



Environment
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protection de
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ENVIRO

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Information for

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Problem

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Spills

SULPHUR

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1984

March 1984

Canada

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The manual has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

SULPHUR

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1984

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS



Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Ottawa, Ontario

March 1984

FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor any other group.

ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who rewrote the text, drafted illustrations and incorporated all comments and additions.

The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation, and Waterloo Engineering Limited. The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review. The Sulphur Development Institute of Canada (SUDIC) is especially acknowledged for its review and input to the manual.

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1 SUMMARY

SULPHUR (S₈)

Solid: yellow powder, slates, granules, lumps, prills

Molten: yellow to orange-red/brown liquid (temperature dependent)

SYNONYMS

Bensulfoïd, Colloidal-S, Colsul, Crystex, Brimstone, Flowers of Sulphur, Sulfur

IDENTIFICATION NUMBERS

UN No. 1350 (solid), 2448 (molten); CAS No. 7704-34-9; OHM-TADS No. 7216913

GRADES & PURITIES

Grades: technical, crude, refined - high purity

IMMEDIATE CONCERNS

Fire: Combustible. Produces toxic sulphur dioxide gas during combustion. Dust may explode if there is an ignition source. May react violently in contact with oxidizing agents or powdered metals. Fire hazard is increased if hydrogen sulphide is present

Human Health: Elemental sulphur is virtually nontoxic. Burning sulphur produces a toxic gas (sulphur dioxide). Crude molten sulphur may evolve hydrogen sulphide due to the presence and decomposition of mercaptans

Environment: May be harmful to aquatic life in high concentrations as a suspended solid

PHYSICAL PROPERTY DATA

State (15°C, 1 atm): solid

Boiling Point: 444.6°C

Melting Point: 112.8 to 120°C

Flammability: combustible

Flash Point: 168-261°C

Behaviour (in water): generally sinks in water; powder may tend to float

Odour Threshold: pure sulphur is odourless; commercial farms may smell of hydrogen sulphide

Specific Gravity (water=1): 1.79 (138°C) (liquid), 2.07 (20°C) (molten)

Solubility: insoluble in water

ENVIRONMENTAL CONCERNS

Elemental sulphur may pose a serious hazard in high concentrations especially in colloidal form. Covering of the bottoms of water bodies may also cause problems. Molten sulphur will solidify, sink to the bottom and similarly pose a threat to bottom life.

There is no potential for accumulation or food chain concentration. Elemental sulphur will undergo slow oxidation in water, generating acidic conditions (probably a mixture of sulphurous and sulphuric acids).

HUMAN HEALTH

Exposure Effects

Inhalation: Sulphur dust can irritate the mucous membranes of the respiratory tract and the inner surfaces of the eyelid

Contact: Skin irritation may result from repeated exposures to sulphur dust. If spilled on clothing and allowed to remain, it may cause smarting and reddening of the skin. Molten sulphur can cause serious burns

Ingestion: Sulphur is nontoxic. Pharmaceutical sulphur has been used internally as a laxative and parasiticide

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "COMBUSTIBLE". Call fire department and notify supplier. Stop flow and contain spill, if safe to do so. Avoid contact and inhalation of dust.

Fire Control

Use water spray, dry chemical, foam or sand to extinguish. Avoid straight streams of water which will scatter molten sulphur and dust.

COUNTERMEASURES

Emergency Control Procedures in/on:

Soil: Construct barriers to contain spill if molten or solid. Dust can be controlled by keeping oxygen surface wet. Shovel solid sulphur into containers with covers for recovery or disposal. If sulphur is wet, some lime should be added to react with any acid formed by reaction with water or impurities. Let molten sulphur solidify and shovel into containers with covers when cool. Dampen area with water spray and cover with limestone. Pick up for recovery.

Water: Contain discharge by damming or water diversion. Remove solidified material and precipitate from bottom, with suction hoses or mechanical dredges.

NAS HAZARD RATING (MOLTEN)

Category Rating

Fire.....1-3

Health

Vapour Irritant.....1

Liquid or Solid Irritant.....1

Poison.....1

Water Pollution

Human Toxicity.....0

Aquatic Toxicity.....1

Aesthetic Effect.....1

Reactivity

Other Chemicals.....4

Water.....0

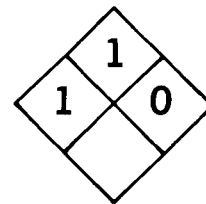
Self-reaction.....0

NFPA
HAZARD
CLASSIFICATION
(SOLID)

Non-Fire

Flammability

Health

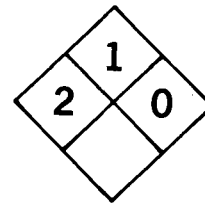


Reactivity

Fire

Flammability

Health



Reactivity

2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance	Solid: yellow powder, granules, lumps, prills Molten: yellow to orange-red/brown liquid
Usual shipping states	Solid α : rhombic crystal (predominant form); liquid molten sulphur maintained between 149 and 154°C (Ashland MSDS; CE 1978)
Physical state at 15°C, 1 atm	Solid in rhombic or monoclinic crystal or amorphous form (CRC 1980; Kirk-Othmer 1979)
Melting point	general range: 110-119°C (Meyer 1977) α : 112.8°C (CRC 1980) β : 119.0°C (CRC 1980) γ : 106.8°C (Cotton 1972)
Freezing point	115°C (MCA 1959)
Boiling point	444.6°C (CRC 1980)

