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# Hazardous Materials in Petroleum Processing

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### Abstract

Although the fire hazard is always a primary concern in the refining of petroleum, there are other hazards present that need to be addressed. Among these are the handling of some of the chemicals that are used or generated in the refining processes. This chapter provides general information on the hazards and handling of several chemicals. The information is not intended to substitute for regulatory, local, or company standards or medical expertise. Included here, are discussions of: amines, ammonia, benzene, carbon monoxide, catalysts and sorbents, caustic soda, furfural, hydrofluoric acid, hydrogen, hydrogen sulfide, methyl ethyl ketone, nickel carbonyl, nitrogen, sulfiding chemicals, and sulfuric acid.

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### Keywords

Refinery • Hazardous materials • Materials handling • Safety • Toxicity • Exposure limits

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## Introduction to Handling Hazardous Materials

*Disclaimer:* Please note that the discussions presented in this chapter are for informational purposes only. They are not meant to be specifications and are not all-encompassing. We defer to industrial hygiene, medical, and other experts and to your company to evaluate and determine the appropriate, current methods for handling these hazardous materials and for emergency responses and procedures relevant to each chemical. Many resources (e.g., MSDSs, chemical suppliers, licensors) are available to assist in these efforts.

From the very nature of crude oil, its refining and processing can create potentially hazardous situations. The most commonly recognized hazard we expect is, of course, the danger of fire. Considerable effort is made to prevent fires and, if a fire does occur, to combat and restrain it in the most effective manner. Fire prevention and firefighting are discussed in detail in the chapter “[Fire Prevention and Firefighting in Petroleum Processing](#)” of this handbook.

Although the fire hazard is always a primary concern in the refining of petroleum, there are other hazards that are present and always need to be addressed. Among these are the handling of toxic and dangerous chemicals that are used in the refining processes. For many of the chemicals used in refining, there is also a danger to life or health from exposure to toxic materials that are produced in some of the refining processes. Perhaps the most notable is hydrogen sulfide, which is common to all modern refineries.

This chapter deals with the nature and handling of some of the common hazardous materials used or produced in refining. The specific materials addressed are:

- Amines
- Ammonia
- Benzene
- Carbon monoxide
- Catalysts and sorbents
- Caustic soda (AKA sodium hydroxide, NaOH)
- Furfural
- Hydrofluoric acid (HF, AHF)
- Hydrogen
- Hydrogen sulfide
- Methyl ethyl ketone
- Nickel carbonyl
- Nitrogen
- Sulfiding chemicals
- Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>)

Some of these materials are discussed in other chapters, but we have tried to pull the relevant materials all together here.

In all cases, it is strongly recommended that you consult the material safety data sheet (MSDS) for each material for the most up-to-date information about its hazards and handling.

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## **Amines for Gas Treating**

### **Discussion and Hazards of Amines**

Amine solvents are used in petroleum and natural gas refining to remove hydrogen sulfide and carbon dioxide from the various streams. In petroleum refining, the monoethanolamine (MEA) compound of the homologue used to be common in the treating processes. Diethanolamine (DEA) and methyl diethanolamine (MDEA) have become much more common. Proprietary compounds of amine such as Sulfinol and ADIP follow in usage. All of these amines, however, are similar with respect to their hazards, handling, and health effects.

**Table 1** Properties of amines used in petroleum refining

Type	MEA	DEA	MDEA	DGA	ADIP	Sulfinol
Mole weight	61.1	105.1	119.16	105.14	133.19	120.17
Boiling Pt °F (°C)	338.5 (170)	515.1 (268)	477 (247)	405.5 (208)	479.7 (249)	545 (285)
Boiling range 5–95 % °F (°C)	336–341 (169–172)	232–237 (111–114)	477 (247)	205–230 (96–110)	–	–
Freezing Pt °F (°C)	50.5 (10.2)	77.2 (25.1)	–9.3 (–23)	9.5 (–12.5)	107.6 (42)	81.7 (27.6)
S.G. @ 77 °F (25 °C)	1.0113	1.0881	1.0418 (20 °C)	1.0572	0.99	1.256
Viscosity @ 77 °F (25 °C)	18.95 cP	351.9 cP	36.8 cSt (100 °F [38 °C])	40 cP	870 cP	12.1 cP
Viscosity @ 140 °F (60 °C)	5.03 cP	–		6.8 cP	86 cP	4.9 cP
Flash Pt °F (°C)	200 (93.3)	295 (146)	265 (129)	260 (127)	255 (124)	350 (177)
Fire Pt °F (°C)	205 (96)	330 (166)	–	285 (141)	275 (135)	380 (193)
Typical solvent concentration, wt%	15–25	25–35	50	50–70	NA	Varies

For the purpose of this work, only MEA will be considered. However, as a point of reference, Table 1 provides the physical properties of those amines used in petroleum refining (see also the chapter entitled “► [Refinery Gas Treating Processes](#)”).

MEA is corrosive and a combustible liquid and requires special handling and personnel protection considerations.

All amines are injurious to personnel. As a guide, the effects of exposure to MEA are as follows:

- *Target organs:* Kidneys, central nervous system, and liver.
- *Potential health effects*
  - *The eyes:* MEA causes severe eye irritation and burning.
  - *The skin:* May be absorbed through the skin in harmful amounts. Causes moderate skin irritation.
  - *Ingestion:* Causes gastrointestinal tract burns.
  - *Inhalation:* Inhalation of high concentrations may cause central nervous system effects. This is characterized by headaches, dizziness, unconsciousness, and coma. Also causes respiratory tract irritation.
  - *Chronic:* May cause liver and kidney damage.

## Safe Handling of Amines

MEA is transported by road or rail tanker in its concentrated form. It is transferred in the normal way to an onsite storage bullet or tank, which is blanketed by an inert gas. MEA is degraded on exposure to air. The use of this, and other ethanolamines, in the refinery processes is in a dilute form. This dilution and its onsite storage are very often in a suitably constructed pit, usually in the proximity of the user plant. In some cases, a cone roof tank may be used for onsite storage. In all cases, though, the product must be kept free from exposure to air by inert gas blanketing. The dilution of MEA for use in the refinery process is between 15 and 25 wt%. The water for this dilution is usually treated boiler feed water or condensate, which are essentially free of impurities.

Vessels and piping in the process in which the amine is used should be of a suitable grade of carbon steel. The amine process temperatures should not exceed 300 °F (149 °C) anywhere in the process.

Personnel likely to be exposed to the amine should wear protective clothing, including eye protection (goggles and/or face shield in addition to safety glasses). As in the case of handling AHF, the minimum protection for operating and maintenance personnel should be:

- Coveralls, with sleeves to the wrist
- Chemical safety goggles
- Hard hat
- Gauntlets (polyvinyl chloride)
- Standard safety footwear

In addition to the standard, protective clothing listed, certain operating and maintenance work requires the use of a respirator. Such an instance would be in the changing of the amine filter (see the chapter entitled “► [Refinery Gas Treating Processes](#)”) cartridge. Although the filter will have been steam cleaned prior to opening the filter vessel, respiratory protection is essential until no presence of amine or H<sub>2</sub>S is verified. The verification is established by gas testing and the special processes to determine the absence of the sulfide (lead acetate test).

In some services, such as hydrogen plants, where MEA is used, arsenic is sometimes used as a corrosion inhibitor. This can increase the hazards of the amine and the equipment during servicing. Procedures to operate and decontaminate equipment for maintenance must ensure the operators and maintenance hands do not come in contact with the arsenic compounds.

## Equipment and Piping for Amines

As is the case with all alkaline substances, amines cause stress corrosion. Consequently, all vessels and piping (welds) are stress relieved. Valves and piping are normally carbon steel, as are pumps and heat exchanger tubes.

## Ammonia (NH<sub>3</sub>)

### Discussion of Ammonia

In petroleum processing facilities, ammonia may be used for NO<sub>x</sub> control in combustion flue gases and for refrigeration. In some facilities it is used to control corrosion in tower overheads and to suppress catalyst activity during hydrocracker startup.

Ammonia is produced in a refinery by hydroprocessing, when nitrogen compounds are removed from petroleum products. It is a major constituent of sour water stripper gases. When economic, some facilities recover ammonia as a by-product.

Ammonia itself may be present as a colorless, pressurized liquid or a colorless gas with a characteristic, pungent smell. Under typical ambient conditions, it is a gas. It is common to handle ammonia in an anhydrous liquid form under pressure or as an aqueous solution (5–30 % ammonia, AKA aqua ammonia) at ambient conditions. A typical aqua ammonia concentration is 19 wt% (for SCR-grade ammonia). See the separate topic “► [Utilities in Petroleum Processing](#)” for a discussion of ammonia systems and uses in the refinery.

### Properties of Ammonia

Table 2 summarizes some of the key properties of anhydrous and aqua ammonia grades.

### Ammonia Hazards

Ammonia, in any form, is an irritant and corrosive to the skin, eyes, respiratory tract, and mucous membranes. It can cause severe chemical burns to eyes, lungs, and skin. Any existing skin or respiratory illnesses are aggravated by exposure to ammonia. Ammonia is not recognized as a carcinogen. Evaporating anhydrous ammonia can produce frostbite if skin contacts equipment where it is being vaporized.

When mixed with air, ammonia vapor is flammable between 15 and 28 vol%. Because the autoignition temperature is high, a fairly hot ignition source is needed to start combustion. Welding and similar activities are hot enough, so care should be taken to ensure equipment that has contained ammonia is completely clear before welding. Ensure there are no vapors in the area if welding near an ammonia storage tank or a line.

Ammonia does not normally corrode steel or iron but can react rapidly with copper, brass, zinc, and many alloys, especially those containing copper. Experience has shown that aqua ammonia will corrode carbon steel slowly, however. Only steel and ductile iron are normally used in ammonia service. For aqua ammonia, stainless steel should be used ahead of any vaporizers.

The exposure limits for ammonia (as vapor) are summarized in Table 3.

**Table 2** Some key ammonia properties

Concentration	Anhydrous	29.4 wt% (26° Baumé)	19 wt% (~20.5° Baumé) SCR grade
Specific gravity	Vapor: 0.59 (Air = 1)	0.8974 (60/60 °F, 15/15 °C)	0.9294 (60/60 °F, 15/15 °C)
	Liq: 681.9 kg/m <sup>3</sup> (-33.3 °C), 42.6 lb/ft <sup>3</sup> (-28 °F)		
Boiling point	-28.01 °F (-33.34 °C)	85 °F (29 °C)	123 °F (~51 °C)
Freezing point	-107.9 °F (-77.7 °C)	-110 °F (-79 °C)	-30 °F (-34 °C)
Solubility in water	47 wt% @ 32 °F (0 °C)		
	31 wt% @ 77 °F (25 °C)		
	28 wt% @ 122 °F (50 °C)		
Solution pH		13.5	~12.9
Viscosity	0.276 cP (-40 °F, -40 °C)		
Autoignition temperature	1204 °F (651 °C)		
Explosive limits	15–28 vol%		

**Table 3** Ammonia exposure limits and toxicity

Agency	Limit type	ppm	mg/m <sup>3</sup>	Basis
US OSHA	PEL	50	35	8 h TWA
US NIOSH	STEL	35	27	15 min
	REL	25	18	10 h TWA
	IDLH	300		
ACGIH	TLV	25	18	8 h TWA
	STEL	35	27	15 min

Toxicity: LD50 (Oral, Rat) =350 mg/kg

## Clothing and Personal Protective Equipment for Ammonia

Proper ammonia handling PPE includes safety goggles and/or face shield, rubber gloves, in addition to the normal flame-retardant clothing, safety glasses, safety-toe shoes, and hardhat. Do not wear contact lenses when handling ammonia. It is also a good idea to wear ammonium hydroxide impervious clothing and rubber boots when loading or unloading.

Adequate ventilation should be provided in any ammonia handling area. There should be a safety shower and eyewash near any ammonia handling area.

If there is a possibility that the inhalation exposure limits may be approached, then respiratory protection approved by NIOSH/MSHA (or equivalent agencies) should be used. For escape in emergencies, approved respiratory protection that consists of a full-face mask, and canisters or SCBA are needed. Regulations 29 1910.134 and ANSI: Z88.2 apply. Only a positive-pressure SCBA should be used for entry into an ammonia-contaminated area if the atmosphere could contain over 300 vppm ammonia (IDLH).



For hazardous materials response to an ammonia spill, Level A and/or Level B gear should be used, including a positive-pressure SCBA.

## Release Measures

In the event of a significant ammonia release, the following steps are recommended:

- Initiate the facility emergency response system.
- Evacuate the immediate area. This evacuation area may need to be very large if the spill is large.
- Eliminate all possible ignition sources in the area.
- Shutoff or isolate the leak, if possible. This will either stop or minimize the amount.
- Control ammonia vapors with water spray around the spill. The runoff water will be contaminated and may require treatment.
- Response personnel should have SCBAs with escape bottles. They should be in chemical-resistant suits with resistant gloves for major spills.

## Storage and Handling

Anhydrous ammonia is shipped in pressurized tank trailers and tank wagons. Aqua ammonia is normally shipped in 6,700 gal (~26,000 l or ~25 MT) tank trucks (at low or ambient pressure) or in drums.

Refer to the topics entitled “► [Utilities in Petroleum Processing](#)” and “► [Environmental Control and Engineering in Petroleum Processing](#)” for discussions of the types of bulk storage facilities used for ammonia. For drum storage of aqua ammonia, the drums should be kept cool and out of the weather. The ammonia in the drums will be near its boiling point at about 85 °F (29 °C).

Sometimes anhydrous ammonia is supplied in pressurized cylinders. These should also be stored in a covered location out of the sun.

Proper PPE as discussed in section “[Clothing and Personal Protective Equipment for Ammonia](#)” should be used when handling cylinders or transferring ammonia. Gloves are especially important in handling cylinders and drums. Cylinders and drums should never be dragged.

Proper safety showers and eye washes should be available near any handling area.

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## Benzene

### General Discussion of Benzene

Benzene is found in many processes and petroleum products within a refinery and related facilities. In some cases, the product may be benzene that is deliberately recovered. In other streams, such as gasoline or reformat, the benzene is present as part of the hydrocarbon mixture.

Some benzene finds its way into waste water effluents, where it is governed by both water and air regulations (NESHAP).

We will briefly discuss benzene in a petroleum processing setting along with handling hazards. Many of the hazards and protective measures for benzene are also applicable to other aromatics (like toluene and xylene) which are a little less hazardous but still need some of the same precautions.

## Key Properties of Benzene

Benzene is the simplest aromatic compound found in petroleum. It occurs naturally but is also made in refining. Some of the key chemical and physical properties of benzene are listed in Table 4.

## Hazards of Benzene

There are two primary areas where benzene presents hazards in handling:

- Health hazards
- Fire hazard

The fire hazard can be perceived from the key properties table. Benzene can cause a flash fire.

From a health standpoint, the exposure limits and toxicity of benzene are summarized in Table 5.

