, shall be used. This will avoid the risk of backfeeding via the purge gas system into another incompatible process gas supply system.

Precautions should be taken to ensure that hydrogen selenide does not inadvertently come into contact with any oxidizing gas or a source of ignition.

10.2 Regulators

Regulators are used in hydrogen selenide delivery systems to reduce and control the pressure from a high pressure source to a safe working pressure for use. All internal regulator parts should be compatible with hydrogen selenide under normal operating conditions.

A regulator for semiconductor applications is functionally the same but has different features than those of a regulator designed for general duty use. Regulators designed for controlling hydrogen selenide in semiconductor processes are typically constructed of 316 or 316L stainless steel (SS) and at times are electropolished. Regulators with stainless steel diaphragms should be used to avoid the potential of hydrogen selenide diffusion through porous elastomeric diaphragms and the potential diffusion of contaminants that are adsorbed on elastomeric diaphragms. Once a regulator has been used in hydrogen selenide service, it should not be used for other gas service.

11 Gas abatement systems

Since hydrogen selenide is a highly toxic material, a gas abatement system shall be used to control any emission whether anticipated or not.

The best method of abatement depends on whether the hydrogen selenide is being handled as a pure product, diluted in a mixture, or mixed with other by-products. Full product recovery tends to be practiced at manufacturing facilities. After use in a process, contamination and other issues utilizing chemical abatement may offer better solutions. Such an abatement system could be capable of dealing with other contaminants in the system. Disposal of hydrogen selenide by any means shall be done in an environmentally acceptable manner in compliance with all applicable regulations. For more information on disposal of gases, see AIGA Doc 83 [43].

A competent person knowledgeable in the handling and processing hydrogen selenide should design the equipment.

11.1 Basic principles of abatement [42, 43, 44, 45]

The following are the typical chemical reactions and physical adsorptions:

- Reclamation or recovery via cryogenic recovery

- Oxidation via incineration
$$2\text{H}_2\text{Se} + 3\text{O}_2 \rightarrow 2\text{SeO}_2 + 2\text{H}_2\text{O}$$
- Oxidation via wet scrubber
$$\text{H}_2\text{Se} + \text{OH}^- \rightarrow \text{HSe}^- + \text{H}_2\text{O}$$
- Absorption/adsorption and reaction on a treated solid (with metallic oxides)
$$2\text{CuSO}_4 + 2\text{H}_2\text{Se} \rightarrow \text{Cu}_2\text{Se}_2 + 2\text{H}_2\text{SO}_4$$
$$2\text{FeCl}_3 + 3\text{H}_2\text{Se} \rightarrow \text{Fe}_2\text{Se}_3 + 6\text{HCl}$$
$$\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{Se} \rightarrow \text{Fe}_2\text{Se}_3 + 3\text{H}_2\text{O}$$
- Physical adsorption on solid media
$$\text{H}_2\text{Se} + \text{C} \rightarrow \text{C}[\text{H}_2\text{Se}] \text{ (C : Activated Carbon)}$$

11.1.1 Reclamation or recovery

Reclamation of hydrogen selenide is not a disposal method, as usually understood. This technique is for reclaiming residual gas and returning the hydrogen selenide safely to suitable containers. Once reclaimed, hydrogen selenide has to be reprocessed, purified, and analyzed before being reused.

All types of reclamation are strongly recommended both in the interest of the environment and the conservation of materials and energy.

The supplier of the material who will have the necessary product handling and container filling expertise is best suited for reclamation of gaseous hydrogen selenide. Hydrogen selenide should not be reclaimed to a container and returned without the written authority of the owner of the container.

Some users collect the hydrogen selenide into the cylinders for treatment offsite.

11.1.2 Oxidation via incineration

While burning the hydrogen selenide molecule can be done satisfactorily, capturing the toxic solid by-product requires extensive equipment. Cleanup procedures and employee protection from the selenium oxide dust are critical.

For complete reaction, hydrogen selenide shall be introduced directly into the burning flame.

11.1.3 Oxidation via wet scrubber

The typical wet scrubber used for hydrogen selenide is a counter current packed tower.

Suitable arrangements should be made to ensure the system is monitored and shut down in the event of waste gas breakthrough. Factors to be taken into account when utilizing a wet scrubber include:

- Hydrogen selenide input flow rate;
- pH control of the absorbent liquor;
- Temperature of the absorbent liquor;
- Provisions should be made to monitor both the inlet and outlet stream for hydrogen selenide concentration;
- Flow control should be installed in the waste hydrogen selenide stream to enable the gas flow to be matched to the capacity of the scrubber;

- Pressure control should be installed in the waste hydrogen selenide stream to enable the gas flow to be matched to the operating capacity of the scrubber;
- Use of inert purge as necessary to facilitate process line clean-up; and
- Consideration of a discharge point from the scrubber exhaust, well away from air intake systems, downdrafts, and personnel areas.

To prevent the risk of absorbent liquor sucking back into the system, controls should be in place. Consideration should be given to the use of non-sparking equipment as hydrogen selenide is flammable. To ensure safe and efficient performance, monitoring of process conditions as well as the scrubber gas discharge effectiveness should be carefully considered.

Oxidizing solutions may consist of liquid solutions of potassium permanganate or sodium hypochlorite and work well for low concentrations of hydrogen selenide.

11.1.4 Absorption/adsorption and reaction on a treated solid (with metallic oxides)

Hydrogen selenide is fed directly into a vessel containing a bed of solid adsorbent. There are many solid adsorbents available that strongly and readily absorb/adsorb and react with hydrogen selenide. Simplicity and portability of a small solid-state absorber may favor the choice of this method under certain emergency conditions. In this publication, the terms absorption and adsorption are used interchangeably.