Densities

Density	Liquid: 1,790 kg/m ³ (138°C) (MCA 1959)
Bulk density:	Prills: 1,090-1,200 kg/m ³ (SUDIC 1983) Solid: 1,201-1,394 kg/m ³ (form not stated) (MCA 1959)
Specific gravity	α : 2.07 (20°C) (CRC 1980) β : 1.96 (20°C) (CRC 1980) γ : 1.92 (20°C) (CRC 1980) Liquid: 1.79 (138°C) (MCA 1959)

Fire Properties

Flammability	Combustible (all states). Forms ignitable/explosive mixtures with air (powdered/dispersed) 248-261°C (CE 1978) 168-188°C (Meyer 1977)
Flash point	207°C (NFPA 1978) 188°C (MCA 1959)
Ignition temperature in air (liquid)	248-261°C (Meyer 1977) 190°C (dispersed in air) (MCA 1959; Meyer 1977) 220°C (undispersed) (Meyer 1977)
Autoigniton temperature (solid)	232°C (NFPA 1978)

Upper explosive limit	1,400 g/m ³ (MCA 1959); as dust in air (Meyer 1979) 2,000 g/m ³ (Orchard 1982)
Lower explosive limit	35 g/m ³ (MCA 1959); as dust (Ashland MSDS) 25.1 g/m ³ (Meyer 1977)
Burning characteristics	Burns with a pale blue flame (CHRIS 1978)
Heat of combustion (solid)	-9,254 kJ/kg (Meyer 1977) -9,378 kJ/kg (monoclinic) (CRC 1982) -9,211 kJ/kg (rhombohedral) (CRC 1982)
Combustion products	Sulphur dioxide
Explosiveness	Dust or vapour forms explosive mixtures with air (NFPA 1978)

Other Properties

Atomic weight	32.06 (CRC 1982)
Molecular weight of pure substance (S ₈)	265.512 (CRC 1980)
Usual purity	>99.9 percent sulphur (molten or liquid) (SUDIC 1983)
Resistivity	1.9 x 10 ¹⁷ ohm•cm (20°C) (Kirk-Othmer 1979)
Refractive index	α: 1.957 (CRC 1980) β: 2.038 (CRC 1957)
Viscosity (liquid sulphur)	11 mPa•s (123°C) (CRC 1982) 23 mPa•s (160°C) (CRC 1982)
Liquid interfacial tension with air	0.061 N/m (liquid at 120°C) (Kirk-Othmer 1979)
Liquid interfacial tension with water	0.05 N/m (liquid at 127°C) (CHRIS 1978)
Latent heat of fusion	α: 49.8 J/g (112.8°C) (Kirk-Othmer 1979) S: 38.5 J/g (118.9°C) (monoatomic sulphur) (CRC 1982)
Latent heat of vaporization	290 J/g (440°C) (Kirk-Othmer 1979)
Heat of formation	S-Monoclinic: 0.33 kJ/mole (25°C) (NBS 1982) S-gas: 278.8 kJ/mole (25°C) (NBS 1982) S ₈ -gas: 102.3 kJ/mole (25°C) (NBS 1982)
Ionization potential (as S ₈ ⁺)	9.04 eV (Rosenstock 1977)
Heat capacity constant pressure (C _p)	961.5 J/kg•K (molten at 120°C) (Kirk-Othmer 1979) 310.5 J/kg•K (S _α at 24.9°C) (Kirk-Othmer 1979)

constant volume (C_V)	98.6 J/mole (est.) (JANAF 1971; CHRIS 1978)
Critical temperature	1,040°C (Kirk-Othmer 1979)
Critical pressure	11,750 kPa (Kirk-Othmer 1979)
Coefficient of thermal expansion (linear)	$7.4 \times 10^{-5}/^{\circ}\text{C}$ (from 13°C to 50°C) (rhombic) (Kirk-Othmer 1979)
Coefficient of cubical expansion	$2.23 \times 10^{-4}/^{\circ}\text{C}$ (13.2-50.3°C) (CRC 1957)
Thermal conductivity	$2.7 \times 10^{-3} \text{ W} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$ (25°C) (solid - polycrystalline) (CRC 1982) $2.05 \times 10^{-3} \text{ W} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$ (25°C) (solid and amorphous) (CRC 1982) $1.29 \times 10^{-3} \text{ W} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$ (100°C) (liquid) (CRC 1982)

Solubility

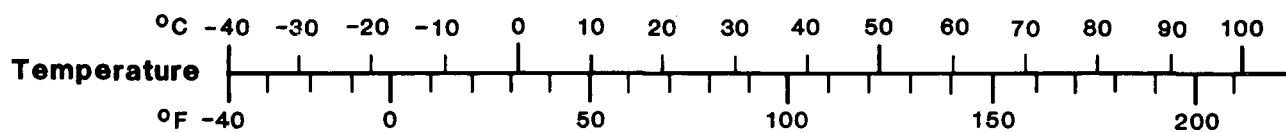
In water	Insoluble (Kirk-Othmer 1979)
In other common materials	(α): Soluble in carbon disulphide and carbon tetrachloride; slightly soluble in toluene, alcohol, benzene, ether and liquid ammonia (CRC 1982)