**Table 4** Some key properties of benzene

Molecular formula	C <sub>6</sub> H <sub>6</sub>
Molecular weight	78.11
Appearance	Clear, colorless, stable liquid
Odor	Sweet aromatic, gasoline-like
Odor threshold	61 ppm
Specific gravity, 20/20 °C (68/68 °F)	0.8765
Boiling point	176.18 °F (80.1 °C)
Vapor pressure	99 mmHg (77 °F, 25 °C)
Freeze/melting point	41.9 °F (5.5 °C)
Solubility in water	1.79 g/l (59 °F, 15 °C)
Flash point	11.9 °F (-11.15 °C) CC
Autoignition temperature	1097 °F (591.65 °C)
Vapor density	2.7 (Air = 1)
Flammable limits in air, vol%	LEL: 1.3; UEL: 7.1
Extremely flammable, especially near open flames	

**Table 5** Exposure limits and toxicity of benzene

Agency	Type	Limit	Notes
ACGIH (2012)	TLV	0.5 ppm	8 h TWA
	STEL	2.5 ppm	15 min
NIOSH (2008)	REL	0.1 ppm	10 h TWA
	STEL	1 ppm	15 min
OSHA (2006)	PEL	1 ppm	8 h TWA
	STEL	5 ppm	15 min
Toxicity data			
LC50 (rate)	Inhalation	10,000 ppm	7 h
LD50 (rat)	Ingestion	930–1,800 mg/kg	

Known carcinogen (leukemia). Suspected mutagen.

Looking at the health hazards and effects from an exposure route standpoint:

- Inhalation: Irritating to mucous membranes and upper respiratory tract. May be fatal in high concentrations. Can cause central nervous system depression, headaches, dizziness, fatigue, and excitation followed by depression.
- Eyes: Irritant.
- Skin: Irritating. Harmful if absorbed through the skin. Skin inflammation characterized by itching, scaling, reddening, or blistering. Prolonged or repeated skin contact can defat the skin and lead to irritation, cracking, and/or dermatitis.
- Ingestion: Aspiration hazard. Can enter lungs and cause damage. May be fatal if swallowed. Can cause dizziness, headaches, breathing difficulties, diarrhea, vomiting, and possible pneumonia.
- Chronic effects: Following low-level exposure, adverse effect on hematological (blood-forming) system and myelodysplastic syndrome (disease that affects bone marrow and blood).
- Benzene is a known carcinogen.

Summarizing, symptoms of over-exposure to benzene include:

- Dizziness
- Excitation
- Pallor followed by flushing
- Weakness
- Headache
- Breathlessness
- Chest constriction
- Irritation of the eyes, skin, nose, and respiratory system
- Nausea
- Staggered gait
- Fatigue

Benzene is extremely reactive or incompatible with oxidizers, nitric acid, and many fluorides and perchlorates.

The HIMA (USA) rating for benzene is 2-3-0 (health-fire-reactivity). The US NFPA rating is also 2-3-0.

## Personnel Protection from Benzene

The primary PPE worn by refinery personnel in the plant will provide some level of protection from limited fire hazards. It does not protect from the chemical and other hazards, however.

Additional PPE for handling high benzene content streams or for spills include:

- Respiratory protection appropriate to the exposure risk
- Impervious gloves
- Chemical splash goggles (possibly face shield)
- Full impervious suit for large quantities or concentrations
- Rubber boots
- SCBA or other positive fresh air equipment

As for most materials discussed in this chapter, an eyewash and safety shower should be immediately available near locations where high concentrations of benzene are handled.

## Storage and Handling of Benzene

Benzene is not corrosive, so handling is normally in carbon steel equipment – tanks, lines, vessels, etc. Metallurgy may be determined more by the other materials mixed with the benzene.

When transferring benzene, the safety precautions required are essentially the same as those for gasoline, including grounding or bonding all equipment involved in the transfer electrically.

For releases of benzene:

- Small spills:
  - Absorb in absorbent material.
  - Put absorbent in metal container.
  - Dispose as hazardous waste.
- Large spills:
  - Flammable liquid risk.
  - Don the appropriate PPE.
  - Contain spill if possible and stop flow.
  - Evacuate area.

- Eliminate possible ignition sources from area – remember the vapors can spread through low-lying areas.
- Ventilate area.
- Absorb benzene in dry earth, clay, sand, or other noncombustible material.
- Do not allow runoff to enter drains or sewers.
- Dike area for containment.
- There will be notifications necessary.

A fire or explosion involving benzene will evolve large amounts CO and CO<sub>2</sub> vapors as well as being very hot. Fresh air equipment must be worn when fighting these fires. Cooling water sprays may be used for equipment containing benzene. Minimize and contain runoff which may contain benzene for subsequent processing. Do not let it enter the wastewater treatment system, drains, or sewers.

Most facilities never handle benzene as a pure substance. Because of this, the normal concerns are with flammability of the product containing the benzene. Higher concentrations of benzene would trigger more diligence toward preventing personnel exposure.

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## Carbon Monoxide (CO)

### Discussion of CO

Large quantities of carbon monoxide are present in all combustion gases (stacks, flares, incinerators, etc.), in partial-burn FCC regenerator gases, and as a by-product of manufacturing hydrogen. It may also be created by smoldering hydrocarbon solids, like coke or coke-coated catalysts. In a plant with cryogenic separation of refinery make gases, CO may be encountered as both gas and liquid. Care is normally taken to ensure the CO is exhausted at a safe location from elevated stacks or, in the case of hydrogen plants, destroyed by further reaction or completion of combustion. Solids are normally kept wet to avoid smoldering.

It is still possible for personnel to encounter CO in a facility. Atmospheric conditions may cause stack gases to drift or settle in locations where someone may be exposed – such as a nearby tower or structure. Sampling of flue gas or hydrogen plant gases can expose someone to CO. Burner problems in furnaces can result in CO outside the firebox and stack.

Precautions and response plans need to consider the possible presence of CO. Here we will discuss the hazards and basic protection methods available.

### Chemical and Physical Properties of CO

Table 6 lists the relevant key physical and chemical properties of CO. Note that CO will normally be a colorless, odorless, tasteless gas at conditions encountered in a refinery. The exception would be in cryogenic units, where it may be a liquid, and in

**Table 6** Some key properties of CO gas

Molecular weight	28.01
Specific gravity	Vapor: 0.97 (Air = 1)
Boiling point	-311.8 °F (-191 °C)
Freezing point	-337 °F (-205 °C)
Solubility in water	27.6 mg/l (77 °F/25 °C)
Autoignition temperature	1121 °F (605 °C)
Explosive limits	12.5–74.2 vol%

flue gases, where it is mixed with other gases that do have a warning odor (like SO<sub>2</sub>). We will focus here on CO as a gas, however.

Things to note in the properties of CO are that it has essentially the same molecular weight as nitrogen, so is likely to be found along with nitrogen. It also has a wide explosive limit, meaning that it will support combustion fairly readily.

## Hazards of CO

CO is a flammable gas and may cause a flash fire. It may be fatal if inhaled in sufficient concentrations. See Table 7 below for exposure limits.

Specific organs at risk from CO include the blood, lungs, nervous system, heart, cardiovascular system, and central nervous system. Frostbite can also occur as a result of rapidly expanding gas or vaporizing liquid, but this is unlikely in a refinery setting.

The primary route of exposure that is most frequently encountered is inhalation. Once in the lungs, CO bonds to the hemoglobin in the blood and reduces the blood's ability to carry oxygen. This is often hard to identify because blood saturated with CO is still red, while the victim is effectively suffocating. Studies indicate that 667 ppm of CO in the atmosphere can bind 50 % of the hemoglobin in the blood. This loss of oxygen capacity may result in seizure, coma, and fatality. Half-life of CO in the blood is about 5 h, so there is a cumulative effect of exposure.

Symptoms of CO poisoning include:

- Headache
- Nausea
- Vomiting
- Dizziness
- Fatigue
- Feeling of weakness
- Confusion
- Disorientation
- Visual disturbances
- Seizures
- Cherry-red blood and appearance (not necessarily reliable)

Most victims of CO poisoning believe they have food poisoning.

**Table 7** Exposure limits for CO

Agency	Limit type	ppm	mg/m <sup>3</sup>	Basis
US OSHA	PEL (2010)	50	55	8 h TWA
US NIOSH	STEL	200	229	
	REL	35	40	10 h TWA
	IDLH	1,200		
ACGIH (USA)	TLV (2010)	25	29	8 h TWA

LC50 (Rat) by inhalation: 6,600 ppm (30 min); 3,760 ppm (1 h); 1,807 ppm (4 h)

## Protective Equipment for CO

The first level of protection against CO exposure is adequate ventilation in locations where CO may accumulate or be encountered. Stack elevations are normally specified to be a minimum height above and a minimum distance from any nearby structure to ensure dissipation of stack gases. These distances are specified by each company.

The normal PPE worn by a refinery worker will not protect against CO inhalation hazards. If exposure to CO is anticipated or possible the following may be used:

- Personal CO monitor with visual, vibration, and audible alarms. In the event of an alarm, the worker should immediately evacuate the area to a safe location.
- Air-purifying respirator up to the maximum CO concentration for the specific respirator. It is advisable to consider this only for escape. These are not for an oxygen-deficient atmosphere.
- Supplied-air respirator with an escape bottle (SCBA or airline respirator) for any significant exposure risk (spills, fires, etc.).

## Handling of CO Streams

The PPE measures for handling streams which may contain CO are listed above.

Aside from small amounts of calibration gases, CO is normally a product of the refining processes. There is normally no reason to receive any bulk CO in a facility. The primary handling focus is on getting rid of the CO produced.

CO in stack gases is dispersed in the atmosphere. Operation of the fired heaters, CO boilers, and other services minimize the amount of CO emitted.

CO from processes, such as hydrogen production, is either burned as fuel gas in the SMR heater or reduced to methane (methanated) in the case of a conventional hydrogen plant.

When exposure to any hazardous level of CO is possible, fresh air respirators should be worn. This would include sampling of hydrogen plant intermediate streams, for instance.

## Catalysts and Sorbents

### General Discussion of Catalysts and Sorbents

Petroleum processing facilities employ a wide range of catalysts and sorbents in the various units. Many of these are designated as hazardous wastes when they are spent. Others may be classified as hazardous wastes based on their characteristics. In some cases, the fresh catalyst or sorbent may present a hazard that should be recognized. Here we will focus on some of the more common materials that present hazards and the methods employed to manage the hazards:

- Fresh and spent hydroprocessing catalysts
- Fresh and spent hydrogen plant nickel catalysts
- PSA adsorbents
- Mole sieve or zeolite adsorbents

### Hazardous Catalyst and Sorbent Properties

Table 8 lists some of the physical properties and hazards of concern for the materials of interest.

Many of these materials are self-heating or pyrophoric. They may combust, generating hazardous gases. Others are hazardous because they heat up on or may release adsorbed hazardous vapors when exposed to moisture, such as in the air. Methods to manage these factors are well established.

The topic titled “► [Environmental Control and Engineering in Petroleum Processing](#)” of this handbook discusses the management of spent catalysts and characteristic hazardous wastes in detail.

Health effects of the above materials by various exposure routes are summarized in Table 9.

### Catalyst and Sorbent Handling

In addition to the normal petroleum facility safety gear (hardhat, safety glasses, flame-retardant clothing, safety boots, gloves), the following PPE are also common when handling the catalysts and sorbents:

- Handling in air:
  - Dust respirator or HEPA half-face mask is adequate normally.
  - If hazardous gases may be released, an appropriate air-purifying or supplied-air respirator may be used.
  - In the case of nickel catalysts, refer to the discussion of nickel carbonyl in this chapter.



**Table 8** Some common catalyst and sorbent properties and hazards

Material	Hydroprocessing catalysts	Hydrogen plant catalysts	PSA adsorbents	Molecular sieves or zeolites
Service	Hydrotreating, hydrocracking	Reforming, methanation	Hydrogen recovery, other	Air drying. O <sub>2</sub> or N <sub>2</sub> generators
Composition				
Fresh	Oxides of Ni, Mo, and Co on alumina base: May contain silica. Sulfided forms, also	NiO and reduced nickel	Activated carbon. Mole sieves (silica)	Mole sieves, zeolite
Spent	Sulfides of the metals. Coke. FeS. Heavy metal or As accumulations. Adsorbed aromatics	NiO and reduced nickel. Adsorbed CO and other gases. Coke	Activated carbon. Mole sieves (silica). Residual adsorbed gases like CO and H <sub>2</sub> S	Mole sieves, zeolite, contaminants picked up in service
Typical density range	25–75 lb/cft (400–1,200 kg/m <sup>3</sup> )	~40–100 lb/cft (640–1,600 kg/m <sup>3</sup> )	30–45 lb/cft (480–720 kg/m <sup>3</sup> )	30–60 lb/cft (480–960 kg/m <sup>3</sup> )
Hazardous properties				
Fresh	Metal dusts. Some may be self-heating	Ni dust	Heat of adsorption for water. Silica dust	Heat of adsorption for water. Silica dust
Spent	Self-heating. Potentially pyrophoric. Desorption of gases	Ni dust. CO. Ni (CO) <sub>4</sub> . Other hazards presented by gases	Heat of adsorption for water. Release of adsorbed CO, H <sub>2</sub> S, and other gases. Silica dust	Heat of adsorption for water. Silica and other dust (coke, metals)
Waste designation	Most are K172 (U.S. RCRA)			
Comments	Refer to the topic on “Environmental control and engineering” for discussion of hazardous waste characteristics for these materials			
	Materials may be tested and reclassified based on actual waste characteristics as defined by US EPA			

- Inert handling:
  - Positive-pressure, supplied-air respirator – the inert atmosphere overrides other risks generally.
  - Refer to the inert entry safety discussion in the separate topic “► [Safety Systems for Petroleum Processing.](#)”
- Suspected hazardous contaminants (e.g., arsenic):
  - Wear protective clothing appropriate for the hazard.
  - Provide decontamination for persons leaving the handling area.
  - Use positive-pressure, supplied-air, full-face respirator.

**Table 9** Health effects of typical catalysis and sorbents

Material	Hydroprocessing catalysis	Hydrogen plant catalysis	PSA adsorbents	Molecular sieves or zeolites
Fresh material				
Inhalation	Excessive dust. Respiratory tract irritation. Cough. Difficulty breathing	High levels of dust irritating to resp. tract. Slow to clear	Irritation of respiratory tract. Potential lung damage (e.g., silicosis)	Irritation of respiratory tract. Potential lung damage (e.g., silicosis)
Ingestion	Irritation of mouth and throat. Discomfort. Malaise, nausea, diarrhea	Low oral toxicity. Irritation of the GI tract	Burns to moist body tissue from heat of adsorption	Burns to moist body tissue from heat of adsorption
Eyes	Irritant	Dust causes irritation to eyes	Irritant. Dust heats up in contact with eyes	Irritant. Dust heats up in contact with eyes
Skin	Skin sensitizer. Irritation	Unlikely to be absorbed	Irritant. Dust heats up in contact with skin. Burns if prolonged, moist contact	Irritant. Dust heats up in contact with skin. Burns if prolonged, moist contact
Chronic	Carcinogenic (Ni, Co)	Carcinogenic (Ni). Liver damage	May cause damage to lungs. May contain silica, which is a carcinogen	May cause damage to lungs. May contain silica, which is a carcinogen
Symptoms	Coughing, difficulty breathing. Delayed onset of flu-like symptoms	Allergic skin reactions. Redness, inflammation, itching, burning. Asthma	Irritation, burns to wet surfaces, respiratory difficulties from heavy dust	Irritation, burns to wet surfaces, respiratory difficulties from heavy dust
Hazard ratings (H/F/R)	HMIS: 3/1/0 NFPA: 3/1/0	HMIS: 2/1/0	NFPA: 1/0/1	NFPA: 1/0/1
Spent material				
Inhalation	Respiratory tract burns. Allergic respiratory response. H <sub>2</sub> S may be evolved	High levels of dust irritating to resp. tract. Slow to clear. Additional hazards may be present from adsorbed gas release	Irritation of respiratory tract. Potential lung damage (e.g., silicosis). Additional hazards may be present from adsorbed gas release	Irritation of respiratory tract. Potential lung damage (e.g., silicosis). Additional hazards may be present from adsorbed gas release

Ingestion	May be fatal. Burns to mucous membranes, throat, esophagus, and stomach	Low oral toxicity. Irritation of the GI tract	Burns to moist body tissue from heat of adsorption	Burns to moist body tissue from heat of adsorption
Eyes	Causes eye burns	Dust causes irritation to eyes	Irritant. Dust heats up in contact with eyes	Irritant. Dust heats up in contact with eyes
Skin	Skin burns. Allergic skin reaction. May be fatal if materials absorbed through skin	Unlikely to be absorbed	Irritant. Dust heats up in contact with skin. Burns if prolonged, moist contact	Irritant. Dust heats up in contact with skin. Burns if prolonged, moist contact
Chronic	Allergic respiratory and skin reactions. As and Ni may increase cancer risk. Co and Ni are carcinogens	Carcinogenic (Ni). Liver damage	May cause damage to lungs. May contain silica, which is a carcinogen	May cause damage to lungs. May contain silica, which is a carcinogen
Symptoms	Burns to skin, eyes, and mucous membranes. Aggravates preexisting conditions. See H <sub>2</sub> S discussion	Allergic skin reactions. Redness, inflammation, itching, burning. Asthma	Irritation, burns to wet surfaces, respiratory difficulties from heavy dust	Irritation, burns to wet surfaces, respiratory difficulties from heavy dust
Hazard ratings (H/F/R)	HMIS: 3/1/0 NFPA: 3/1/0	Normally HMIS: 2/1/0	Normally NFPA: 1/0/1	Normally NFPA: 1/0/1
Environmental effects	Toxic to aquatic life. Long effect	Limited information. Product is insoluble, so limited aquatic exposure	Limited information. Products not particularly hazardous once wetted	Limited information. Products not particularly hazardous once wetted

To avoid release of hazardous gases, keep the solids dry or coated with an oil film. It is also possible to fully saturate the materials with enough water to manage the heat of adsorption, but this will generate gases that will require control. Dust management is normally the key control measure to prevent exposure or release of the materials.

