



MATERIAL SAFETY DATA SHEET

Spent Sulfidic Caustic

VALERO MARKETING & SUPPLY COMPANY
and Affiliates
P.O. Box 696000
San Antonio, TX 78269-6000

Emergency Phone Numbers

24 Hour Emergency: 866-565-5220
Chemtrec Emergency: 800-424-9300

General Assistance

General Assistance: 210-345-4593

BRAND NAMES: Valero, Diamond Shamrock, Shamrock, Ultramar, Beacon, Total

Section 1. Chemical Product and Company Identification

Common / Trade name : Spent Sulfidic Caustic

SYNONYMS/Common Names: This Material Safety Data Sheet applies to the listed products and synonym descriptions for Hazard Communication purposes only. Technical specifications vary greatly depending on the product and are not reflected in this document. Consult specification sheets for technical information. This product contains ingredients that are considered to be hazardous as defined by the OSHA Hazard Communication Standard (29 CFR 1910.1200).

Material uses : This product is intended for use as a refinery feedstock, fuel, or for use in engineered processes. Use in other applications may result in higher exposures and require additional controls, such as local exhaust ventilation and personal protective equipment.

MSDS # : 615

CAS # : Mixture

Section 2. Composition, information on ingredients

<u>Name</u>	<u>CAS number</u>	<u>Concentration (%)</u>
Sodium Sulfide	1313-82-2	1 - 15
Sodium Hydroxide	1310-73-2	0 - 15
Hydrogen Sulfide	7783-06-4	0.1 - 0.2

Section 3. Hazards Identification

DANGER: Corrosive material. Avoid contact with eyes and skin in mist or liquid form. Do not eat, drink, or smoke while using this product. Store in properly labeled tanks or containers. Do not store near strong acids, organic chemicals, e.g. solvents, alcohols, etc. contact with acids may generate toxic gas hydrogen sulfide.

The fumes may contain hydrogen sulfide, avoid breathing fumes. Wash with soap and water before eating, drinking, smoking or using toilet facilities.

Physical state : Liquid.

Emergency overview : Warning!

MAY BE FATAL IF INHALED.

HARMFUL IF SWALLOWED.

CAUSES SKIN IRRITATION.

CONTAINS MATERIAL WHICH CAUSES DAMAGE TO THE FOLLOWING ORGANS:
LUNGS, RESPIRATORY TRACT, SKIN, EYE, LENS OR CORNEA.

Avoid contact with skin and clothing. Wash thoroughly after handling.

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Routes of entry : Dermal contact. Eye contact. Inhalation. Ingestion.

Potential acute health effects

Eyes : Severely corrosive to the eyes. Inflammation of the eye is characterized by redness, watering and itching. May cause corneal opacity. Liquid, spray or mist may produce tissue damage, particularly to mucous membranes of eyes, mouth and respiratory tract. May cause severe irritation, redness, tearing, blurred vision and conjunctivitis. Severe eye damage may result. Liquid in the eye can cause severe destruction and blindness. These effects can occur rapidly effecting all parts of the eye. Mists at high concentrations can cause destructive burns.

Skin : Corrosive to skin on contact. Skin contact can produce inflammation and blistering. Skin inflammation is characterized by itching, scaling, reddening or, occasionally, blistering. Major potential hazard to skin. Contact with the skin can cause severe burns with deep ulcerations. Contact with solution or mist can cause multiple burns with temporary loss of hair at burn site. Solutions of 4% Sodium Hydroxide may not cause irritation and burning for several hours, while 25-50% solutions cause these effects in less than 3 minutes. Prolonged or repeated contact may cause moderate irritation, defatting (cracking), redness, itching, inflammation, dermatitis and possible secondary infection. High pressure skin injections are **SERIOUS MEDICAL EMERGENCIES**. Injury may not appear serious at first. Within a few hours, tissues will become swollen, discolored and extremely painful.