Structural Properties

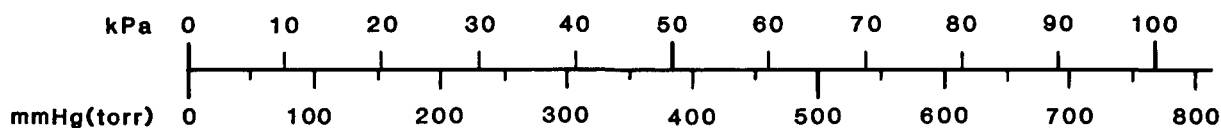
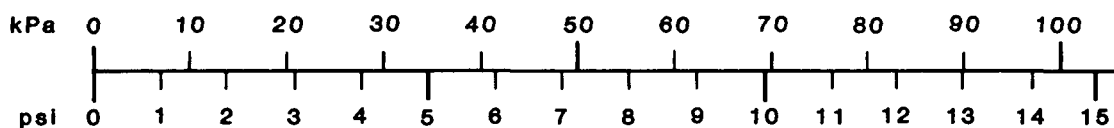
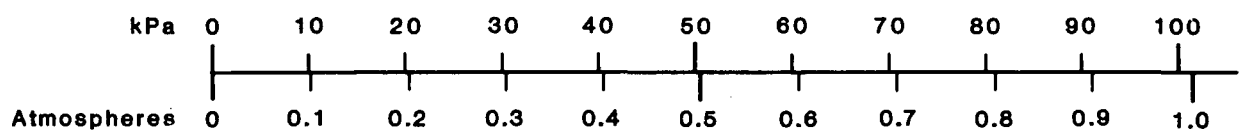
Because the structural relationships of sulphur in all three phases are exceedingly complex, a brief summary is thought to be pertinent and is presented in this section. All modifications of solid sulphur contain rings or chains of sulphur atoms. The most common form, cyclooctasulphur (S_8), has three main allotropes (crystal forms). Rhombic (orthorhombic) sulphur, S_{α} , is thermodynamically the most stable form. It melts at 112.8°C. Rhombic sulphur transforms slowly to monoclinic sulphur, S_{β} , at 95.5°C. The latter form melts at 119°C; however, because the transformation is slow, rapid heating will produce the melting point of the more stable allotrope. Monoclinic sulphur slowly converts back to rhombic sulphur at normal conditions. Other monoclinic forms have been identified microscopically, but must be obtained by special procedures. One such form is S_{γ} which melts at 106.8°C and slowly transforms back into S_{β} and/or S_{α} . Other cyclic sulphur with more or less sulphur atoms can be prepared, but all are unstable at normal conditions. A plastic sulphur, thought to contain helical chains of sulphur atoms, can be obtained by pouring molten sulphur into ice water. The plastic mass will slowly transform to S_{α} . Cyclooctasulphur is a yellow, transparent, mobile liquid upon melting which becomes brown and increasingly viscous above 160°C. The viscosity increases until the temperature reaches about 200°C, then decreases to the boiling point, 444.60°C. At this

point, the sulphur is a mobile, dark red liquid. The changes in the viscosity and the colour are due primarily to ring cleavage and chain formation. Sulphur vapour contains not only S_8 molecules, but S_n species in a temperature-dependent equilibrium (Kirk-Othmer 1979).

CONVERSION NOMOGRAMS



Pressure 1 kPa = 1,000 Pa



Viscosity

Dynamic 1 Pa·s = 1,000 centipoise (cP)

Kinematic 1 m²/s = 1,000,000 centistokes (cSt)

Concentration (in water)

1 ppm \approx 1 mg/L

Energy (heat) 1 kJ = 1,000 J

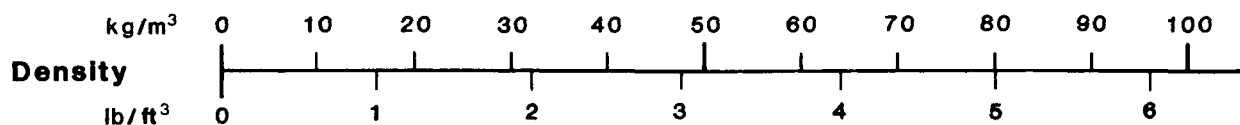
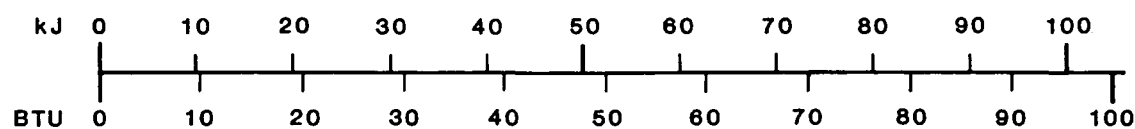
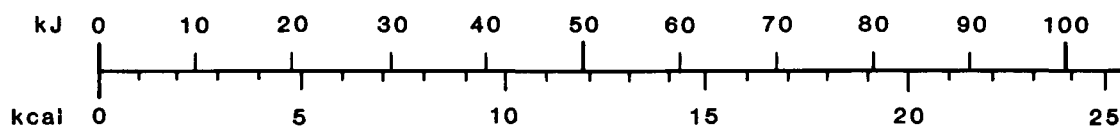