If the materials are potentially self-heating, pyrophoric, or otherwise present a hazard if exposed to air, they should be handled in purged and/or sealed systems and stored in purged and sealed containers. Refer to the discussion of inert handling of solids.

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## Caustic Soda (Sodium Hydroxide, NaOH)

### Discussion and Hazards of Caustic Soda

Caustic soda solution is used in oil refining mostly for the absorption of hydrogen sulfide or light mercaptans from light petroleum products from LPG through the kerosene cut. Very often the compound is delivered to the refinery in a strong aqueous solution to be further diluted on site to the strength required by a specific process. Sodium hydroxide in a solution is a white, odorless, nonvolatile liquid. It will not burn, but it is highly reactive. It can react violently with water and numerous commonly encountered materials, generating enough heat to ignite nearby combustible materials. Contact with many organic and inorganic chemicals may cause fire or explosion. Reaction with some metals (like aluminum and zinc) releases flammable hydrogen gas.

Sodium hydroxide is produced mainly in three forms:

- ~50 % aqueous solution (most commonly used)
- ~73 % aqueous solution
- Anhydrous sodium hydroxide in the form of solid cakes, flakes, or beads

The major impurities include sodium chloride, sodium carbonate, sodium sulfate, sodium chlorate, potassium, and heavy metals such as iron and nickel. The following discussion reviews the information relevant to solutions.

Chemical data are in Table 10.

### Handling Hazards for Caustic Soda

#### Skin

Sodium hydroxide is extremely corrosive and is capable of causing severe burns with deep ulceration and permanent scarring. It can penetrate to deeper layers of the skin, and corrosion will continue until removed. The severity of injury depends on the concentration of the solution and the duration of exposure. Burns may not be immediately painful; onset of pain may be delayed minutes to hours. Several human

**Table 10** Physical and chemical properties of caustic soda

Molecular weight	40.00
Melting point	12 °C (53.6 °F) (50 % soln.; freezing point)
	62 °C (143.6 °F) (70–73 % solution)
Boiling point	140 °C (284 °F) (50 % solution)
Specific gravity	1.53 (50 % solution)
	2.0 at 15.5 °C (70–73 % solution)
Solubility in water	Soluble in all proportions
Solubility in other liquids	Soluble in all proportions in ethanol, methanol, and glycerol
pH values	12 (0.05 % solution)
	13 (0.5 % solution)
	14 (5 % solution)

studies and case reports describe the corrosive effects of sodium hydroxide. A 4 % solution of sodium hydroxide, applied to a volunteer's arm for 15–180 min, caused damage which progressed from destruction of cells of the hard outer layer of the skin within 15 min to total destruction of all layers of the skin in 60 min. Solutions as weak as 0.12 % have damaged healthy skin within 1 h. Sodium hydroxide dissolved the hair and caused reversible baldness and scalp burns when a concentrated solution (pH 13.5) dripped onto a worker's head and treatment was delayed for several hours.

Owing to its corrosive nature, repeated or prolonged skin contact with dust and weak solutions would be expected to cause drying, cracking, and inflammation of the skin (dermatitis).

### Eyes

Sodium hydroxide is extremely corrosive to the eye tissues. The severity of injury increases with the concentration of the solution, the duration of exposure, and the speed of penetration into the eye. Damage can range from severe irritation and mild scarring to blistering, disintegration, ulceration, severe scarring, and clouding. Conditions which affect vision such as glaucoma and cataracts are possible late developments. In severe cases, there is progressive ulceration and clouding of eye tissue which may lead to permanent blindness.

### Inhalation

A worker, exposed for 2 h per day over 20 years to mists from boiling a solution of sodium hydroxide in two large containers in a small room with inadequate ventilation, developed severe obstructive airway disease. It was concluded that the massive and prolonged exposure induced irritation and burns to the respiratory system eventually leading to the disease. It was noted that chronic exposure had not previously been reported, probably since the strong and immediate irritation would normally deter workers from further exposure. Actual exposures to sodium hydroxide aerosols were not measured, and it could not definitely exclude late onset asthma as a cause of the man's condition.

A report of workers exposed to sodium hydroxide aerosol for at least 16 months was confounded by the presence of high concentrations of Stoddard solvent and other solvent vapors, as well as other chemicals.

There was no trend of increased mortality in relation to duration (up to 30 years) or intensity of exposure ( $0.5\text{--}1.5\text{ mg/m}^3$ ) among 291 workers exposed to sodium hydroxide dust during the production of flakes or beads of concentrated sodium hydroxide from chlorine cell effluent. This study was limited by the small population size.

### **Ingestion**

There are no reported cases of industrial workers ingesting sodium hydroxide solutions. Non-occupational ingestion has produced severe corrosive burns to the esophageal tissue, which has in some cases progressed to stricture formation. Should ingestion occur, severe pain; burning of the mouth, throat, and esophagus; vomiting; diarrhea; collapse; and possible death may result.

### **Long-Term Effects**

Sodium hydroxide has been implicated as a cause of cancer of the esophagus in individuals who have ingested it. The cancer may develop 12–42 years after the ingestion incident. Similar cancers have been observed at the sites of severe thermal burns. These cancers may be due to tissue destruction and scar formation rather than the sodium hydroxide itself.

A case-control study reported an association between renal cancer and history of employment in the cell maintenance area of chlorine production. The major exposures in this work were presumed to be to asbestos and sodium hydroxide. An association was made between renal cancer and sodium hydroxide exposure. This study was limited by factors such as small numbers of exposed workers, multiple exposures, and reliance on work histories and is not considered sufficiently reliable.

## **First Aid and Personal Safety for Caustic Soda**

### **Contact with the Skin**

Avoid direct contact with this chemical. Wear chemical-resistant protective clothing, if necessary. As quickly as possible, remove contaminated clothing, shoes, and leather goods (e.g., watchbands, belts). Flush contaminated area with lukewarm, gently flowing water for at least 60 min, by the clock. **DO NOT INTERRUPT FLUSHING.** If necessary, keep emergency vehicle waiting. Transport victim to an emergency care facility immediately. Discard contaminated clothing, shoes, and leather goods.

### **Contact with the Eyes**

Avoid direct contact. Wear chemical-resistant gloves, if necessary. Quickly and gently blot or brush away excess chemical. Immediately flush the contaminated eye (s) with lukewarm, gently flowing water for at least 60 min, by the clock, while

holding the eyelid(s) open. Neutral saline solution may be used as soon as it is available. **DO NOT INTERRUPT FLUSHING.** If necessary, keep emergency vehicle waiting. Take care not to rinse contaminated water into the unaffected eye or onto the face. Quickly transport victim to an emergency care facility.

### **Suffering from Inhalation**

Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention immediately.

### **Ingestion**

**DO NOT INDUCE VOMITING!** Give large quantities of water or milk if available. Never give anything by mouth to an unconscious person. Get medical attention immediately.

## **Protective Clothing for Caustic Soda**

### **Personal Respirators (NIOSH Approved)**

If the exposure limit is exceeded and engineering controls are not feasible, a half-face piece particulate respirator (NIOSH type N95 or better filters) may be worn for up to 10 times the exposure limit or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier, whichever is lowest. A full-face-piece particulate respirator (NIOSH type N100 filters) may be worn up to 50 times the exposure limit or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier, whichever is lowest. If oil particles (e.g., lubricants, cutting fluids, glycerin, etc.) are present, use a NIOSH type R or P filter. For emergencies or instances where the exposure levels are not known, use a full-face-piece positive-pressure, air-supplied respirator. **WARNING:** Air-purifying respirators do not protect workers in oxygen-deficient atmospheres.

### **Skin Protection**

Wear impervious protective clothing, including boots, gloves, lab coat, apron, or coveralls, as appropriate, to prevent skin contact.

### **Eye Protection**

Use chemical safety goggles and/or a full-face shield where splashing is possible. Maintain eye wash fountain and quick-drench facilities in work area.

## **Materials of Construction for Caustic Soda**

Carbon steel can be used throughout at moderate temperatures. At temperatures in excess of 350 °F (177 °C), nickel or nickel alloy is recommended. All carbon steel piping, flanges, welds, and vessel must be stress relieved. Caustic soda solution also attacks glass and dissolves it to some extent. As caustic soda is used in cleaning

process plants during commissioning, sight glasses and level gauges are removed and replaced with silica glasses for this cleaning phase of the commissioning. Plastic or plastic lined-pipe can also be used for handling caustic soda at low temperatures. Consult plastic manufacturers for compatibility information.

## Furfural

### Discussion and Hazards of Furfural

Furfural is used in petroleum refining for the production of lube oils. It is a solvent in the extraction of undesirable compounds such as naphthenes and aromatics from lube oil stocks to improve the color of the lube oil product (see the separate topic “► [Non-energy Refineries in Petroleum Processing](#)”). Furfural or furfuraldehyde,  $C_4H_3OCHO$ , is a viscous, colorless liquid that has a pleasant aromatic odor, which upon exposure to air turns dark brown or black. It boils at about 160 °C (320 °F). It is commonly used as a solvent. It is soluble in ethanol and ether and somewhat soluble in water.

Furfural is the aldehyde of pyromucic acid. It has properties similar to those of benzaldehyde. A derivative of furan, it is prepared commercially by dehydration of pentose sugars obtained from cornstalks and corncobs, husks of oat and peanut, and other waste products. It is used in the manufacture of pesticides, phenolfurfural resins, and tetrahydrofuran. Tetrahydrofuran is used as a commercial solvent and is converted in starting materials for the preparation of nylon.

Chemical properties of furfural are in Table 11.

### Hazards Associated with Handling Furfural

#### Inhalation

Causes irritation to the mucous membranes and upper respiratory tract. Symptoms may include sore throat, labored breathing, and headache. Higher concentrations act on the central nervous system and may cause lung congestion. Inhalation may be fatal.

**Table 11** Physical properties of furfural

Appearance	Colorless to yellowish liquid
Odor	Almond odor
Solubility	8 g/100 g water @ 70 °F (21 °C)
Specific gravity	1.16 @ 77 °F (25 °C)
% Volatiles by volume @ 70 °F (21 °C)	100
Boiling point	324 °F (162 °C)
Melting point	−38 °F (−39 °C)
Vapor density (Air = 1)	3.3
Vapor pressure (mm Hg)	1 @ 64 ° F (18 °C)



**Ingestion**

Highly toxic. May cause gastrointestinal disorders. Can cause nerve depression and severe headache. May be fatal. Other effects are not well known.

**Skin Contact**

Irritant to skin. May cause dermatitis and possibly eczema, allergic sensitization, and photosensitization. May be absorbed through the skin with possible systemic effects.

**Eye Contact**

Vapors irritate the eyes, causing tearing, itching, and redness. Splashes may cause severe irritation or eye damage.

**Chronic Exposure**

Can cause numbness of the tongue, loss of sense of taste, and headache. Other effects are not well known.

**Aggravation of Preexisting Conditions**

Persons with preexisting skin disorders or eye problems or impaired liver, kidney or respiratory function may be more susceptible to the effects of the substance.

**First Aid and Personal Safety with Furfural****Inhalation**

Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention immediately.

**Ingestion**

If swallowed, give large quantities of water to drink and get medical attention immediately. Never give anything by mouth to an unconscious person.

**Skin Contact**

Immediately flush skin with plenty of soap and water for at least 15 min while removing contaminated clothing and shoes. Get medical attention, immediately. Wash clothing before reuse. Thoroughly clean shoes before reuse.

**Eye Contact**

Immediately flush eyes with plenty of water for at least 15 min, lifting lower and upper eyelids occasionally. Get medical attention immediately.

**Protective Clothing and Equipment for Furfural Handling****Airborne Exposure Limits**

The recommended airborne exposure limit is between 2 and 5 ppm.

## Ventilation System

A system of local and/or general exhaust is recommended to keep employee exposures below the airborne exposure limits. Local exhaust ventilation is generally preferred because it can control the emissions of the contaminant at its source, preventing dispersion of it into the general work area. Please refer to the ACGIH document, *Industrial Ventilation, A Manual of Recommended Practices*, most recent edition, for details.

## Personal Respirators (NIOSH Approved)

If the exposure limit is exceeded, a full-face-piece respirator with organic vapor cartridge may be worn up to 50 times the exposure limit or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier, whichever is lowest. For emergencies or instances where the exposure levels are not known, use a full-face-piece positive-pressure, air-supplied respirator. **WARNING:** Air-purifying respirators do not protect workers in oxygen-deficient atmospheres.

## Skin Protection

Wear impervious protective clothing, including boots, gloves, lab coat, apron, or coveralls, as appropriate, to prevent skin contact.

## Eye Protection

Use chemical safety goggles and/or a full-face shield where splashing is possible. Maintain eye wash fountain and quick-drench facilities in work area.

## Fire Prevention and Firefighting for Furfural

### Fire

The relevant combustion properties of furfural are in Table 12.

### Explosion

Above the flash point, vapor-air mixtures are explosive within flammable limits noted above. Reacts violently with oxidants. Reacts violently with strong acids and bases causing fire and explosion hazards. Sealed containers may rupture when heated. Sensitive to static discharge.

### Fire Extinguishing Media

Water spray, dry chemical, alcohol foam, or carbon dioxide can be used as fire extinguishing media. Water spray may be used to keep fire-exposed containers cool.

**Table 12** Furfural combustion properties

Flash point	140 °F (60 °C) Pensky-Martens
Autoignition temperature	601 °F (316 °C)
Flammable limits in air % by volume	LEL: 2.1; UEL: 19.3
Flammable liquid and vapor!	

Water may be used to flush spills away from exposures and to dilute spills to nonflammable mixtures.