Inhalation : Corrosive to the respiratory system. Inhalation of the spray or mist may produce severe irritation of respiratory tract, characterized by coughing, choking or shortness of breath. Possible risk of irreversible effects. After the initial episode, individuals should be followed for the delayed appearance of pulmonary edema and chemical pneumonitis. Warning - Hydrogen sulfide (H₂S) and other hazardous vapors may evolve and collect in the headspace of storage tanks or other enclosed vessels. Inhalation of vapors, mist or fumes (generated at high temperatures) may cause irritation to the eyes, nose, throat and respiratory tract. Additionally, inhalation of high concentrations may cause CNS (Central nervous System) depression and/or chemical pneumonitis. In worst cases immediate comma and death may occur. Hydrogen sulfide is an extremely toxic gas.

Inhalation of solution mists can cause mild irritation at 2 mg/m³. More severe burns and tissue damage at the upper respiratory tract, can occur at higher concentrations.

Ingestion : Irritating to mouth, throat and stomach. May cause burns to mouth, throat and stomach. May be fatal if swallowed. This product may be harmful or fatal if swallowed. This product may cause nausea, vomiting, diarrhea and restlessness. **DO NOT INDUCE VOMITING**. Aspiration into the lungs can cause severe chemical pneumonitis or pulmonary edema/hemorrhage, which can be fatal. Accidental ingestion of sodium hydroxide can cause severe burning and pain in lips, mouth, throat and stomach. Severe scarring of the throat can occur after swallowing. Death can result from ingestion.

Medical conditions aggravated by over-exposure : Preexisting eye, skin, and respiratory disorders may be aggravated by exposure to this product.

Over-exposure signs/symptoms : After the initial episode, individuals should be followed for the delayed appearance of pulmonary edema and chemical pneumonitis.

See toxicological information (section 11)

Section 4. First Aid Measures

- Eye contact** : In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical attention immediately. May cause severe irritation, redness, tearing, blurred vision and conjunctivitis. Severe eye damage may result. Liquid in the eye can cause severe destruction and blindness. These effects can occur rapidly effecting all parts of the eye. Mists at high concentrations can cause destructive burns.
- Skin contact** : In case of contact, immediately flush skin with plenty of water. Remove contaminated clothing and shoes. Wash clothing before reuse. Clean shoes thoroughly before reuse. Get medical attention. Major potential hazard to skin. Contact with the skin can cause severe burns with deep ulcerations. Contact with solution or mist can cause multiple burns with temporary loss of hair at burn site. Solutions of 4% Sodium Hydroxide may not cause irritation and burning for several hours, while 25-50% solutions cause these effects in less than 3 minutes. Prolonged or repeated contact may cause moderate irritation, defatting (cracking), redness, itching, inflammation, dermatitis and possible secondary infection. High pressure skin injections are **SERIOUS MEDICAL EMERGENCIES**. Injury may not appear serious at first. Within a few hours, tissues will become swollen, discolored and extremely painful.
- Inhalation** : If inhaled, remove to fresh air. If breathing is difficult, give oxygen. If not breathing, give artificial respiration. Get medical attention. Warning - Hydrogen sulfide (H₂S) and other hazardous vapors may evolve and collect in the headspace of storage tanks or other enclosed vessels. Inhalation of vapors, mist or fumes (generated at high temperatures) may cause irritation to the eyes, nose, throat and respiratory tract. Additionally, inhalation of high concentrations may cause CNS (Central nervous System) depression and/or chemical pneumonitis. In worst cases immediate comma and death may occur. Hydrogen sulfide is an extremely toxic gas.
- Inhalation of solution mists can cause mild irritation at 2 mg/m³. More severe burns and tissue damage at the upper respiratory tract, can occur at higher concentrations.
- Ingestion** : Do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. If potentially dangerous quantities of this material have been swallowed, call a physician immediately.
- Notes to physician** : In case of ingestion, treat symptomatically. Consideration should be given to the use of an intratracheal tube, to prevent aspiration. Individuals intoxicated by the product should be hospitalized immediately. Positive pressure ventilation may be necessary. After the initial episode, individuals should be followed for the delayed appearance of pulmonary edema and chemical pneumonitis. Individuals with chronic pulmonary disease will be more seriously impaired, and recovery from inhalation exposure may be complicated. In case of skin injection, prompt debridement of the wound is necessary to minimize necrosis and tissue loss.