Factors to be taken into account when utilizing the solid-state absorber include:

- Required hydrogen selenide disposal rate;
- Quantity of hydrogen selenide to be disposed;
- Acceptable frequency of changing the absorbent bed or system;
- Concentration of the hydrogen selenide stream delivered into the absorber bed;
- Temperature rise effects from reaction between the hydrogen selenide and the absorbent;
- Distribution system within the absorber bed to prevent channeling and premature breakthrough of unreacted hydrogen selenide;
- Absorbent particle size: Generally small particles give a high contact area, which corresponds to greater efficiency. However, small particle sizes can lead to plug gage or high pressure drops and a tendency of channeling and premature breakthrough of unreacted hydrogen selenide;
- Provisions should be made to monitor both the inlet and outlet stream for hydrogen selenide concentration;
- Flow control should be installed in the waste hydrogen selenide stream to enable the gas flow to be matched to the capacity of the absorber bed;
- Pressure control should be installed in the waste hydrogen selenide stream to enable the gas flow to be matched to the operating capacity of the absorber bed;
- Use of inert purge as necessary to facilitate process line clean-up; and
- Consideration of discharge point from the absorber bed exhaust, well away from air intake systems and personnel areas.

11.1.5 Physical adsorption on solid media

Hydrogen selenide is fed directly into a vessel containing a bed of solid media. There are many types of solid media available that adsorb hydrogen selenide. Adsorption capacity varies with solid type. Offgassing of hydrogen selenide from solid media can occur so it is important to have controls and hydrogen selenide monitoring in place. Heat is generated during hydrogen selenide adsorption as a function of adsorption rate and hydrogen selenide concentration. Temperature profiles through the bed containing solid media that are flammable shall be monitored to prevent the solid media from igniting.

Simplicity and portability of a small solid-state adsorber may favor the choice of this method under certain emergency conditions. Factors to be taken into account when adsorption on carbon are similar as those identified in 11.1.4.

11.2 User requirements

All personnel involved with the handling of hydrogen selenide shall be trained in the procedures for abatement control used at the site. A thorough knowledge of the product and its associated hazards is required. This would include, but is not limited to:

- physical characteristics and toxicological properties of hydrogen selenide;
- physical properties of abatement material; and
- operating documents.

11.3 Waste stream disposal

Dispose in accordance with all applicable regulations. Waste streams can contain selenium and be considered a toxic, hazardous waste. Management and control of waste is required. Refer to local and national regulations as they apply to waste management.

12 Emergency response

12.1 Preparation

The purpose of preparation is to establish a system and assign responsibility in the event of an accident or other emergency situation.

The hydrogen selenide user shall have procedures in place to address emergency situations that affect public health and environmental concern in the event of an accident. The emergency plan identifies potential emergencies that are reasonably foreseeable, and specifies actions to prevent, prepare for, respond to, and recover from these emergencies. The emergency plan includes methods used to prevent and mitigate environmental impacts, which could be associated with emergency situations.

The emergency plan shall be reviewed and updated periodically as applicable. Updated copies are provided to the local emergency planning committees and government officials as applicable. Training is provided for all personnel who could be involved with emergency response.

The emergency plan is tested periodically to ensure its effectiveness, including tests of related leak detection equipment, PPE, protective systems, and emergency communications. The emergency contact list is reviewed and updated with each change as applicable. Latest versions shall be maintained.

Hydrogen selenide incidents vary considerably and the emergency plan shall consider the chemicals and quantities involved, types of hazard, response efforts required, number of responders needed, and effects produced. Incidents can require immediate control measures (emergency) or long term activities (remedial action) to restore acceptable conditions. The plan activities are divided into interacting elements:

- recognition;
- evaluation;
- control;
- information; and
- safety.

12.1.1 Recognition

Recognizing the type and degree of the hazard presented by hydrogen selenide is usually one of the first steps in responding to an incident.

12.1.2 Evaluation

The responder will predict the behavior and anticipated problems associated with the material. Anticipated problems that could extend beyond the company property will require support/involvement from local officials. SDS or other product information will be used to help evaluate the nature and affect to the environment and public health.

12.1.3 Control

Control refers to those methods that prevent or reduce the impact of an incident. Control is addressed by remedial action in the form of documented procedures (plans). It is the responsibility of each facility and its personnel to ensure procedures are in place and followed.

12.1.4 Information

An integral component of response is information. Notification of employees, local emergency response officials, corporate compliance, corporate safety, and government agencies is completed per established procedures. All accidents are documented and reviewed by a safety committee and/or emergency response team to determine the root cause and to implement the corrective actions of the accident, the effectiveness of the response, corrective action warranted, and notification to prevent a repeat occurrence. Reference documents may include:

- SDS;
- Emergency plan;
- Standard operating procedures (SOP);
- PHA reviews; and
- Technical gas data books.

12.1.5 Safety

All hazardous material responses pose varying dangers (health and safety) to responders, the environment, and the neighborhood. Safety considerations are an input to every activity that is undertaken and are an outcome of each response taken. It is the responsibility of all employees to work in a safe manner and follow established safety rules and regulations.

12.2 Response

Always ensure that personnel responding to an emergency situation are trained and PPE is worn. Only those employees trained in responding to an incident shall do so and only to the level of their training. The company's emergency plan shall identify the procedures and policies that will be followed in an emergency response [42, 43, 44, 45].

Off-site response requires interaction with other company's emergency plan. It could occur during transportation or at the customer site. Whether on site or offsite, detailed information on how to handle such issues can be found in AIGA 004, EIGA Doc 80, *Handling Gas Container Emergencies* and the *Emergency Response Guidebook (ERG)* [42, 50, 11]. Also refer to EIGA Doc 30 *Disposal of Gases* [44].

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