### Special Information

In the event of a fire, wear full protective clothing and NIOSH-approved self-contained breathing apparatus with full-face piece operated in the pressure demand or other positive-pressure mode.

## Materials of Construction and Storage for Furfural

There are no special materials of construction required for furfural. A suitable grade of carbon steel is adequate. Storage and handling of furfural must exclude air. Furfural polymerizes readily on exposure to air. In refinery practices, startup of furfural extraction plants usually requires that the equipment which handles furfural be first filled with either the lube oil feed or a suitable middle distillate to eliminate air.

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## Hydrofluoric Acid (HF, AHF)

### Discussion and Hazards of HF

Because of anhydrous hydrofluoric acid's (AHFs) highly toxic and corrosive nature, this section highlights its characteristics and the safe handling of the acid.

Anhydrous hydrofluoric acid is a colorless, mobile liquid which boils at 67 °F (19.4 °C) at atmospheric pressure and therefore requires pressure containers. The acid is also hygroscopic; therefore, its vapor combines with the moisture of air to form "fumes." This tendency to fume provides users with a built-in detector of leaks in AHF storage and transfer equipment. On the other hand, care is needed to avoid accidental spillage of water into tanks containing AHF. Dilution is accompanied by a high release of heat. The physical properties of AHF are given in Table 13.

AHF vapor, even at very low concentrations in air, has a sharp penetrating odor that is an effective deterrent to willful overexposure by operating personnel. Both the vapor and liquid forms of AHF cause severe and painful burns on contact with the skin, eyes, or mucous membranes.

Hydrofluoric acid is very corrosive. It attacks glass, concrete, and some metals – especially cast iron and alloys which contain silica (e.g., Bessemer steels). The acid

**Table 13** The physical properties of anhydrous hydrofluoric acid (AHF)

Boiling point at 1 atm, °F (°C)	66.9 (19.4)
Freezing point, °F (°C)	−117.4 (−83)
Specific gravity at 32 °F (0 °C)	1.00
Weight per gallon at 32 °F (0 °C), lb (MT/m <sup>3</sup> )	8.35 (1.0)
Viscosity at 32 °F (0 °C), cP	0.31

also attacks such organic materials as leather, natural rubber, and wood, but does not promote their combustion.

Although AHF is nonflammable, its corrosive action on metals, particularly in the presence of moisture, can result in hydrogen forming in containers and piping to create a fire and explosion hazard. Potential sources of ignition (sparks and flames) should be excluded from areas around equipment containing hydrofluoric acid.

Despite its corrosive nature, AHF can be handled with relative safety if the hazards are recognized and the necessary precautions taken. The next few sections describe certain procedures for the safe handling of large bulk quantities of AHF.

### **Safe Handling Practices for HF**

The safe handling of AHF requires that well-designed equipment be properly operated and maintained by well-trained, adequately protected, responsible personnel.

Tanks and other containers of AHF should be protected from heat and the direct rays of the sun. Storage-area temperatures should preferably remain below 100 °F (38 °C). If they reach or exceed 125 °F (51.7 °C), means for cooling the containers must be applied.

Acid transfer lines between the unloading station and the storage tank should be designed to free drain toward the storage tank. Thermal relief valves should be installed in those sections of acid transfer lines where acid may be entrapped between two closed valves in the line, because expansion of the liquid might create excessive pressure and rupture the line. The relief will need to discharge toward the tank, not to atmosphere.

No open fires, open lights, or matches should be allowed in or around acid containers or lines. The possibility of acid acting on metal to produce hydrogen gas is ever present. Only non-sparking tools and spark-proof electrical equipment should be used in the AHF storage and handling areas.

Safety showers should be readily accessible at the unloading station, in the storage area, and at other locations where acid is handled. The showers should be capable of supplying volume flows of 30 GPM (114 l/min) through quick-opening valves in 2 in. (50 mm) water lines. Handles at hip level should actuate the valves which, with a 0.25 in. (6.4 mm) weep hole directly above the valve, should be positioned below the frost line and surrounded by crushed rock or gravel to provide drainage.

A water hydrant and hose should also be available in the unloading area to flush away spilled acid. Good drainage should be provided and also a supply of dry soda ash, ground limestone, or hydrated builders lime. Accidental spills of acid on walkways or equipment should be washed off immediately with large volumes of water and, if necessary, neutralized with one of the agents mentioned.

## Personal Protective Equipment Requirements for HF

Personal protective equipment is not a substitute for good, safe working conditions. Its purpose is to protect the wearer in the event of an accident – major or minor. The extent of protection needed depends upon the degree of potential exposure attending the particular job at hand. Protective equipment should not be worn or carried beyond the operating area. It should be thoroughly washed with sodium bicarbonate solution immediately after each use.

The minimum protection required for operating and maintenance personnel includes the following items:

- Coveralls with sleeves to the wrists
- Face shield or chemical safety goggles
- Hard hat
- Poly(vinyl chloride) – or neoprene-dipped gauntlets
- Poly(vinyl chloride) – or neoprene-soled rubber shoes

When taking acid samples, opening equipment which may contain hydrofluoric acid, or performing similar hazardous duties, operators should wear the following:

- Poly(vinyl chloride) or neoprene overalls
- Poly(vinyl chloride) or neoprene boots
- Lightweight poly(vinyl chloride) or neoprene gloves under poly(vinyl chloride) – or neoprene-dipped gauntlets
- Poly(vinyl chloride) or neoprene jumper
- Airline hood

Air should be applied to the hood until the absence of fumes in the work area has been fully established.

## Unloading and Transfer of AHF

AHF is shipped in rail tank cars having capacities ranging from approximately 5,400 to 25,000 gal (~20–94 MT) and in road tank trucks of approximately 5,250 gal (~20 MT) AHF capacity. Compressed dry gas (air, hydrocarbon, or nitrogen) is the preferred means for transferring bulk quantities of AHF, but a centrifugal, rotary, or positive-pressure pump can be used, if necessary.

The unloading of AHF tank cars or tank trucks, with transfer of the acid to plant storage, consists of five steps:

1. Spotting the tank car or tank truck at the unloading station
2. Connecting the plant compressed-gas (or vapor) and AHF-unloading lines to the proper valves on the carrier tank

3. Transferring the AHF from the carrier tank to the storage tank
4. Disconnecting the plant compressed-gas (or vapor) and AHF-unloading lines from the carrier tank valves
5. Releasing the tank car or tank truck for return to the shipper

## Equipment for HF Service

Mild steel is satisfactory for storing and handling AHF at temperatures up to 150 °F (~65 °C) maximum. Type 300 stainless steels are useful up to 200 °F (~93 °C). “Monel” nickel-copper alloy and “Hastelloy” C nickel steel are suitable for higher temperatures. TEFLON TFE fluorocarbon resin is completely resistant to all concentrations of hydrofluoric acid at temperatures up to 500 °F (260 °C).

Steel should not be used for movable parts because the corrosion-product film will cause movable parts to “freeze.” Cast iron, type 400 stainless steel, and hardened steels are unsatisfactory for AHF handling. Copper is velocity sensitive. Stressed Monel may stress crack if exposed to moist vapors or aerated acid containing water. Welds in Monel corrode rapidly.

The selection of construction materials used for AHF equipment depends very much on such corrosion-affecting variables as moisture, temperature, aeration, fluid velocity, and impurities. Each storage and handling situation requires separate study to evaluate these factors before selecting materials which must meet the requirements of the installation.

Additional information on metallurgy and materials for HF service can be found in API Recommended Practice 571 and is available from process licensors.

## Storage Tank

The capacity of the storage system should be approximately 1.5 times the maximum quantity normally ordered to insure against running out of acid between receipts of shipments. As a rule, too large a storage system is preferable to too small a system. The additional investment required for the larger installation is not great. The larger installation permits further expansion, less precise scheduling of shipments, and larger inventories when desired.

The horizontal cylindrical storage tank should be manufactured according to the current ASME Code for Unfired Pressure Vessels or other equivalent codes which meet state or local mandatory requirements. It is further recommended that the wall thickness of the tank be at least 1/8 in. (3.2 mm) in excess of the ASME Code requirements. The tank should be double-welded, butt-joint construction, the welds to be slag-free (conforming to ASME Code, Section 8) and ground smooth inside to facilitate inspection. X-ray inspection of welds is recommended.

The storage tank should be suitably supported above ground level. Structural steel supports or concrete saddles (protected with an acid-resistant paint) are satisfactory. Secondary containment is normally required. An emergency water wall system may also be required.

Safety devices for relieving abnormal internal tank pressures should be obtained from qualified manufacturers who are familiar with AHF. The maximum working pressure of the storage system should not exceed two thirds the rated relief or bursting pressure of the safety devices. A dual relief system is recommended which has a two-way valve and rupture disks ahead of the relief valves and also a separate rupture-disk line in case of relief valve failure.

### **Piping**

All pipe lines should be installed so that they drain toward the storage tank or toward the point of consumption. This will prevent the accumulation of acid in low points, thereby eliminating possible safety hazards when repairs are necessary. Relief valves should be installed in the various sections of the lines in case acid becomes confined between two closed valves in the line. All flanges in the lines should preferably be coated with an acid-indicating paint, such as Mobil #220-Y-7 hydrofluoric acid-detecting paint, which changes in color from orange to yellow in the presence of AHF liquid or vapor.

The line from the unloading station to the storage tank should be equipped with a gate valve so acid flow can be stopped at any time. The line should also be securely anchored to the storage tank as considerable vibration may occur, especially when unloading by means of compressed gas.

Extra heavy (Schedule 80) or, better, triple extra-heavy black seamless or welded steel pipe, which is free from non-metallic inclusions, is satisfactory.

### **Fittings**

Larger lines (2 in. [50 mm] and larger) should preferably be welded to conform to ASME Code, Section 8. Alternatively, properly gasketed forged steel flanges can be used.

On smaller lines, extra-heavy forged steel, screw-type unions with steel-to-steel seats can be used for pipe joints. Graphite-and-oil is satisfactory as lubricant.

### **Gaskets**

Gaskets made of TEFLON TFE fluorocarbon resin are recommended.

### **Valves**

Jamesbury "Double-Seal" ball valves have given excellent service to AHF manufacturing operations. The valve seats are preferably of TEFLON TFE; the balls and bodies of 316 stainless steel, Durimet 20 austenitic stainless steel alloy, or equivalent. Gate valves should be of the O, S, and Y flange type, with a ring of TEFLON TFE or "Kel-F" fluorocarbon thermoplastic material on the plug seat and packing of either TEFLON TFE or Kel-F.

Globe valves can be of Monel nickel-copper alloy or have a forged steel body and trim of Monel.

Good service has been reported for Hills-McCanna diaphragm valves with body of Durimet 20 or equivalent, or Monel alloy; diaphragm of polyethylene, Kel-F, or a laminate of neoprene and TEFLON TFE; and a wheel closure.

Plug valves of Monel with a sleeve of TEFLON TFE have been found satisfactory. Check valves should be of the forged ball and body type – made of Monel metal.

### **Pressure Gauges**

Pressure gauges should be constructed of 316 stainless steel or Monel metal Bourdon tubes. The bottom connection of the gauge should be 1/2 inch. The case should have a “blow-out” back.

### **Pumps**

Centrifugal, rotary, or positive-pressure types of pumps are satisfactory. The 300 series stainless steels; Durimet 20 or equivalent, Hastelloy C, Monel alloys; nickel, bronze, and acid bronze have been recommended as construction materials.

### **Level Gauges**

AHF Manufacturers suggest the use of a magnetic-type level gauge, such as a Fischer & Porter Model 13 C 2265 W Liquid “Levelrator” with donut-type float.

An alternative means for monitoring storage-tank content is to set the tank on load cells or strain gauges.

### **Filters**

Where the critical nature of the process has warranted, cartridge-type filters in the storage tank-to-process line have been recommended. Two such filters are normally mounted in parallel to permit replacing the cartridge in one line while diverting the acid flow through the other. Construction materials used in fabricating the filters are the same or similar to those described above for other auxiliary equipment.

Polypropylene can be used as filter material for AHF alone if the liquid temperature remains below 200 °F (93 °C).

When a fouled filter is removed for replacement, it should be promptly flushed with water, neutralized with a solution of soda ash, and rinsed before discard.

## **Personal Safety When Handling HF**

Liquid AHF causes immediate and serious burns to any part of the body on contact.

Dilute solutions of hydrofluoric acid often do not cause an immediate burning sensation where they came in contact with skin. Several hours may pass before the solution penetrates the skin sufficiently to cause redness or a burning sensation.

Wearing clothing which may have absorbed small amounts of hydrofluoric acid (such as leather shoes or gloves) can result in painful delayed effects similar to those caused by dilute acid solutions.

Hydrofluoric acid vapor causes skin irritation and inflammation of the mucous membranes; the burns become apparent a few hours after exposure. Inhaling the vapor in high concentrations may cause lung damage (pulmonary edema).

In the United States, the American Conference of Governmental Industrial Hygienists recommends a threshold limit value of 3 parts (by volume) AHF



vapor (hydrogen fluoride) per million parts air. This value refers to a time weighted concentration for a seven- or 8-h workday and 40-h work week.

The 3 vppm figure is based on both experimental and occupational evidence; however, nosebleeds and sinus troubles have reportedly occurred among metal workers exposed to even lower concentrations of a fluoride or fluorine in air. Therefore, for protection against acute irritation, 3 ppm should be considered a ceiling limit.

Anyone who knows or even suspects he has come in contact with hydrofluoric acid should immediately seek first aid.

In the event of an accident, the medical response should be called immediately; however, all plant supervisors should be aware of first aid procedures for HF burns. All affected persons should be referred to a physician even when the injury seems slight.

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## Hydrogen

### General Discussion of Hydrogen

Hydrogen is present throughout refining and petroleum processes today. It is:

- Generated in reformers and hydrogen plants
- Recovered from fuel and refinery make gases
- Consumed in hydrotreaters, hydrocrackers, isomerization units, benzene saturators, and sulfur plants

It is critical to meeting modern product specifications.

Most hydrogen is produced within a facility and used within the facility. In some cases, hydrogen may be received in bulk from a supplier for specific purposes, such as naphtha reformer startup or calibration gases. Hydrogen may also be supplied in bulk by pipeline from an outside facility.

The primary hazards presented by hydrogen are fire and explosion. When released to the atmosphere, hydrogen quickly rises and dissipates, but local concentrations may present risks.

High velocity releases of hydrogen (as in a vent) may generate a static electrical charge that can create a spark to ignite the vent.

### Physical and Chemical Properties of Hydrogen

Table 14 summarizes the key properties of hydrogen of concern here.

Hydrogen gas is extremely flammable and easily ignites, even from hot equipment. It is colorless, odorless, and tasteless.

Hydrogen has the unusual property of a reverse Joule-Thompson effect – it will heat up when it rapidly expands.

**Table 14** Key properties of hydrogen gas

Molecular weight	2.02
Specific gravity	Vapor: 0.0696 (air =1)
Boiling point	-423.4 °F (-253 °C)
Freezing point	-434.5 °F (-259.15 °C)
Solubility in water	27.6 mg/l (77 °F/25 °C)
Autoignition temperature	932–1060 °F (500–571 °C)
Explosive limits	4–76 vol%

## Hazards of Hydrogen

The most obvious and well-known hazard of hydrogen is its flammability. It burns with a clear flame that is hard to detect. Personnel have been known to walk into a hydrogen flame without seeing it.

The heat generated from the reverse Joule-Thompson effect of hydrogen, along with the static electricity generated in a leak, can result in fires or explosions from hydrogen leaking from pressures over about 1,000 psig (69 barg).