FIGURE 1

SULPHUR

LIQUID DENSITY vs TEMPERATURE

Reference: CRC 1982

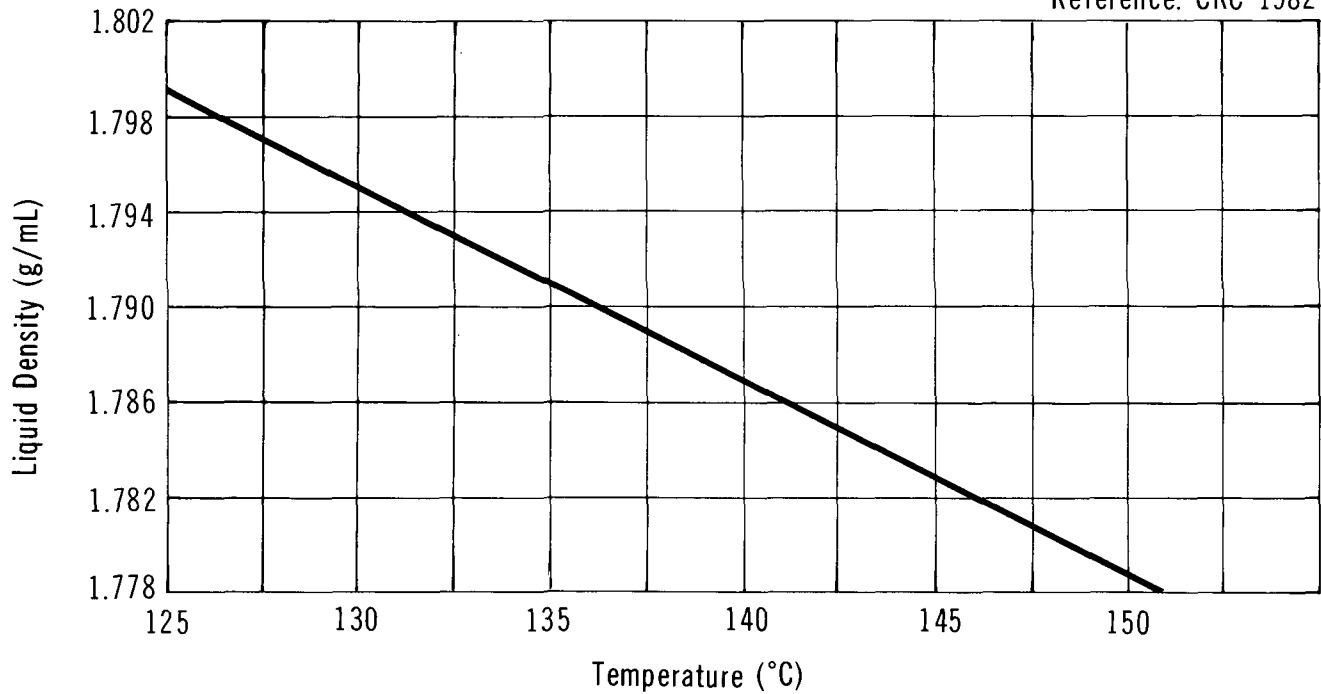
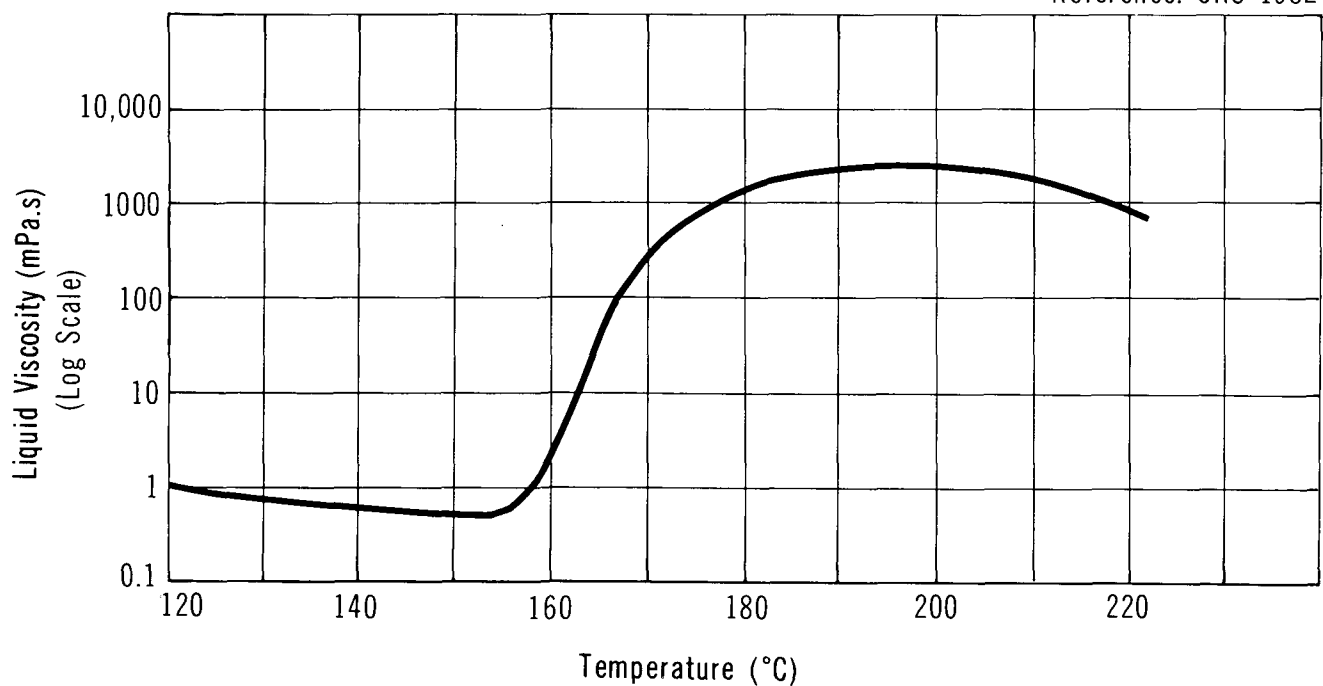