Section 5. Fire Fighting Measures

- Flammability of the product** : May be combustible at high temperature.
- Products of combustion** : These products are sulfur oxides (SO₂, SO₃ etc.). Some metallic oxides.
- Fire-fighting media and instructions** : Use an extinguishing agent suitable for the surrounding fire. Foam, dry chemical or carbon dioxide type extinguishing agents may all be suitable for product, depending on size or potential size of fire and circumstances related to the situation. Plan fire protection and response strategy through consultation with local fire protection authorities or appropriate specialists.
- Fires involving small amounts of combustibles may be smothered with suitable dry chemical. Use water on combustibles burning in vicinity of this material but use care as water applied directly to this acid results in evolution of heat and causes spattering. Use water to flush spills away from sources of ignition. Do not flush down public sewers.

No specific hazard.

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- Special protective equipment for fire-fighters** : Fire-fighters should wear appropriate protective equipment and self-contained breathing apparatus (SCBA) with a full face-piece operated in positive pressure mode.
- Special remarks on fire hazards** :
- Special remarks on explosion hazards** :

Section 6. Accidental Release Measures

- Personal precautions** : Immediately contact emergency personnel. Keep unnecessary personnel away. Use suitable protective equipment (section 8).
- Environmental precautions** : If facility or operation has an "oil or hazardous substance contingency plan", activate its procedures. Stay upwind and away from spill. Wear appropriate protective equipment including respiratory protection as conditions warrant. Do not enter or stay in area unless monitoring indicates that it is safe to do so. Isolate hazard area and restrict entry to emergency crew. Extremely flammable. Review Fire Fighting Measures section before proceeding with clean up. Keep all sources of ignition (flames, smoking, flares, etc.) and hot surfaces away from release. Contain spill in smallest possible area. Recover as much product as possible (e.g., by vacuuming). Stop leak if it can be done without risk. Use water spray to disperse vapors. Spilled material may be absorbed by an appropriate absorbent, and then handled in accordance with environmental regulations. Prevent spilled material from entering sewers, storm drains, other unauthorized treatment or drainage systems and natural waterways. Contact fire authorities and appropriate federal, state and local agencies. If spill of any amount is made into or upon navigable waters, the contiguous zone, or adjoining shorelines, contact the National Response Center at 800-424- 8802. For highway or railway spills, contact Chemtrec at 800-424-9300.

Section 7. Handling and Storage

- Handling** : Avoid contact with skin and clothing. Keep container closed. Use only with adequate ventilation. Avoid breathing vapor or mist. Wash thoroughly after handling. To avoid fire or explosion, dissipate static electricity during transfer by grounding and bonding containers and equipment before transferring material. Use good personal hygiene practices. After handling this product, wash hands before eating, drinking, or using toilet facilities.
- Storage** : Keep container tightly closed. Keep container in a cool, well-ventilated area.

Section 8. Exposure controls, personal protection

- Engineering controls** : Provide a readily-accessible eyewash facility and quick-drench safety shower. Keep container tightly closed and in a well-ventilated place. Local exhaust ventilation should be provided.
- Personal protection**
- Eyes** : Safety eyewear complying with an approved standard should be used when a risk assessment indicates this is necessary to avoid exposure to liquid splashes, mists or dusts. face shield splash goggles
- Skin** : Personal protective equipment for the body should be selected based on the task being performed and the risks involved and should be approved by a specialist before handling this product.
- Respiratory** : Use a properly fitted, air-purifying or air-fed respirator complying with an approved standard if a risk assessment indicates this is necessary. Respirator selection must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected respirator.
- Hands** : Chemical-resistant, impervious gloves complying with an approved standard should be worn at all times when handling chemical products if a risk assessment indicates this is necessary.

Personal protective equipment (Pictograms) : Consult your Supervisor or S.O.P. for special handling directions.



Personal protection in case of a large spill : Splash goggles. Full suit. Boots. Gloves. Suggested protective clothing might not be adequate. Consult a specialist before handling this product. Wear MSHA/NIOSH-approved self-contained breathing apparatus or equivalent and full protective gear.

Component

Sodium Hydroxide

Exposure limits

ACGIH TLV (United States, 1/2005).

CEIL: 2 mg/m³ Form: All forms

NIOSH REL (United States, 12/2001).