Sometimes hydrogen is received as compressed gas (2,000 psig [138 barg] plus). In these cases, additional hazard is presented by the high pressure.

Hydrogen will burn aggressively with any oxidizer.

Hydrogen is not particularly toxic but may cause asphyxiation in high enough concentrations, e.g., near a hydrogen vent. The rapid dissipation of vented hydrogen normally limits asphyxiation risk.

## Protective Equipment for Hydrogen Handling

The common refinery PPE (hardhat, safety glasses, flame-retardant clothing, and safety shoes) provide some protection against a hydrogen flash fire. They will not provide protection from a significant fire or explosion, an oxygen deficiency, or physical hazard from high pressures involving hydrogen. Major events involving hydrogen require SCBA and flash suits. There should be an SCBA nearby when handling bulk hydrogen.

It is best to focus on preventing a hydrogen fire from affecting surrounding equipment until the hydrogen can be stopped at the source.

Ventilation of areas where hydrogen may accumulate is the best way to protect personnel.

## Storage and Handling of Bulk Hydrogen

Hydrogen is normally generated and used within a facility or may be received by pipeline over the fence. As such, no more handling is involved than for the hydrocarbon streams. Precautions and PPE used for handling hydrocarbon gases are adequate for hydrogen in general.

When hydrogen is received in bulk, normally pressurized gas in tube trailers or in cylinders, the normal precautions that apply to compressed gases are adequate.

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## Hydrogen Sulfide (H<sub>2</sub>S)

### Discussion and Hazards of H<sub>2</sub>S

Hydrogen sulfide in a refinery is usually formed during the desulfurizing processes used to sweeten product streams. Hydrogen sulfide (H<sub>2</sub>S) is a colorless, extremely poisonous gas that has a very disagreeable odor, much like that of rotten eggs, in low concentrations. In high concentrations that are IDLH, it deadens the sense of smell.

It is slightly soluble in water and is soluble in carbon disulfide. Dissolved in water, it forms a very weak dibasic acid. Hydrogen sulfide is flammable, and in excess air, it burns to form sulfur dioxide and water. Where less than stoichiometric oxygen is present, it forms elemental sulfur and water.

It may be made by reacting hydrogen gas with molten sulfur or with sulfur vapors or by treating a metal sulfide (e.g., ferrous sulfide, FeS) with an acid. Hydrogen sulfide reacts with most metal ions to form sulfides; the sulfides of some metals are insoluble in water and have characteristic colors that help to identify the metal during chemical analysis.

Hydrogen sulfide also reacts directly with silver metal, forming a dull, gray-black tarnish of silver sulfide (Ag<sub>2</sub>S). One method of detecting small concentrations of hydrogen sulfide is to expose it to a filter paper impregnated with lead acetate. The paper turns black (due to the precipitation of lead sulfide). The degree of H<sub>2</sub>S concentration is measured by the shade of “blackness” of the lead acetate paper compared with standard colors.

The relevant properties of hydrogen sulfide are given in Table 15.

### Hazards and Toxicity of Hydrogen Sulfide

Table 16 indicates the toxicity of hydrogen sulfide.

The following discussion uses the present US OSHA limits as a basis.

At 1 ppm, most people can smell the gas. A strong smell does not necessarily mean a high concentration, and a slight smell does not mean a low concentration. A person could work in a 10 ppm concentration of H<sub>2</sub>S for 8 h. If the concentration exceeds 10 ppm for a short period of time, then the time must be reduced.

A concentration of 15 ppm can be tolerated for a period of time not exceeding 15 min. There can be no more than four exposures of 15 ppm in an 8 h shift with 1 h between exposures. If the concentration of H<sub>2</sub>S exceeds 20 ppm, a worker must wear approved breathing apparatus. If the concentration is not known, a worker must wear breathing apparatus until the concentration is determined.

**Table 15** Properties of hydrogen sulfide

Chemical formula	H <sub>2</sub> S
Relative density	1.189 (air = 1.0)
Autoignition temperature	500 °F (260 °C)
Flammability	Very flammable
Lower explosive limit	4.3 vol% in air
Upper explosive limit	46 vol% in air
Color	Colorless, invisible
Odor	Strong rotten egg at low concentrations; cannot smell at IDLH concentrations
Vapor pressure	17.7 atm at 20 °C (68 °F)
Boiling point	-77 °F (-61 °F)
Melting point	-122 °F (-86 °F)
Reactivity	Dangerous with acids and oxidizers
Solubility	In water, hydrocarbons, alcohol

Quoted from National Safety Council Data Sheet 1-284-67

**Table 16** Toxicity of hydrogen sulfide

ppm	Percent	Comments
1	0.0001	Most people can smell the gas
10	0.001	Occupational exposure limit. Maximum continuous exposure for 8 h
15	0.0015	Occupational exposure for 15 min
20	0.002	Ceiling occupational exposure limit. This level of exposure cannot be exceeded at any time without respiratory protection
100	0.01	Dulls sense of smell. Causes burning sensation in the eyes and throat
500	0.05	Attacks the respiratory center of brain; causes loss of reasoning and balance
700	0.07	Victim quickly loses consciousness; breathing will stop, and death will result if not rescued promptly
1,000	0.1	Unconscious immediately; permanent brain damage or death occurs if victim is not rescued and resuscitated immediately

If exposed to a concentration of 100 ppm (1/100 of 1 %), the sense of smell will be lost or become ineffective within 2–15 min. The H<sub>2</sub>S might cause a burning sensation to the eyes, throat, and lungs and could cause headache or nausea.

A 200 ppm concentration will cause immediate loss of smell and a burning sensation in the eyes, throat, nose, and lungs. (The hydrogen sulfide combines with alkali in body fluids to form caustic sodium sulfide.)

At a concentration of 500 ppm, the victim will appear to be intoxicated, and will lose his sense of balance and reasoning. In this state, the victim may attempt to continue with the job he was doing when he encountered the gas. For this reason, a person *must* know the people he works with and be able to detect any unusual behavior of a coworker. Obviously, persons under the influence of alcohol, or any other mind-altering drugs, should never be allowed in an area which may contain

sour gas. A victim must be watched very closely and may require resuscitation. A victim should be taken for medical attention and not allowed to return to work for at least 8 h.

At 700 ppm, the victim will be rendered unconscious very quickly and may develop seizures similar to those caused by epilepsy. Loss of bladder and bowel control can be expected. Breathing will stop, and death will result, if not rescued and resuscitated promptly. At a concentration of 1,000 ppm (1/10 of 1 %), the victim will be rendered unconscious immediately. **THE VICTIM WILL NOT BEGIN BREATHING VOLUNTARILY IF BROUGHT TO FRESH AIR. ARTIFICIAL RESUSCITATION MUST BE COMMENCED WITHIN THREE MINUTES OF EXPOSURE TO THIS LEVEL OF HYDROGEN SULFIDE!**

## **Protective Clothing and Personal Safety for H<sub>2</sub>S**

The appropriate personal protective equipment when working around gaseous H<sub>2</sub>S, or in areas where H<sub>2</sub>S may be present and is typically the same as the minimum required in a facility:

- Hardhat
- Flame-retardant clothing
- Safety glasses
- Safety-toe shoes

In addition, many (if not most) refiners now require workers to wear personal H<sub>2</sub>S monitors, which provide an audible and visual alarm at a specified concentration of H<sub>2</sub>S. These personal monitors complement area H<sub>2</sub>S monitors in many facilities.

In areas where H<sub>2</sub>S exposure is possible, appropriate supplied-air respirators must be readily available, if not actually worn. If exposure to H<sub>2</sub>S is expected, such as during sampling of sour gas streams or when setting blinds on a sour line, procedures generally call for the use of fresh air equipment.

In confined areas, such as enclosed compressor or pump houses which handle sour gas or liquids, constant monitoring for H<sub>2</sub>S concentration in the atmosphere by automatic area air analyzers with alarms is common. Failing this, a routine analysis using a lead acetate paper should be made. In addition, all such buildings should always be properly vented using an exhaust fan system.

## **Materials of Construction in H<sub>2</sub>S Service**

Atmospheres containing hydrogen sulfide and completely or almost free of oxygen give rise to rapid corrosion of unalloyed steel by forming a sulfide film on its surface. The corrosion rate in hydrogen/hydrogen sulfide increases as the content of hydrogen sulfide increases up to about 5 vol.%, while increases beyond that point generally only

have a slight effect on the corrosion rate. Steels alloyed with chromium and aluminum have improved resistance to hydrogen sulfide, while nickel has no deleterious effect.

Moist and aqueous solutions of hydrogen sulfide cause some minor pitting in unalloyed steel, and there is a risk of stress corrosion. This pitting corrosion is about 1 mm/year. This rate can be considerably reduced to about 0.1 mm/year using an alloyed steel of 18 % chrome and 9 % nickel. Vessels and piping should all be stress relieved.

The API provides detailed guidance on materials of construction for various types of H<sub>2</sub>S services.

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## Methyl Ethyl Ketone (MEK)

### Discussion of MEK

Methyl ethyl ketone (MEK) is used in oil refining for the removal of wax from lube oil stock (see the separate chapter “► [Non-energy Refineries in Petroleum Processing](#)”). Methyl ethyl ketone is a colorless liquid with a sweet/sharp, fragrant, acetone-like odor. It is extremely flammable in both the liquid and vapor phase. The vapor is heavier than air and may spread long distances, and distant ignition and flashback are possible. MEK is highly volatile. Its basic properties are in Table 17.

### Hazards Associated with MEK

#### Inhalation

Causes irritation to the nose and throat. Concentrations above 200 ppm may cause headache, dizziness, nausea, shortness of breath, and vomiting. Higher concentrations

**Table 17** Properties of methyl ethyl ketone

Appearance	Clear, colorless, stable liquid
Purity, % minimum	99.5
Water content, % maximum	0.30
Acidity, % maximum (as acetic acid)	0.003
Color, Pt-Co maximum	10
Specific gravity, 20/20 °C (68/68 °F)	0.805–0.807
Nonvolatile matter (g/100 ml), maximum	0.002
Boiling point	176 °F (80 °C)
Vapor pressure	3 in Hg @ 68 °F (76 mmHg @ 20 °C)
Flash point	–9 °C (16 °F) CC
Autoignition temperature	404 °C (759 °F)
Flammable limits in air, vol%	LEL: 1.4; UEL: 11.4
Extremely flammable	

may cause central nervous system depression and unconsciousness. The airborne exposure limits are:

- Permissible exposure limit (PEL): 200 ppm (TWA)
- Threshold limit value (TLV): 200 ppm (TWA), 300 ppm (STEL)

### **Ingestion**

May produce abdominal pain, nausea. Aspiration into lungs can produce severe lung damage and is a medical emergency. Other symptoms expected to parallel inhalation.

### **Skin Contact**

Causes irritation to skin. Symptoms include redness, itching, and pain. May be absorbed through the skin with possible systemic effects.

### **Eye Contact**

Vapors are irritating to the eyes. Splashes can produce painful irritation and eye damage.

### **Chronic Exposure**

Prolonged skin contact may defat the skin and produce dermatitis. Chronic exposure may cause central nervous system effects.

### **Aggravation of Preexisting Conditions**

Persons with preexisting skin disorders or eye problems or impaired respiratory function may be more susceptible to the effects of the substance.

## **First Aid and Personal Protection**

### **Inhalation**

Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

### **Ingestion**

Aspiration hazard. If swallowed, vomiting may occur spontaneously, but DO NOT INDUCE. If vomiting occurs, keep head below hips to prevent aspiration into lungs. Never give anything by mouth to an unconscious person. Call a physician immediately.

### **Skin Contact**

Immediately flush skin with plenty of soap and water for at least 15 min while removing contaminated clothing and shoes. Get medical attention. Wash clothing before reuse. Thoroughly clean shoes before reuse.

### **Eye Contact**

Immediately flush eyes with plenty of water for at least 15 min, lifting upper and lower eyelids occasionally. Get medical attention.

## Clothing and Protective Equipment

### Ventilation System

A system of local and/or general exhaust is recommended to keep employee exposures below the airborne exposure limits. Local exhaust ventilation is generally preferred because it can control the emissions of the contaminant at its source, preventing dispersion of it into the general work area.

### Personal Respirators

If the exposure limit is exceeded and engineering controls are not feasible, a full-face-piece respirator with organic vapor cartridge may be worn up to 50 times the exposure limit or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier, whichever is lowest. For emergencies or instances where the exposure levels are not known, use a full-face-piece positive-pressure, air-supplied respirator. **WARNING:** Air-purifying respirators do not protect workers in oxygen-deficient atmospheres.

### Skin Protection

Wear impervious protective clothing, including boots, gloves, lab coat, apron, or coveralls, as appropriate, to prevent skin contact. Butyl rubber is a suitable material for personal protective equipment.

### Eye Protection

Use chemical safety goggles and/or a full-face shield where splashing is possible. Maintain eye wash fountain and quick-drench facilities in work area.

## Fire Prevention and Fighting

### Fire

MEK is extremely flammable. Refer to Table 17 for flammability data.

### Explosion

Above the flash point, vapor-air mixtures are explosive within flammable limits noted in Table 17. Vapors can flow along surfaces to distant ignition sources and flash back. Contact with strong oxidizers may cause fire. Sealed containers may rupture when heated. They are sensitive to static discharge.

### Fire Extinguishing Media

Dry chemical, foam, or carbon dioxide are suitable extinguishing agents. Water spray may be used to keep fire-exposed containers cool, dilute spills to nonflammable mixtures, protect personnel attempting to stop leaks, and disperse vapors.



### Special Information

In the event of a fire, wear full protective clothing and NIOSH-approved self-contained breathing apparatus with full-face piece operated in the pressure demand or other positive-pressure mode. This highly flammable liquid must be kept from sparks, open flame, hot surfaces, and all sources of heat and ignition.

### Accidental Release Measures

Ventilate the area of any leak or spill. Remove all sources of ignition. Wear appropriate personal protective equipment as noted above. Isolate the hazard area. Keep unnecessary and unprotected personnel from entering. Contain and recover liquid when possible. Use non-sparking tools and equipment. Collect liquid in an appropriate container or absorb with an inert material (e.g., vermiculite, dry sand, earth) and place in a chemical waste container. Do not use combustible materials, such as sawdust. Do not flush to sewer! If a leak or spill has not ignited, use water spray to disperse the vapors, to protect personnel attempting to stop leak, and to flush spills away from exposures.

### Storage and Handling

MEK is usually delivered to a refinery by road or rail truck. It may be stored in small bullets or a cone roof tank under an inert gas blanket. The materials of construction normally include appropriate grades of carbon steel.

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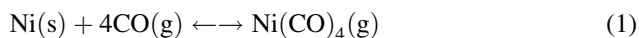
## Nickel Carbonyl (Ni(CO)<sub>4</sub>)

### General Discussion of Nickel Carbonyl

Nickel carbonyl is one of the most toxic substances which may be encountered in a petroleum processing facility anywhere CO is present along with nickel in a reduced state. From experience, the nickel does not need to be present as metal directly; Ni(CO)<sub>4</sub> has been detected when spent NiMo hydrotreating catalyst has been exposed to air and smoldered.

It is stable at ambient pressure below ~400 °F (~204 °C).

Nickel carbonyl is formed by the reaction of CO with nickel via the equation:



While most literature on Ni(CO)<sub>4</sub> discusses it as a liquid, it would be most likely encountered as a gas in the refining environment. It has been found in hydrogen plant vapors from the reforming furnace (Ni catalyst and CO present) and is likely to be present in methanator reactor effluent (also CO and Ni). As noted above, it has

been detected in gases from smoldering spent NiMo hydrotreating catalysts. It can also be adsorbed on NiMo catalysts and released on exposure to air.