FIGURE 2

SULPHUR

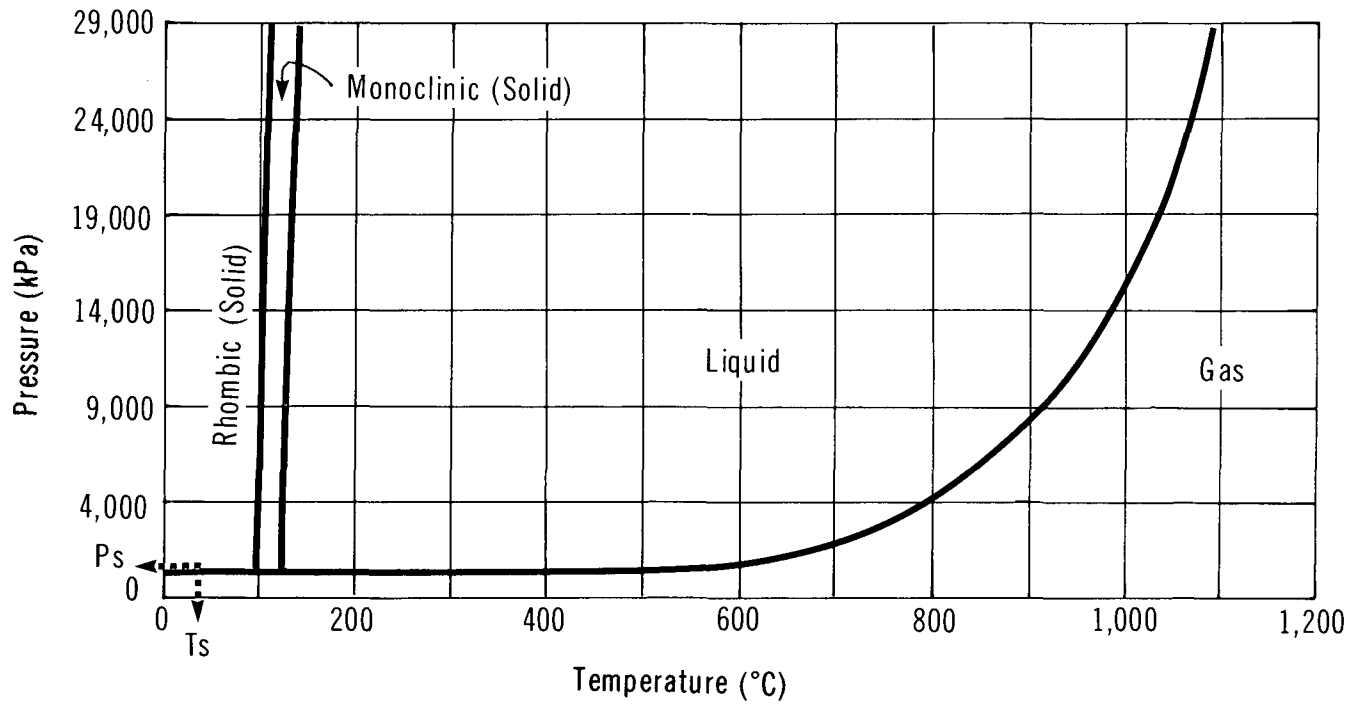
LIQUID VISCOSITY vs TEMPERATURE

Reference: CRC 1982



SULPHUR

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (CMI 1980)

The primary forms of sulphur in the Canadian market are slates, granules, or prills (solid form), and molten (liquid form). Slates are defined as a layer about 0.64 to 1.3 cm thick and 3 to 6 cm wide. The length is random. By the end of 1981, about 60 percent of exported sulphur was in granular or prill form.

3.2 Domestic Manufacturers (CBG 1980; DNACP 1979; SUDIC 1983)

These are corporate headquarters addresses and are not intended as spill response contacts.

Amerada Minerals Corporation
of Canada Ltd.
540-5th Avenue S.W.
Calgary, Alberta
T2P 0M3
(403) 267-4110

Chevron Canada Resources Ltd.
500-5th Avenue S.W.
Calgary, Alberta
T2P 0L7
(403) 262-0500

Amoco Canada Petroleum Co. Ltd.
444-7th Avenue S.W.
Calgary, Alberta
T2P 0Y2
(403) 233-1313

Cominco Limited
200 Granville Street
Vancouver, British Columbia
V6C 2R2
(604) 682-0611

Canterra Energy Ltd.
P.O. Box 1051
505-5th Street S.W.
Calgary, Alberta
T2P 2K7
(403) 267-9111

Dome Petroleum Ltd.
330-7th Avenue S.W.
P.O. Box 200
Calgary, Alberta
T2P 2Z1
(403) 260-5100

Canadian Superior Oil Ltd.
3 Calgary Place
355-4th Avenue S.W.
Calgary, Alberta
T2P 0J3
(403) 267-4110

Esso Resources Canada Limited
Esso Plaza
237-4th Avenue S.W.
Calgary, Alberta
T2A 0H6
(403) 237-3737