CEIL: 2 mg/m³ Form: All forms

OSHA PEL (United States, 8/1997).

TWA: 2 mg/m³ 8 hour/hours. Form: All forms

Hydrogen Sulfide

ACGIH TLV (United States, 9/2004).

TWA: 10 ppm 8 hour/hours. Form: All forms

STEL: 15 ppm 15 minute/minutes. Form: All forms

NIOSH REL (United States, 12/2001).

CEIL: 10 ppm 10 minute/minutes. Form: All forms

OSHA PEL Z2 (United States, 8/1997).

CEIL: 20 ppm Form: All forms

AMP: 50 ppm 10 minute/minutes. Form: All forms

Consult local authorities for acceptable exposure limits.

Section 9. Physical and Chemical Properties

Physical state	: Liquid.
Color	: Dark Orange. Green. Light brown.
Odor	: Sulfurous.
pH	: >11 [Basic.]
Boiling point	: >104°C (219.2°F)
Melting/freezing point	: 0.5°C (32.9°F)
Specific gravity	: 1.13 to 1.18 (Water = 1) (@ 60 °F)
Solubility	: Soluble in cold water.

Section 10. Stability and reactivity data

Stability and reactivity	: The product is stable.
Incompatibility with various substances	: Extremely reactive or incompatible with oxidizing agents, reducing agents, organic materials, acids, water.

Section 11. Toxicological Information

Toxicity data

HYDROGEN SULFIDE can affect the body if it is inhaled or if it comes into contact with the eyes, skin, nose or throat. It can also affect the body if it is swallowed. It is colorless and has the odor of rotten eggs. However, its odor cannot be used as an indication of its presence since one of the first effects of H₂S exposure is the loss of the sense of smell. Inhalation of high concentrations of hydrogen sulfide, 1000 to 2000 ppm, may cause coma after a single breath and may be rapidly fatal, convulsions can also occur. Hydrogen sulfide gas is a rapidly acting systemic poison which causes respiratory paralysis with consequent asphyxia at high concentrations (500 to 1000 ppm). A case of polyneuritis and encephalopathy from one day's exposure to a concentration insufficient to cause loss of consciousness has been reported. It irritates the eyes and respiratory tract at lower concentrations (50 to 500 ppm). Pulmonary edema and bronchial pneumonia may follow prolonged exposure at concentrations exceeding 250 ppm. Exposure to concentrations of hydrogen sulfide around 50 ppm for one hour may produce rhinitis, pharyngitis, bronchitis, pneumonitis, acute conjunctivitis with pain, lacrimation and photophobia, in severe form this may progress to keratoconjunctivitis and vesiculation of the corneal epithelium. In lower concentrations, hydrogen sulfide may cause headache, fatigue, irritability, insomnia, and gastrointestinal disturbances, as well as central nervous system disturbances, causing excitation

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and dizziness. Repeated exposure to hydrogen sulfide results in increased susceptibility, so that eye irritation, cough and systemic effects may result from concentrations previously tolerated without any effect.

<u>Ingredient name</u>	<u>Test</u>	<u>Result</u>	<u>Route</u>	<u>Species</u>
Sodium Sulfide	LD50	208 mg/kg	Oral	Rat
	LD50	205 mg/kg	Oral	Mouse
Sodium Hydroxide	LDLo	500 mg/kg	Oral	Rabbit
Hydrogen Sulfide	LC50	444 ppm (1 hour/hours)	Inhalation	Rat
	LC50	673 ppm (1 hour/hours)	Inhalation	Mouse

IDLH :

Chronic effects on humans : Contains material which causes damage to the following organs: lungs, upper respiratory tract, skin, eye, lens or cornea.

Other toxic effects on humans : Very dangerous in case of skin contact (corrosive, irritant, sensitizer, permeator), eye contact (irritant), ingestion or inhalation.

Specific effects

Carcinogenic effects : No known significant effects or critical hazards.

Target organs : Contains material which causes damage to the following organs: lungs, upper respiratory tract, skin, eye, lens or cornea.