There should be no reason to handle nickel carbonyl in bulk. Your primary concern is the possible presence of it as a trace gas and managing it as a hazardous material within the process equipment, especially during maintenance activities.

## Chemical and Physical Properties of Nickel Carbonyl

Some of the key chemical and physical properties of nickel carbonyl are listed in Table 18.

Note that it is a heavy vapor that may accumulate in low elevations.

The formation of stable nickel carbonyl depends strongly on the partial pressure of CO, assuming nickel is present. The equilibrium equation is:

$$P_{\text{Ni}(\text{CO})_4} = [P_{\text{CO}}]^4 \times 10^{[8546/T - 21.64]} \quad (2)$$

where:

$P_{\text{Ni}(\text{CO})_4}$  = partial pressure of nickel carbonyl, atmospheres

$P_{\text{CO}}$  = partial pressure of CO, atmospheres

$T$  = absolute temperature, °K

Once formed, the dissociation back to nickel and CO is not instantaneous but may require several minutes. The formation of Ni(CO)<sub>4</sub> is hindered by the oxide

**Table 18** Some key properties of nickel carbonyl

Chemical formula	Ni(CO) <sub>4</sub>
Molecular weight	170.73
Relative density	5.9 (air = 1.0)
Autoignition temperature	140 °F (60 °C)
Flammability	Very flammable
Explosive limits	2–34 vol% in air
Color	Colorless, invisible
Odor	Musty, like brick dust (don't try to find out, however) (threshold = 1–3 ppm)
Boiling point	109 °F (43 °C)
Melting point	1.0 °F (–17.2 °C)
Reactivity	Dangerous with oxidizers and bases
Solubility in water	0.018 g/100 ml (50 °F, 10 °C)
Solubility in organics	Soluble

coating of Ni catalyst and oxygen. Formation of  $\text{Ni}(\text{CO})_4$  is accelerated by ammonia and  $\text{H}_2\text{S}$ .

## Hazards of Nickel Carbonyl

This is one of the most toxic materials encountered in refining (or any industry for that matter). Table 19 lists the applicable exposure limits.

Via the various exposure routes, the toxic effects are:

- Inhalation:
  - Short-term: Cough, fever, nausea, vomiting, diarrhea, chest pain, difficulty breathing, irregular heartbeat, headache, dizziness, disorientation, bluish skin color, blood disorders, liver enlargement, convulsions, and death
  - Long term: Reproductive effects and cancer
- Skin contact:
  - Short-term: Irritation, allergic reactions, rash, itching. It may be absorbed through the skin and produce effects similar to inhalation.
  - Long term: Irritation and allergic reactions. May experience reactions similar to inhalation.
- Eye contact:
  - Short-term: irritation.
  - Long term: No information available.
- Ingestion:
  - Short-term: Cough, fever, nausea, vomiting, diarrhea, chest pain, difficulty breathing, irregular heartbeat, headache, dizziness, disorientation, and bluish skin color
  - Long term: No information available

In addition to the health impacts, nickel carbonyl in sufficient quantities is highly flammable and can be detonated by shock, friction, or moderate heating. You should not normally encounter it in any concentration that would cause these hazards, however.

NFPA rating for nickel carbonyl is 4 (health) – 3 (flammability) – 3 (reactivity).

**Table 19** Exposure limits and toxicity of nickel carbonyl

Agency	Limit type	ppb	mg/m <sup>3</sup>	Basis
US OSHA	PEL	1	0.007	8 h TWA
US NIOSH	REL	1	0.007	10 h TWA
	IDLH	(~3 ppm)		
ACGIH (USA)	TLV	1	0.007	10 h TWA

LC50 (Rat) by inhalation: 35 ppm (30 min)

Known human carcinogen

## Protective Equipment for Nickel Carbonyl

If exposure to significant amounts of nickel carbonyl may be possible, the normal precautions (in addition to the normal hardhat, safety glasses, flame-retardant clothing, and safety shoes) are:

- Provision of adequate ventilation, which may include explosion-resistant fans.
- Eye protection: splash-resistant chemical goggles with face shield. Emergency eyewash in immediate area.
- Clothing: chemical-resistant clothing if liquid may be present.
- Gloves: chemical-resistant gloves if liquid may be present.
- Respirator: Full-face, self-contained, or supplied-air respirator operating on pressure demand (or other positive-pressure mode) with an escape bottle. A full-face, air-purifying respirator with a suitable canister is only usable for emergency escape.

If there is any possibility of IDLH atmosphere with nickel carbonyl, a supplied-air breathing apparatus is required. Do not take any chances.

Note that these precautions apply for personnel at catalyst dump points (such as at the top of flow bins) as well as those working in enclosed spaces with catalysts.

## Management of Nickel Carbonyl Hazards

The primary focus of nickel carbonyl management in a refinery is prevention of its formation.

In hydroprocessing units, where nickel catalysts and deposits are common, it is normal practice to cool reactors to about 450–500 °F (232–260 °C) and then test the circulating gases for CO. Different companies and units use different limits, but the CO in the gas must normally be less than 10–100 ppm before cooling further. This ensures the nickel carbonyl content will not exceed 1 ppb as the catalyst is cooled. Purging with nitrogen further reduces the risk of formation. You have to be careful to avoid introducing any more CO after the test through the hydrogen or nitrogen used. After testing, it is normally best to avoid bringing in anything except vaporized, cryogenic nitrogen.

If the CO test shows a CO level above the allowable, the reactor should be held at temperature (or re-heated above 450 °F). The system should be purged and any possible CO (or oxygen or CO<sub>2</sub>) sources eliminated until the CO level drops to the allowable range. Once a CO source is stopped in a circulating system with hydrogen, the remaining CO will be methanated and disappear from the system.

In hydrogen production, CO and reduced nickel catalysts are part of the process. To eliminate the possibility of nickel carbonyl formation in hydrogen plants on shutdown, the feedstock should be pulled at high temperature. No oxygen, CO<sub>2</sub>, or

other possible CO formation sources should be permitted to reenter the system during cooling. The system should be thoroughly purged with nitrogen (CO-free) before cooling below 400 °F (204 °C).

Precautions during catalyst handling include:

- Continuous monitoring of the inert atmosphere for CO and oxygen. Stop and purge if these are detected above allowable limits.
- Use fresh air equipment at the dump point where catalyst smoldering may occur.
- Keep catalyst spills wet to prevent smoldering.
- Dump potentially self-heating catalysts into inert-purge containers or flood and dump wet.

CO testing by detection tubes is normally employed to verify no CO is present. Follow the detector tube manufacturer's instructions. For Dräger tubes:

- Hydrogen gas atmosphere: use tube 8/a for CO with solid sodium hydroxide and carbon pre-tubes.
- Nitrogen or natural gas atmosphere: use tube 5/c for CO with the NaOH and carbon pre-tubes.
- Olefins present in the gas will interfere with the analysis.

While detector tubes are available for nickel carbonyl, the detector range is 0.1 ppm (100 ppb), which is too high to help in this case.

Nickel carbonyl itself can be analyzed using wet chemical or adsorption/desorption methods. US NIOSH has procedures available. These tests are too slow for most practical monitoring, however.

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## Nitrogen (N<sub>2</sub>, LN<sub>2</sub>)

### General Discussion of Nitrogen

The uses and hazards of nitrogen are addressed somewhat under the topics “► [Utilities in Petroleum Processing](#)” and “► [Safety Systems for Petroleum Processing](#)” of this handbook. We will explore the hazards of handling these materials a little more quantitatively here.

As background and refresher, nitrogen is used extensively in most refineries today. Some of the common uses are:

- Purging of equipment and piping to eliminate air or hydrocarbons/hydrogen
- Purging of compressor seals
- Storage tank or vessel blanketing to prevent air contact
- As emergency backup pneumatic gas
- Chilling of some analytical instruments

In normal practice, the nitrogen is received as a refrigerated liquid. The liquid is stored in a double-walled, insulated cryogenic storage tank and is vaporized as needed to supply facility needs. For large, intermittent uses, nitrogen trailers and fired vaporizers are used. Some facilities generate their own nitrogen cryogenically or, more commonly, using a PSA or membrane system. This is discussed in more detail in the chapter on “► [Utilities in Petroleum Processing](#).”

## Chemical and Physical Properties of Nitrogen

Table 20 lists the key properties of nitrogen relevant to the current discussion.

Nitrogen may be found in a refinery as a refrigerated liquid or as a vapor. The most common exposure risk is from inhalation of excessive nitrogen vapors.

Note that the cryogenic liquid that is normally handled in bulk is extremely cold.

Nitrogen will not support combustion at any condition normally encountered in a refinery.

## Hazards of Nitrogen

Nitrogen, as used in a petroleum processing facility, presents the following hazards:

- Oxygen depletion in the atmosphere
- Risk of burns or frostbite from cryogenic liquid contact
- Physical injury from high pressure gas

The most important of these hazards is normally asphyxiation from an oxygen-deficient atmosphere. Since nitrogen is colorless and odorless, it provides no warning of oxygen deficiency.

Otherwise, nitrogen is not toxic and causes no other issues. These hazards are discussed more fully in the handbook topic “► [Safety Systems for Petroleum Processing](#).”

Symptoms of oxygen deficiency from a nitrogen atmosphere would include:

- Headache
- Dizziness

**Table 20** Some key properties of nitrogen

Molecular weight	28.02
Specific gravity	Vapor: 0.967 (air = 1)
	Liquid: 50.46 lb/ft <sup>3</sup> (808.3 kg/m <sup>3</sup> )
Boiling point	−320 °F (−196 °C)
Freezing point	−346 °F (−210 °C)
Autoignition temperature	Will not support combustion
Explosive limits	Not applicable

- Fatigue
- Nausea
- Euphoria
- Or simply unconsciousness without warning (within seconds at low oxygen levels)

Most often, unconsciousness is so rapid there is no time for other symptoms to manifest.

In working with the cryogenic liquid, any exposure of personnel to the liquid (as in skin) will result in immediate/instantaneous, severe burns.

## Protective Equipment for Nitrogen Handling

The best protection against nitrogen creating an oxygen deficiency is adequate ventilation and exclusion of all personnel from areas near inerted equipment. Anyone that must approach inerted equipment must wear fresh air breathing apparatus (SCBA or supplied air).

In addition to the normal refinery PPE, areas where there may be a nitrogen deficiency are normally monitored by fixed or personal monitors for oxygen with audible, vibration, and visual alarms. Any alarm would require immediate evacuation.

Refer to the topic “► [Safety Systems for Petroleum Processing](#)” for additional discussion.

When handling cryogenic liquid nitrogen, chemical-resistant, insulated gloves, and face shield should be worn.

Large spills of liquid will require fresh air breathing apparatus.

## Storage and Handling of Nitrogen

Refer to “► [Utilities in Petroleum Processing](#)” for a detailed discussion of nitrogen handling systems and to “► [Safety Systems for Petroleum Processing](#)” for a discussion of managing potentially oxygen-deficient atmospheres.

Fresh air equipment (e.g., SCBAs) should be immediately available where liquid nitrogen is handled and in areas where oxygen deficiency may occur.

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## Sulfiding Chemicals

### General Discussion of Sulfiding Chemicals

Most hydroprocessing catalysts are not very active as received. The most active forms of these materials are the sulfides or the catalytic metals. To create the active forms, the catalysts are activated or “sulfided” using H<sub>2</sub>S or one of several other sulfiding agents in a circulating hydrogen stream. Today, H<sub>2</sub>S is not commonly used.

At one time carbon disulfide ( $\text{CS}_2$ ) would have been included here; but it is rarely used today because of the extreme fire hazard it represents.

In another application, sulfiding chemicals are used to temporarily suppress cracking activity in naphtha reformers during startup.

Aside from  $\text{H}_2\text{S}$ , the most common sulfiding agents include:

- Dimethyl sulfide (DMS)
- Dimethyl disulfide (DMDS)
- Di-tertiary butyl polysulfide (TBPS)
- Di-tertiary nonyl polysulfide (TNPS)

There are proprietary versions of some of these chemicals, such as Sulfrzol<sup>®</sup> 54, but the hazards are similar.

These chemicals present a range of hazards from relatively low hazard to suspected carcinogens. We will explore the hazards and their management here.

## Chemical and Physical Properties of Sulfiding Agents

Table 21 provides some of the key, relevant properties for various sulfiding agents.

Most of these chemicals have an unpleasant smell. Often the smell is associated with residual traces of the mercaptans left over from manufacturing.

Note that the polysulfides decompose on heating before they boil. The decomposition products include mercaptans and  $\text{H}_2\text{S}$ . Under some conditions, the polysulfides may form solid deposits and plug lines, especially if boiled at high temperatures without the presence of other liquid hydrocarbons.

Some of these compounds are excellent solvents for many common materials, especially shoes.

## Hazards of Sulfiding Agents

The odors of these materials provide an early warning of potential exposure. Spills of the heavier liquids, however, just look like water.

Note that some people react much more strongly to even the slightest odor of some of these compounds. Reactions may include nausea and vomiting.

All the compounds present a fire hazard, in addition to health hazards. DMS is especially volatile and tends to load up the treat gas circulation with methane. It is not used much anymore. DMDS, TBPS, and TNPS (or their branded counterparts) are most common.

Table 22 summarizes the key hazards and exposure limits for these materials.

All of these materials are flammable. They are all toxic to fish and long lasting in an aquatic environment, so they should not be allowed into storm drains or effluents without treatment.

The products of combustion will include  $\text{CO}$ ,  $\text{SO}_2$ , and  $\text{H}_2\text{S}$  if the materials burn.



**Table 21** Some key properties of sulfiding agents

Chemical	Dimethyl sulfide (DMS)	Dimethyl disulfide (DMDS)	Di- <i>t</i> -butyl polysulfide (TBPS)	Di- <i>t</i> -nonyl polysulfide (TNPS)
Formula	(CH <sub>3</sub> ) <sub>2</sub> S	(CH <sub>3</sub> ) <sub>2</sub> S <sub>2</sub>	C <sub>8</sub> H <sub>18</sub> S <sub>x</sub> (x = avg ~2.8)	C <sub>18</sub> H <sub>38</sub> S <sub>x</sub> (x = avg 5.0)
Molecular weight	62.13	94.2	~204 avg	414 avg
Color (liq)	Clear	Pale yellow	Yellow	Yellow to yellow-orange
Odor	Stench	Strong garlic-like odor	Slightly acrid	Mildly unpleasant
Odor threshold	<1 ppm	~8–10 ppb		
Sulfur, wt%	51.5	67.9	~44 avg	35–39
Specific gravity	Gas: 2.1 (air=1)	Gas: 3.25 (air=1)	Liq: 1.07 (68 °F, 20 °C)	Liq: 1.05 (68 °F, 20 °C)
	Liq: 0.85 (68 °F, 20 °C)	Liq: 1.06 (39 °F, 4 °C)		
Boiling point	99 °F (38 °C)	228 °F (109 °C)	342–356 °F (172–180 °C) (decomposes)	407–507 °F (208–264 °C) (decomposes)
Freezing point	–145 °F (–98.3 °C)	–121 °F (–85 °C)	37 °F (3 °C)	<–4 °F (<–20 °C)
Flash point	–54 °F (–48 °C)	59 °F (15 °C)	217 °F (103 °C) CC	277–291 °F (136–144 °C) PMCC
Solubility in water	2.0 wt% (68 °F/20 °C)	~0.25 wt% (68 °F/20 °C)	Insoluble	Insoluble
Autoignition temperature	403 °F (206 °C)	Not available	437 °F (225 °C)	464 °F (240 °C)
Explosive limits	2.2–19.7 vol%	1.1–16 vol%	Not available	Not available
Viscosity (liq)	0.29 cP (68 °F, 20 °C)	0.62 cP (68 °F, 20 °C)	10 cP (68 °F, 20 °C)	24–34 cP (122 °F, 50 °C)

## Protective Equipment for Sulfiding Chemicals Handling

In addition to the normal petroleum processing facility PPE (hardhat, flame-retardant clothing, safety glasses, safety shoes), the recommended personal protective equipment when handling these materials includes:

- Eye/face protection: Goggles, face shield. Eye wash station should be available nearby.