Chevron Canada Ltd.
1500-1050 West Pender Street
Vancouver, British Columbia
V6C 3T4
(604) 681-4271

Gulf Canada Ltd.
130 Adelaide St. W.
Toronto, Ontario
M5H 3P5
(416) 869-8600

Home Oil Co. Limited
2300 Home Oil Tower
324-8th Avenue S.W.
Calgary, Alberta
T2P 2Z5
(403) 232-7100

Husky Oil Ltd.
505-5th Street S.W., 19th Floor
P.O. Box 6525, Station "D"
Calgary, Alberta
T2P 3G7
(403) 267-6111

Imperial Oil Ltd.
111 St. Clair Avenue West
Toronto, Ontario
M5W 1K3
(416) 968-4111

Inco Metals
Inco Ltd.
1 First Canadian Place
P.O. Box 44
Toronto, Ontario
M5X 1C4(403) 234-6700
(416) 361-7511

Irving Oil Ltd.
Refining Division
P.O. Box 1260
Saint John, New Brunswick
E2L 4H6
(506) 652-7710

Maynard Exploration Company
2319 Sun Oil Bldg.
T2P 2V6
(403) 269-4993
Calgary, Alberta

Mobil Oil Canada Ltd.
Mobil Tower
330-5th Avenue S.W.
P.O. Box 800
Calgary, Alberta
T2P 2J7
(403) 268-7910

Norcen Energy Resources Ltd.
4600 Toronto Dominion Centre
Toronto, Ontario
M3K 1E5
(416) 866-4000

Pan Canadian Petroleum
Pan Canadian Plaza
150-9th Avenue S.W.
P.O. Box 2850
Calgary, Alberta
T2P 2S5
(403) 290-2000

Petro-Canada
P.O. Box 2844
Calgary, Alberta
T2P 2M7
(403) 296-8000

Petrogas Processing Ltd.
1600 McFarland Towers
700-4th Avenue S.W.
Calgary, Alberta
T2P 3J5

Saratoga Processing Co. Ltd.
1212 Palliser Square East
125-9th Avenue S.E.
Calgary, Alberta
T2G 0P6
(403) 262-4561

Shell Canada Ltd.
505 University Avenue
Toronto, Ontario
M5G 1X4
(416) 597-7111

Sulconam Inc.
11450 Cherrier
Montreal East, Quebec
H1B 1A6
(514) 645-1636

Sulpetro of Canada Ltd.
3200 Bow Valley Square
255-5th Avenue S.W.
Calgary, Alberta
T2P 3G6
(403) 232-1500

Texaco Canada Inc.
90 Wynford Drive
Don Mills, Ontario
M3C 1K4
(416) 443-7811

Suncor Inc.
Sunoco Group Offices
56 Wellesley Street West
Toronto, Ontario
M5S 2S4
(416) 924-4111

Westcoast Transmission Co. Ltd.
1333 West Georgia Street
Vancouver, British Columbia
V6E 3K9
(604) 682-4411

Suncrude Canada Ltd.
10030-107 Street
Edmonton, Alberta
T5J 3E5
(403) 429-9110

Western Decalta Petroleum (1977)
Limited
P.O. Box 2404, 9th Floor
734-7th Avenue S.W.
Calgary, Alberta
T2P 2M7
(403) 294-5566

3.3 Major Transportation Routes

Canadian production and/or utilization of elemental sulphur are widespread, occurring in nine of the ten provinces. Alberta accounts for 90 percent of the total production, with facilities located throughout the province. Both solid and molten forms are shipped to destinations in North America by rail and truck. Molten sulphur is not shipped to offshore markets. Offshore shipments of formed sulphur (prills, slates or granules) occur through the ports of Vancouver and Prince Rupert, B.C., and Thunder Bay, Ontario. Generally, the sulphur reaches these ports by rail. The Canadian market for elemental sulphur totals around 850,000 tonnes per year, half of which remain in Alberta for the manufacture of fertilizer. Transport of molten sulphur by truck is only significant within Alberta in the fertilizer manufacturing industry.

3.4 Production Levels (Corpus 1983)

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1982)
Amerada Mineral, Olds, Alta.	140
Amoco, East Crossfield, Alta.	640
Amoco, Bigstone Creek, Alta.	140