Section 12. Ecological Information

Ecotoxicity data

<u>Ingredient name</u>	<u>Species</u>	<u>Period</u>	<u>Result</u>
Sodium Sulfide	Poecilia reticulata (LC50)	96 hour/hours	15 mg/l
Hydrogen Sulfide	Pimephales promelas (LC50)	96 hour/hours	0.007 mg/l
	Oncorhynchus mykiss (LC50)	96 hour/hours	0.007 mg/l
	Pimephales promelas (LC50)	96 hour/hours	0.0071 mg/l
	Lepomis macrochirus (LC50)	96 hour/hours	0.009 mg/l
	Pimephales promelas (LC50)	96 hour/hours	0.0107 mg/l
	Oncorhynchus mykiss (LC50)	96 hour/hours	0.012 mg/l

Products of degradation :


Toxicity of the products of biodegradation : N/A

Section 13. Disposal Considerations

Waste disposal : Do not puncture or incinerate container. Disposal of this product, solutions and any by-products should at all times comply with the requirements of environmental protection and waste disposal legislation and any regional local authority requirements.

Consult your local or regional authorities.

Section 14. Transport Information

<u>Regulatory information</u>	<u>UN number</u>	<u>Proper shipping name</u>	<u>Class</u>	<u>Packing group</u>	<u>Label</u>	<u>Additional information</u>
DOT Classification	UN1760	Corrosive liquids, n.o.s.	8	II		NAERG #154

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Definitions of Material Safety Data Sheet Terminology

GOVERNMENT AGENCIES AND PRIVATE ASSOCIATIONS

ACGIH - American Conference of Governmental Industrial Hygienists, (private association)
DOT - United States Department of Transportation
EPA - United States Environmental Protection Agency
IARC - International Agency for Research on Cancer, (private association)
NFPA - National Fire Protection Association, (private association)
MSHA - Mine Safety and Health Administration, U.S. Department of Labor
NIOSH - National Institute of Occupational Safety and Health, U.S. Department of Health and Human Services
NTP - National Toxicology Program, (private association)
OSHA - Occupational Safety and Health Administration, U.S. Department of Labor
WHMIS - Workplace Hazardous Material Information System
CSA - Canadian Standards Association

HAZARD AND EXPOSURE INFORMATION

Acute Hazard - An adverse health effect which occurs rapidly as a result of short term exposure.
CAS # - American Chemical Society's Chemical Abstract service registry number which identifies the product and/or ingredients.
Ceiling - The concentration that should not be exceeded during any part of the working exposure
Chronic Hazard - An adverse health effect which generally occurs as a result of long term exposure or short term exposure with delayed health effects and is of long duration
Fire Hazard - A material that poses a physical hazard by being flammable, combustible, pyrophoric or an oxidizer as defined by 29 CFR 1910.1200
Hazard Class - DOT hazard classification
Hazardous Ingredients - Names of ingredients which have been identified as health hazards
IDLH - Immediately Dangerous to Life and Health, the airborne concentration below which a person can escape without respiratory protection and exposure up to 30 minutes, and not suffer debilitating or irreversible health effects. Established by NIOSH.
mg/m³ - Milligrams of contaminant per cubic meter of air, a mass to volume ratio
N/A - Not available or no relevant information found
NA - Not applicable
PEL - OSHA permissible exposure limit; an action level of one half this value may be applicable
ppm - Part per million (one volume of vapor or gas in one million volumes of air)
Pressure Hazard - A material that poses a physical hazard due to the potential of a sudden release of pressure such as explosive or a compressed gas as defined by 29 CFR 1910.1200
Reactive Hazard - A material that poses a physical hazard due to the potential to become unstable reactive, water reactive or that is an organic peroxide as defined by 29 CFR 1910.1200.
STEL - The ACGIH Short-Term Exposure Limit, a 15-minute Time-Weighted Average exposure which should not be exceeded at any time during a workday, even if the 8-hour TWA is less than the TLV.
TLV - ACGIH Threshold Limit Value, represented herein as an 8-hour TWA concentration.
8-hour TWA - The time weighted average concentration for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.
LD₅₀ - Single dose of a substance that, when administered by a defined route in an animal assay, is expected to cause the

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death of 50% of the defined animal population.

LC50 - The concentration of a substance in air that, when administered by means of inhalation over a specified length of time in an animal assay, is expected to cause the death of 50% of a defined animal population.