**Table 22** Hazards and exposure limits of common sulfiding agents

Chemical	Dimethyl sulfide (DMS)	Dimethyl disulfide (DMDS)	Di- <i>t</i> -butyl polysulfide (TBPS)	Di- <i>t</i> -nonyl polysulfide (TNPS)
<b>Exposure effects</b>				
Inhalation	Headache, memory loss, confusion, convulsions, unconsciousness; ACGIH TLV = 10 ppm (8 h)	Nausea, headache, or dizziness, drowsiness, unconsciousness; ACGIH limit 0.5 ppm TWA	Unlikely route of exposure	Unlikely route of exposure
Eyes	Irritation, inflammation	Irritation, may be irreversible	Almost no irritation	Slight irritation
Skin	Stinging, reddening, removal of skin oils	Irritation, redness, rash, removal of oils, may also see central nervous system effects like inhalation	Allergic reaction, redness, rash	Slight irritation
Ingestion	Irritation of the mouth, throat, stomach; nausea, vomiting	Irritation of the mouth, throat, stomach; nausea, vomiting	Aspiration hazard to lungs, increased breathing and heart rate, coughing, respiratory distress	Slightly toxic
Chronic	None identified	Sensitizer	Sensitizer	No effects expected
Preexisting conditions	Aggravates respiratory diseases	No information	No information	No information
Carcinogenic	Not listed	Suspected	No information	No information
<b>Toxicity</b>				
Inhalation	LD50 = 40,250 ppm (102 mg/l, rat)	Slightly toxic, LC50 805 ppm (rat, 4 h)	Not available	LC50 >50 mg/l (4 h, rat)
Ingestion	LD50 = 3,700 mg/kg (mouse)	Moderately toxic, LD50 = 290–500 mg/kg (rats)	Slightly toxic, LD50 >2,000 mg/kg (rat)	Slightly toxic, LD50 = 19,550 mg/kg (rat)

Dermal	LD50 = 10,200 mg/kg (rat)	Slightly toxic, LD50 >2,000 mg/kg	Slightly toxic, LD50 >2,000 mg/kg (rat)	Slightly toxic, LD50 >2,000 mg/kg (rabbit)
Skin irritation	Mild (rabbit), LD50 >5 g/kg	Slight (rabbit)	Slight (rabbit)	Slight
Eye irritation	Severe (rabbit)	May cause irreversible eye damage	Slight (rabbit)	Slight
Fire				
Flammability	High, vapors may ignite from remote sources, possible explosion	High, vapors may ignite from remote sources, possible explosion	Moderate	Moderate
Hazardous combustion products	Sulfur dioxide, H <sub>2</sub> S, CO	Sulfur dioxide, H <sub>2</sub> S, CO	Sulfur dioxide, H <sub>2</sub> S, CO	Sulfur dioxide, H <sub>2</sub> S, CO
Hazard ratings (health/flammability/reactivity)				
HMIS	2/4/0	3/3/1	1/2/0	Not available
NFPA	1/4/0	2/4/0	2/1/0	0/1/0

References: Various MSDSs and product data sheets from manufacturers and distributors. These are the best data available, but there are conflicts among some of the data sources on effects, exposures, and ratings

- Respiration: if strong vapor or mist present, use appropriate organic vapor cartridge respirator, SCBA, or supplied-air breathing apparatus. For vessel entry or high levels of potential exposure, use SCBA or supplied air only.
- Skin/clothing: Butyl or nitrile rubber gloves (not leather). In some cases, aprons, rubber boots, or a rubber suit may be needed. A safety shower should be available in the immediate area.
- Other: Do not smoke in areas where these chemicals may be present. Wash hands and other potentially exposed areas of skin thoroughly with soap and water before eating, smoking, or using toilet facilities.

In the event of a fire involving the chemicals, wear SCBA, protective clothing (which may include a rubber suit), and gloves.

Have bleach (2–5 %) or LAB solution available in a sprayer to manage odors from small spills. See below.

### Storage and Handling of Sulfiding Chemicals

These chemicals can be handled like other hydrocarbons of similar vapor pressure. They are stable under normal conditions, but the vapors can ignite readily.

Carbon and stainless steels are suitable for vessels and piping. When making up threaded piping, normal pipe compound is not suitable. Makeup temporary threaded piping with Teflon<sup>®</sup> (Rect-R-Seal<sup>™</sup> or equal). Pressure test all temporary piping before allowing any sulfiding chemical into the lines. It is a big, stinky mess if the lines leak once they contain the sulfiding chemicals.

The sulfiding chemicals are normally brought into a facility by truck or iso-container. Some may also be handled in barrels or tote-bins, depending on the quantity required. Small quantities may be kept onsite for activities like naphtha reformer startup, but large quantities are seldom stored onsite. They are normally used directly from the tank truck or iso-container.

The trucks are staffed by experienced and trained personnel (supplied by the chemical vendor or trucking company) around the clock until the sulfiding activity is completed. Sulfiding chemicals are normally pressured out of the trucks or iso-containers by nitrogen through metering and an injection pump into the process.

In the event of small spills, spray the chemical with a *dilute* solution (~2–5 %) of bleach to neutralize odors. This converts the chemicals to dimethyl sulfoxide, which may be treated in a wastewater treatment plant. “Liquid Alive Bacteria (LAB)” solution is also effective when used in accordance with the manufacturer’s instructions. Concentrated bleach or solid bleach should *not* be used as it may react violently or cause a fire.

Absorb small spills in a sorbent. Collect the sorbent in a metal container and dispose of as a hazardous waste.

In the event of a large spill or fire:

- Get people out of the area.
- Contain the spill if possible. Avoid disposal or runoff. Runoff will be an ecological problem. Get your environmental department involved.

- Eliminate all ignition sources – remember the vapors of these chemicals are heavy and can follow low spots or sleeperways for a long distance to an ignition source.
- Wear impervious gloves, skin protection (including a rubber suit).
- If the material ignites or explodes:
  - Combustion and thermal decomposition products will be toxic (CO, SO<sub>2</sub>, H<sub>2</sub>S), so full-face, positive-pressure fresh air equipment is required.
  - Extinguishing media: dry chemicals, CO<sub>2</sub>, alcohol-resistant foam, and other foams. Water spray may be used also to cool and protect equipment, but contain runoff. High volume water jets are *not* suitable.
  - Keep surrounding equipment cool with water spray.

These materials are routinely handled in petroleum facilities without incident. Their odor reminds people to use care in handling them.

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## Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>)

### General Discussion of Sulfuric Acid

Sulfuric acid is found in several locations in refineries or other processing facilities. It is used for pH control in cooling towers and other services. It is the primary catalyst in some alkylation processes. Some refineries even have sulfuric acid plants associated with them to dispose of sulfur removed by other processes.

Sulfuric acid is safely handled in bulk regularly in facilities, but it can be very hazardous if not handled properly. The most common form of H<sub>2</sub>SO<sub>4</sub> is concentrated acid. Dilute acid is corrosive to steel, whereas concentrated acid is not very corrosive to steel at most ambient conditions. Hence, we like to handle the acid as a concentrate.

### Properties of Concentrated Sulfuric Acid

Table 23 presents the relevant properties of concentrated acid, the most common used in refining. More dilute grades may be encountered.

### Hazards of Sulfuric Acid

Sulfuric acid presents a number of hazards. Table 24 summarizes the exposure limits and toxicity data.

Health effects described by exposure route include:

- Inhalation: May cause severe irritation of respiratory tract with sore throat, coughing, shortness of breath, and delayed lung edema. Causes chemical burns to respiratory tract. May cause inflammation. Destructive to mucous membranes. May cause headache, vomiting, nausea, pulmonary edema. Corrosive and toxic. May be fatal.
- Eyes: Severe eye burns. May be irreversible.

**Table 23** Some key properties of concentrated sulfuric acid

Chemical formula	H <sub>2</sub> SO <sub>4</sub>
Molecular weight	98.079
Appearance	Clear, colorless, odorless liquid
Purity, %	98
pH, 1N solution	0.3
Specific gravity	1.841 (~1.84 kg/l)
Boiling point	554 °F (290 °C)
Vapor pressure	<0.00005 in Hg @ 68 °F (<0.0012 mmHg @ 20 °C)
Freezing point	50.6 °F (10.3 °C)
Vapor density	1.2 kg/m <sup>3</sup>
Decomposition temperature	644 °F (340 °C)
Viscosity	26.7 cP (68 °F, 20 °C)

**Table 24** Exposure and toxic effects of concentrated sulfuric acid

Agency	Limit type	mg/m <sup>3</sup>	Basis
US OSHA	Limit	1	8 h TWA
US NIOSH	REL	1	10 h TWA
ACGIH (USA)	TLV	1	10 h TWA
	STEL	3	
Toxicity			
Inhalation	LC50 (rat)	51 mg/m <sup>3</sup>	2 h
Oral	LD50 (rat)	2140 mg/kg	
Ecology	Harmful to aquatic life in very low concentrations		
Workers exposed to sulfuric acid mist showed increase in laryngeal, nasal, sinus, and lung cancer			

- Skin: Skin burns. Defatting dermatitis with prolonged exposure. May be fatal.
- Ingestion: May cause severe and permanent damage to digestive tract, burns in mouth, pharynx, and gastrointestinal tract. May cause nausea, vomiting, and abdominal pain. Corrosive and toxic. May be fatal.
- Chronic exposure: Nosebleeds, nasal congestion, erosion of teeth, perforation of nasal septum, chest pain, and bronchitis. Eye exposure may cause conjunctivitis. May cause death. Corrosive to body tissues.

## PPE for Handling Sulfuric Acid

The following minimum PPE are recommended beyond the typical refinery worker's PPE when handling sulfuric acid:

- Eye protection: Splash-proof chemical safety goggles and face shield.
- Skin protection: Neoprene or polyethylene gloves.
- Clothing: Apron or other impervious clothing (e.g., rain coat), rubber boots, other clothing to prevent skin contact.

- Respiratory protection: Use a US NIOSH-approved (or equal) respirator when necessary.
- Ventilation: Use only with adequate ventilation. In a lab, hand the acid in a fume hood.
- Other: Eye wash and safety shower should be immediately available in any area where sulfuric acid is handled.

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## Storage and Handling of Sulfuric Acid

For concentrated sulfuric acid, carbon steel tanks and piping are normally adequate. Temperature must be kept low in carbon steel to prevent corrosion. If higher temperatures or dilute acid are handled, higher alloys are required. Consult with a metallurgist on the proper alloys for your application.

The acid is normally stored in atmospheric vessel vented through a desiccant cartridge to prevent moisture from the air entering the tank. Sulfuric acid is a desiccant in its own right, so avoiding any moisture is critical. The storage tanks are typically within chemical containment dikes (epoxy-coated concrete). The dike drain is managed closed to ensure any leaks are not sent to the sewer uncontrolled.

There should always be an eyewash and safety shower immediately adjacent to the acid storage area.

Acid is generally unloaded and moved by nitrogen or air pressure among users. The final users will generally use pumps for controlled injection.

Sulfuric acid will not burn but can decompose to yield poisonous sulfur oxide vapors if the storage area becomes involved in a fire. Positive-pressure, supplied-air respiratory equipment is required if fighting a fire near an acid storage tank. Use water spray on the outside of the tank to keep it cool.

Do not allow water to be pumped into an acid storage tank. The heat of solution will cause foaming and possible tank failure.

Safe handling of concentrated sulfuric acid is common in a refinery, in spite of the hazards. The key points to remember are:

- Keep the acid contained and cool.
- Do not allow any personnel contact with the acid.
- Keep water away from the concentrated acid until you are ready for use, then add acid into a large excess of water.

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## Hazardous Materials Handling Summary

Table 25 pulls together some of the most important information from the foregoing sections of this chapter for convenience. For more details, consult the individual sections and the MSDS sheets from your supplier or company for the specific materials of interest.

Table 25 Summary of key hazardous materials handling information

Material	Amines for gas treating									
	Monoethanolamine	Dietanolamine	Methyldiethanolamine	Diglycolamine	Diisopropanolamine	Sulfino	Ammonia	26 1B6	20.5 B6	
Abbreviation/alias	MEA	DEA	MDEA	DGA	DIPA	–	–	Aqua ammonia	Aqua ammonia	
Chemical formula	$\text{HOC}_2\text{H}_4\text{NH}_2$	$(\text{HOC}_2\text{H}_4)_2\text{NH}$	$(\text{HOC}_2\text{H}_4)_2\text{NCH}_3$	$\text{H}(\text{OC}_2\text{H}_4)_2\text{NH}_2$	$(\text{HOC}_3\text{H}_7)_2\text{NH}$	Mixture	$\text{NH}_3$	$\text{NH}_3$	$\text{NH}_3$	
Molecular weight	61.1	105.1	119.16	105.14	133.19	120.17	17.0305	–	–	
Physical states	Pure liquid, as received	Pure liquid, as received	Pure liquid, as received	Pure liquid, as received	Pure liquid, as received	Aq. solution	Liq. vap	Aq. liq. vap	Aq. liq. vap	
Color	Colorless	Colorless to yellow	Colorless to Lt. yellow	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
Odor	Ammoniacal	Ammoniacal	Amine-like	Mild amine	Ammonia-like	Fishy hydrocarbon	Strong acid	Strong acid	Strong acid	Strong acid
Vapor Sp. Gr. (air = 1)	2.1	3.6	4.1	3.6	4.6	4.6	0.59	0.59	0.59	0.59
Liquid Sp. Gr. (nominal)	1.01	1.09	1.04	1.06	0.99	1.26	0.68	0.90	0.93	0.93
Boiling point, °F/°C	338.5/170	515.1/268	477/247	405.5/208	479.7/249	545/285	–28/–33	85/29	123/51	123/51
Freeze point, °F/°C	50.5/10.2	77.2/25.1	–9/–23	9.5/–12.5	107.6/42	81.7/27.6	–108/–78	–110/–79	–30/–34	–30/–34
Flash point, °F/°C	200/93.3	295/146	265/129	260/127	255/124	350/177	Not available	Not available	Not available	Not available
Autoignition, °F/°C	Not available	Not available	509/265	698/370	545/285	Not Available	1,204/651	See anhydrous	See anhydrous	See anhydrous
Decomposition, °F/°C	Not available	Not available	Not available	Not available	Not available	Not available	Not available	Not available	Not available	Not available

a



Flammability limits (air)	Not available	Not available	0.9–8.4	2.6–11.7	1.1–8.5	Not available	15–28 %	See anhydrous	See anhydrous
Exposure limits (always verify current values)	TLV=3 ppm STEL=6 ppm	TLV=2 mg/m <sup>3</sup>	Not available	Not available	US PEL=5 ppm, UK STEL=15 ppm	Not available	TLV=25 ppm STEL=35 ppm IDLH = 300 ppm	See anhydrous	See anhydrous
Primary hazard routes	Skin, inhalation	Skin, inhalation	Skin, inhalation	Skin, inhalation	Skin, inhalation	Skin, inhalation	Inhalation, skin, eyes	Inhalation, skin, eyes	Inhalation, skin, eyes
Exposure type									
Fire/explosion	Remote	Remote	Remote	Remote	Remote	Remote		Unlikely	Unlikely
Toxicity	X	X	X	X	X	X	X	X	X
Ecological impacts									
Aqueous env.	Toxic	Medium toxic	Slightly toxic	Slightly toxic	Not Available	Not Available	Highly toxic	Moderately toxic	Moderately toxic
Biodegradable	Yes	Yes	Yes	Yes	Not available	Not available	Yes	Yes	Yes
Firefighting media	Water spray/fog, foam, dry chemical, CO <sub>2</sub>	Water spray/fog, foam, dry chemical, CO <sub>2</sub>	Water spray/fog, foam, dry chemical, CO <sub>2</sub>	Water spray/fog, foam, dry chemical, CO <sub>2</sub>	Water spray/fog, foam, dry chemical, CO <sub>2</sub>	Water spray/fog, alc. foam, dry chemical, CO <sub>2</sub>	Water spray/fog, dry chemical, CO <sub>2</sub>	Water spray/fog, dry chemical, CO <sub>2</sub>	Water spray/fog, dry chemical, CO <sub>2</sub>
Possible added PPE <sup>1</sup>									
Handling area (normal)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots), vapor respirator or supplied air	Goggles, face shield, impermeable clothing (gloves, coveralls, boots), vapor respirator or supplied air	Goggles, face shield, impermeable clothing (gloves, coveralls, boots), vapor respirator or supplied air
Fire or large spill (additional)	SCBA or =, eye protection, protective clothes	SCBA or =, eye protection, protective clothes	SCBA or =, eye protection, protective clothes	SCBA or =, eye protection, protective clothes	SCBA or =, eye protection, protective clothes	SCBA or =, eye protection, protective clothes	SCBA or =, eye protection, protective clothes	SCBA or =, eye protection, protective clothes	SCBA or =, eye protection, protective clothes