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1982)
Amoco, Canterra, Windfall, Alta.	430
Canadian Occidental Petroleum, Paddle River, Alta.	7.1
Canadian Superior Oil, Harmattan, Alta.	180
Canadian Superior Oil, Lone Pine Creek, Alta.	57
Canterra Energy, Rainbow Lake, Alta.	50
Canterra Energy, Ram River, Alta.	1 670
Canterra Energy, Okotoks, Alta.	167.5
CDC Oil & Gas, Brazeau River, Alta.	15.5
Chevron Canada, Burnaby, B.C.	3.5
Chevron Development, Sinclair, Alta.	90
Chevron Standard, Kaybob, Alta.	1 285
Chevron Standard, Nevis, Alta.	95
Cominco, Trail, B.C.	40
Consumers Corp. REF., Regina, Sask.	7.2
Dome Petroleum, Brazeau River, Alta.	40.2
Dome Petroleum, Caroline, Alta.	8
Dome Petroleum, Edson, Alta.	103.5
Dome Petroleum, Kaybob South I, Alta.	388
Dome Petroleum, Kaybob South II, Alta.	388
Dome Petroleum, Lone Pine Creek, Alta.	103
Dome Petroleum, Sturgeon Lake S., Alta.	27
Esso Resources, Joffre, Alta.	6.2
Esso Resources, Quirk Creek, Alta.	109.5
Esso Resources, Redwater, Alta.	12
Gulf Canada, Clarkson, Ont.	15
Gulf Canada, Edmonton, Alta.	37.5
Gulf Canada, Hanlan-Robb, Alta.	251
Gulf Canada, Nevis, Alta.	108.5
Gulf Canada, Pincher Creek, Alta.	58.5
Gulf Canada, Port Moody, B.C.	9
Gulf Canada, Rimbey, Alta.	121.5
Gulf Canada, Strachan, Alta.	344
Home Oil, Carstairs, Alta.	26.5
Hudson's Bay Oil & Gas, Zama, Alta.	27
Husky Oil, Prince George, B.C.	2
Imperial Oil, Edmonton, Alta.	13
Imperial Oil, Ioco, B.C.	6.5
Imperial Oil, Sarnia, Ont.	40
Imperial Oil, Dartmouth, N.S.	26
Inco Metals, Thompson, Man.	30
Irving Refining, Saint John, N.B.	73
Mobil Oil Canada, Teepee Creek, Alta.	11
Mobil Oil Canada, Wimborne, Alta.	63.5
Pan Canadian Petroleum, Morley, Alta.	6.5
Petro-Canada, Gold Creek, Alta.	15.5
Petro-Canada, Wildcat Hills, Alta.	64.5

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1982)
Petrogas Processing, Crossfield, Alta.	615
Saratoga Processing, Coleman, Alta.	142
Shell Canada, Burnt Timber Cr., Alta.	181.5
Shell Canada, Corunna, Ont.	12.5
Shell Canada, Burnaby, B.C.	5.5
Shell Canada, Innisfail, Alta.	59.5
Shell Canada, Jumping Pound, Alta.	186.5
Shell Canada, Oakville, Ont.	18
Shell Canada, Simonette River, Alta.	97.5
Shell Canada, Waterton, Alta.	1 120
Shell Canada, South Rosevear, Alta.	62.5
Steelman Gas, Steelman, Sask.	2.5
Sulconam Inc., Montreal East, Que.	110
Sulpetro, Minnehik-Buck L., Alta.	16.5
Suncor, Black Diamond, Alta.	4.5
Suncor, Fort McMurray, Alta.	100
Suncor, Rosevear, Alta.	30.5
Suncor, Sarnia, Ont.	4.5
Syncrude, Mildred Lake, Alta.	181.5
Texaco Canada, Bonnie Glen, Alta.	4.5
Texaco Canada, Nanticoke, Ont.	12.5
Westcoast Trans, Fort Nelson, B.C.	400
Westcoast Trans, Pine River, B.C.	385
Westcoast Trans, Taylor Flats, B.C.	118.5
Western Decalta, Turner Valley, Alta.	9
TOTAL	11 458.2
Domestic Production (1982)	6 673
Imports (1982)	2
TOTAL SUPPLY	6 675

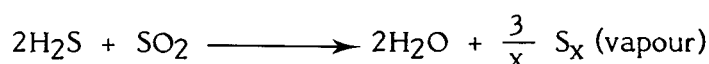
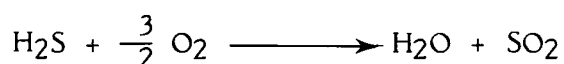
3.5 Manufacture of Sulphur (Shreve 1977; CMI 1980)

3.5.1 General. In Canada, sulphur is obtained from three sources. The primary source of elemental sulphur is from sour natural gas (containing hydrogen sulphide), with smaller amounts from sour petroleum. Other sources include sulphuric acid and sulphur dioxide recovered from smelter gases, and sulphuric acid from pyrite concentrates and minor amounts from direct mining operations.

3.5.2 Raw Materials Occurrence and Extraction. The hydrogen sulphide dissolved in natural gas is extracted by absorption into a solution of either diethanolamine, monoethanolamine, hot potassium carbonate or sulfinol (a mixture of water, an alkanolamine - usually diisopropanolamine - and sulfolane-tetrahydrothiophene dioxide).

The solution is then heated in a stripper tower where the dissolved gas is evolved. Considerable care is taken to ensure that hydrocarbon dissolution in the treating agent is avoided.

3.5.3 Manufacturing Process. The hydrogen sulphide is then burned with sufficient air to oxidize one-third of the hydrogen sulphide to sulphur dioxide; or, in some operations, sulphur dioxide, made by burning sulphur, is added to achieve a two-to-one hydrogen sulphide-to-sulphur dioxide ratio. This mixture is passed over an alumina-based catalyst in a "Claus reactor" or other reactors. The following equations are representative of the transformations occurring in reactors:



A key variable in this reaction is the ratio of sulphur dioxide to hydrogen sulphide. This must be controlled within close limits for good yields of sulphur. (Precision may be achieved by computer-linked spectrophotometric analysis and feed control systems.) Passing the reaction mixture through another, lower temperature, reactor shifts the equilibrium to more complete conversion to sulphur. Similar reactors may be used at progressively lower temperatures to reduce the amounts of unreacted sulphur compounds to acceptable levels prior to final discharge of effluent gases to the atmosphere.