(continued)

**Table 25** (continued)

Category		Amines for gas treating																		
		Monoethanolamine				Diethanolamine		Methyldiethanolamine		Dicycloamine		Diisopropanolamine		Sulfinol		Anhydrous		Aqua ammonia		
Abbreviation/alias	MEA	DEA	MDEA	DGA	DIPA	–	–	–	–	–	–	–	–	–	–	–	–	–	–	
Hazard ratings (health – flammability – reactivity)	NFPA 3-1-0	NFPA 2-1-0	HIMS 1-1-0	HIMS 3-1-0	HIMS 2-1-0	HIMS 3-1-0	HIMS 3-1-0	HIMS 3-1-0	HIMS 3-1-0	HIMS 3-1-0	HIMS 3-1-0	HIMS 3-1-0	HIMS 3-1-0	NFPA expect 2-10 based on ingredients	NFPA 3-1-0	NFPA 3-1-0	NFPA 3-1-0	NFPA 3-1-0	NFPA 3-1-0	
References																				
MSDS SOURCES	Dow	Dow	Acros Organics, Dow, Huntsman	Huntsman, Univar	BASF, Hazel Mercantile	Huntsman	Huntsman	Huntsman	Burlington Resources, Shell	Tanner Industries, Air Products	Tanner Industries, Air Products	Tanner Industries, Air Products	Tanner Industries, Air Products	Tanner Industries, Air Products	Tanner Industries, Air Products	Tanner Industries, Air Products	Tanner Industries, Air Products	Tanner Industries, Air Products	Tanner Industries, Air Products	
ARTICLES; BULLETINS; OTHER																				

Category		Catalysts and sorbents																
		Carbon monoxide			Hydro processing		Hydrogen plant		PSA adsorbents		Mole sieves, zeolites		Caustic soda (50%)		Furfural		Hydrofluoric acid	
Material	Benzene	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Abbreviation/alias	Bz																	
Chemical formula	C <sub>6</sub> H <sub>6</sub>	CO	Co, Ni, Mo, sulfides and oxides; alumina; silicates; coke; with contam	Ni and NiO on ceramic support	Molecular sieves, activated carbon, activated alumina	Molecular sieves, zeolites	Molecular sieves, zeolites	Molecular sieves, zeolites	Molecular sieves, activated alumina	Molecular sieves, zeolites	Molecular sieves, zeolites	NaOH	NaOH	C <sub>5</sub> H <sub>4</sub> OCHO	C <sub>5</sub> H <sub>4</sub> OCHO	AHF, HF	AHF, HF	HF
Molecular weight	78.11	28.01	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	40.00	40.00	96	96	20.01	20.01	20.01

Physical states	Liq. vap	Vap	Solid to oily solid	Solid	Solid	Solid	Solid	Aq. liq. solid	Liq. vap	Liq. Vap
Color	Colorless	Colorless	Varies	Gray	White to black depends on product	White to tan	Colorless to white	Colorless to white	Lt. yellow to brown	Colorless
Odor	Sweet aromatic	Odorless	Hydrocarbon	None	None	None	None	None	Almond	
Vapor Sp. Gr. (air =1)	2.7	0.97	N/A	N/A	N/A	N/A	N/A	N/A	3.3	0.69
Liquid Sp. Gr. (nominal)	0.88	-	N/A	N/A	N/A	N/A	1.53	1.53	1.16	1.00
Boiling point, °F/°C	176/80	-312/-191	N/A	N/A	N/A	N/A	284-140	284-140	324/162	67/19
Freeze point, °F/°C	42/6	-337/-205	N/A	N/A	N/A	N/A	54/12	54/12	-38/-39	-117/-83
Flash point, °F/°C	12/-11	Not available	Varies	N/A	N/A	N/A	N/A	N/A	140/60	N/A
Autoignition, °F/°C	1097/592	1121/605	Not available	N/A	N/A	N/A	N/A	N/A	601/316	N/A
Decomposition, °F/°C	Not available	N/A	Not available (may liberate CO, H <sub>2</sub> S, other gases)	Not available (may liberate CO, H <sub>2</sub> S, or Ni(CO) <sub>4</sub> , or other gases)	Not available (may liberate CO, H <sub>2</sub> S, or other gases if wet)	Not available (may liberate CO, H <sub>2</sub> S, or other gases if wet)	N/A	N/A	Not available - unstable in light and air	Not available - decomposition products include halogens
Flammability limits (air)	1.3-7.1	12.5-74.2	N/A	N/A	N/A	N/A	N/A	N/A	2.1-19.3	N/A
Exposure limits (always verify current values)	TLV=0.5-1 ppm STEL=2.5-5 ppm	TLV=25 ppm STEL=200 ppm	N/A	Refer to nickel hazards	Refer to silica hazards	Refer to silica hazards	2 mg/m <sup>3</sup> mist or dust	2 mg/m <sup>3</sup> mist or dust	TLV=2 ppm STEL=5 ppm	TLV=0.5 ppm skin, STEL=6 ppm
Primary hazard routes	Inhalation, skin	Inhalation	Inhalation (dust, vapors), skin	Inhalation (dust, vapors)	Inhalation (dust, vapors)	Inhalation (dust, vapors)	Skin, eyes, inhaled mist or dust	Skin, eyes, inhaled mist or dust	Inhalation, skin	Inhalation, skin
Exposure type										
Fire/explosion	X	X	Smoldering	N/A	X (act. carbon)	N/A	N/A	N/A	X	N/A

(continued)

Table 25 (continued)

Category	Catalysts and sorbents				Hydrofluoric acid			
	Carbon monoxide	Hydro processing	Hydrogen plant	PSA adsorbents		Mole sieves, zeolites	Caustic soda (50%)	Furfural
Material	Benzene							
Abbreviation/alias	Bz	-	K172	-	-	-	-	AHF, HF
Toxicity	X	X	Ni dust, carcinogen	Low	Low	X	X	High
Ecological impacts								
Aqueous env.	Not major	N/A	Slightly toxic, potential groundwater contamination	Not available	Not available	Toxic, avoid contamination of effluent	Toxic	Not available
Biodegradable	Yes	N/A	No	Not available	Not available	No	Yes	No
Firefighting media	Water spray/fog, alc. foam, dry chemical, CO <sub>2</sub> , Halon	Water spray/fog, alc. foam, dry chemical	Water spray/fog, foam, dry chemical, CO <sub>2</sub>	N/A	N/A	N/A	Water spray/fog, foam, dry chemical, CO <sub>2</sub>	N/A
Possible added PPE <sup>1</sup>								
Handling area (normal)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots), vapor respirator or supplied air	SCBA or =, personal CO monitor	Dust respirator, goggles, face shield, gloves, chemical-resistant clothing	Dust respirator, goggles, gloves	Dust respirator, goggles, gloves	Goggles, face shield, impermeable clothing (gloves, coveralls, boots)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots), vapor respirator or supplied air	Goggles, face shield, impervious acid suit, boots and gloves, SCBA
Fire or large spill (additional)	SCBA or =, eye protection, protective clothes	SCBA or =	SCBA or =	N/A	N/A	N/A	SCBA or =, eye protection, protective clothes	SCBA
Hazard ratings (health – flammability – reactivity)	HIMS 2-3-0, NFPA 2-3-0	HIMS 2-4-0, NFPA 3-4-0	Varies	HIMS 2-1-0, NFPA 2-1-0	NFPA 1-0-1	NFPA 3-0-1	NFPA 3-2-0	NFPA 4-0-1 (acid)

References	Total	Airgas	CRJ/Criterion, Haldor Topsoe, Porocel, Valero	Johnson Matthey	Delta Adsorbents	Orica Chemicals	Int'l Furan Chemicals	Airgas		
MSDS SOURCES	Wikipedia	Wikipedia						Wikipedia		
ARTICLES; BULLETINS; OTHER										
c										
Category	Sulfiding chemicals									
Material	Hydrogen sulfide	Hydrogen sulfide	Methyl ethyl ketone	Nickel carbonyl	Nitrogen	Dimethyl sulfide	Dimethyl disulfide	Di-t-butyl polysulfide	Di-t-nonyl polysulfide	Sulfuric acid (Conc.)
Abbreviation/alias	-	H <sub>2</sub> S	MEK	-	N <sub>2</sub> , LN <sub>2</sub>	DMS	DMS	TBPS	TNPS	SA
Chemical formula	H <sub>2</sub>	H <sub>2</sub> S	CH <sub>3</sub> C(O)CH <sub>2</sub> CH <sub>3</sub>	Ni(CO) <sub>4</sub>	N <sub>2</sub>	H <sub>3</sub> CSCH <sub>3</sub>	H <sub>3</sub> CSSCH <sub>3</sub>	C <sub>8</sub> H <sub>18</sub> S <sub>x</sub>	C <sub>18</sub> H <sub>38</sub> S <sub>x</sub>	H <sub>2</sub> SO <sub>4</sub>
Molecular weight	2.02	34.08	72	170.73	28.02	62.13	94.2	~204	~414	98.08
Physical states	Vap	Vap	Liq, Vap	Vap (Liq unlikely)	Cryogenic Liq, Vap	Liq, Vap	Liq, Vap	Liq	Liq	Liq
Color	Colorless	Colorless	Colorless	Colorless	Colorless	Clear	Pale Yellow	Yellow	Yellow	Colorless
Odor	Odorless	Rotten eggs	Sweet alcohol	Musty/wet brick	Odorless	Stench	Strong garlic	Slightly acrid	Mildly unpleasant	Odorless to slight sulfur odor
Vapor Sp. Gr. (air = 1)	0.0696	1.19	2.4	5.9	0.97	2.1	3.25	-	-	(1.2 kg/m <sup>3</sup> )
Liquid Sp. Gr. (nominal)	-	-	0.81	-	0.81	0.85	1.06	1.07	1.05	1.84
Boiling point, °F/C	-423/-253	-77/-61	176/80	109/43	-320/-196	99/38	228/109	342-356/172-180	407-507/208-264	554/290
Freeze point, °F/°C	-435/-259	-122/-86	-123/-87	1/-17	-346/-210	-145/-98	-121/-85	37/3	≤4/≤20	50.6/10.3
Flash point, °F/°C	-	-	16/-9	4/20	N/A	-54/-48	59/15	217/103	277-291/136-144	N/A
Autoignition, °F/°C	932-1,000/500-571	500/260	759/404	140/60	N/A	403/206	Not available	437/225	464/240	N/A
Decomposition, °F/°C	N/A	N/A	Not available	~300/~149	N/A	Yes (H <sub>2</sub> S, mercaptans)	Yes (H <sub>2</sub> S, mercaptans)	Yes (H <sub>2</sub> S, mercaptans,	Yes (H <sub>2</sub> S, mercaptans,	644/340 (SOx)

(continued)

Table 25 (continued)

Category	Sulfiding chemicals									
	Hydrogen	Hydrogen sulfide	Methyl ethyl ketone	Nickel carbonyl	Nitrogen	Dimethyl sulfide	Dimethyl disulfide	Di-t-butyl polysulfide	Di-t-nonyl polysulfide	Sulfuric acid (Conc.)
Material Abbreviation/alias	-	H <sub>2</sub> S	MEK	-	N <sub>2</sub> , LN <sub>2</sub>	DMS	DMS	TBPS	TNPS	SA
Flammability limits (air)	4-76	4.3-45.5	1.4-11.4	2-34	N/A	2.2-19.7	1.1-16	elemental sulfur	elemental sulfur	N/A
Exposure limits (always verify current values)	N/A	TLV=1 ppm STEL=5 ppm IDLH=100 ppm	TLV=200 ppm STEL=300 ppm	TLV=1 ppb IDLH=3 ppm carcinogen	O <sub>2</sub> depletion hazard	TLV=10 ppm	TLV=0.5 ppm	Not available	Not available	TLV=1 mg/m <sup>3</sup> STEL=3 mg/m <sup>3</sup>
Primary hazard routes	Inhalation	Inhalation	Inhalation, skin	Inhalation, skin (absorption)	Inhalation, skin (cryogenic liquid)	Inhalation, skin (absorption)	Inhalation, skin (absorption)	Skin	Skin	Skin, eyes, inhalation
Exposure type										
Fire/explosion	High	X	X (CO evolved)	Unlikely	N/A	X (CO, SO <sub>2</sub> , H <sub>2</sub> S)	X (CO, SO <sub>2</sub> , H <sub>2</sub> S)	X (CO, SO <sub>2</sub> , H <sub>2</sub> S)	X (CO, SO <sub>2</sub> , H <sub>2</sub> S)	N/A
Toxicity	N/A	High	Moderate	Extreme (CO, Ni)	O <sub>2</sub> depletion hazard	High	Moderate	Slight	Slight	High, tissue damage
Ecological impacts										
Aqueous env.	N/A	Toxic	Moderate to low toxicity	Toxic, but short lived	N/A	Moderate (evaporates so short-lived effect)	Toxic, long lived	Very toxic	Insufficient data	Harmful
Biodegradable	N/A	Yes	Not available	Not available	N/A	Evaporates	No	Not available	Insufficient data	No, but reacts
Firefighting media	Water, steam	Water spray/fog, foam, dry chemical	Water spray/fog, alcohol-resistant foam, dry chemical, CO <sub>2</sub>	Water spray/fog, alcohol-resistant foam, CO <sub>2</sub>	N/A	Alcohol foam, foam, dry chemical, CO <sub>2</sub>	Water spray/fog, alcohol-resistant foam, CO <sub>2</sub>	Water spray/fog, foam, dry chemical, CO <sub>2</sub>	Water spray/fog, foam, dry chemical, CO <sub>2</sub>	N/A