Gas from the reactor enters a condenser-converter series; liquid sulphur is removed in each unit until 95 percent or more of the original sulphur has been drawn off. The molten sulphur can be transported as a liquid or processed to form slates, granules and prills. The latter two forms are generated by water quenching and air quenching sprays of molten sulphur, respectively. The air is blown up through towers to quench counter-current sprays of the molten class product. Water quenching produces relatively lumpy granules in a large range of sizes, while air quenching produces dimpled spheroids of fairly consistent size.

3.6 Major Uses in Canada (CMI 1980)

Consumption of sulphur in 1979 and 1980 was in excess of 1.7 million tonnes, with about half of the tonnage (counted as sulphur equivalent) derived from smelter gases. Three-quarters of this total consumption was in the form of sulphuric acid at some stage.

It is safe to say that the major use of sulphur in Canada is in the production of sulphuric acid. The second largest consumer is the pulp and paper industry. Other industries using significant quantities of sulphur or sulphuric acid are uranium ore processing, metal recovery, petroleum refining, plastics, rubber products, soaps, and food.

3.7 Major Buyers in Canada (Corpus 1981; CBG 1980)

Abitibi-Price, Iroquois Falls, Thorold, Thunder Bay, Ont.; Kenogami, Que.; Grand Falls, Nfld.
 BC Forest Products, Crofton, Mackenzie, B.C.
 Boise Cascade, Kenora, Ont.
 Border Chemical, Transcona, Man.
 Bowater Mersey, Brooklyn, N.S.
 Bowater Newfoundland, Cornerbrook, Nfld.
 Canada Colours, Toronto, Ont.
 Canadian Cellulose, Castlegar, B.C.
 Canadian Forest Products, Port Mellon, B.C.
 Canadian International Paper, Hawkesbury, Ont.; Trois-Rivieres, Matane, Que.
 Canadian Occidental Petroleum, Vancouver, B.C.
 Cariboo Pulp, Quesnel, B.C.
 Chemsolve, Willowdale, Ont.
 Consolidated-Bathurst, Shawinigan, Grand'Mere, Port Alfred, Que.
 Cornwall Chemicals, Cornwall, Ont.
 Crestbrook Timber, Skookumchuck, B.C.
 Domtar, Dolbeau, Donnacona, Que.
 Donohue, Clermont, Que.
 Esso Chemical Canada, Redwater, Alta.
 Fraser, Edmundston, Atholville, N.B.
 Gaspesia Pulp & Paper, Chandler, Que.
 Great Lakes Forest, Thunder Bay, Ont.
 Gulf Minerals, Rabbit Lake, Sask.
 IMC, Port Maitland, Ont.
 Inland Chemicals, Ft. Saskatchewan, Alta.
 Kruger Pulp & Paper, Trois Rivieres, Que.
 Lake Utopia Paper, St. George, N.B.
 MacLaren James, Buckingham, Que.
 MacMillan Bloedel, Harmac, Powell River, B.C.
 NL Chem Canada, Varennes, Que.
 Northwood Pulp, Prince George, B.C.
 Nova Scotia Forest, Pt. Hawkesbury, N.S.
 Ontario Paper, Thorold, Ont.
 QNS Paper, Baie Comeau, Que.
 Rayonier, Port Alice, B.C.
 Reed, Quebec City, Que.
 St. Lawrence Chemical, Montreal, Que.
 St. Raymond Paper, Debiens, Que.
 St. Regis Alberta, Hinton, Alta.
 Sherritt Gordon Mines, Ft. Saskatchewan, Alta.
 Spruce Falls Power, Kapuskasing, Ont.
 Sulco Chemicals, Elmira, Ont.
 Tahsis, Gold River, B.C.

Tembec Forest Products, Temiscaming, Que.
Thio-Pet Chemicals, Ft. Saskatchewan, Alta.
Van Waters & Rogers, Richmond, B.C.
Western Cooperative Fertilizer, Calgary, Alta.
Western Forest Products, Port Alice, B.C.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 Bulk Shipment. Most sulphur is transported in open-topped gondola cars as bulk solid. Molten sulphur and solid bulk sulphur are shipped in specially designed railway tank cars and tank motor vehicles.

4.1.1.1 Railway cars. Solid sulphur is most commonly transported in open-topped gondola cars as illustrated in Figure 4 and detailed in Table 2. The capacity of the most commonly used gondola is 125 m³ (4,400 cu. ft.) or 91 tonnes (100 tons) (ORER 1983). Railway tank cars used in the transportation of molten sulphur are not regulated by CTC or DOT. However, CTC/DOT 111A railway tank cars are generally used. The most commonly used car is a 50,500 L (11,000 Imp. gal.) capacity 111A100W1 tank car as illustrated in Figure 5 and detailed in Table 3.

Cars are equipped for unloading by pump, gravity flow, or air padding through one 102 mm (4 in.) diameter bottom outlet provided with a stainless steel ball valve (Shell 1982). This bottom discharge outlet is furnished with a steam jacket (Shell 1982). In addition to bottom unloading, the cars may be unloaded from the top by compressed air. In this case, the molten sulphur is withdrawn through an eduction pipe which extends from the bottom of the tank to the top operating platform where it terminates at a blind flange, usually 51 mm (2 in.) in size. Air pressure of 138 kPa (20 psi) is applied through the 25 mm (1 in.) air connection valve (MCA 1959). Outside heating coils and glass wool insulation are required. Constructed from 203 mm (8 in.) diameter type A53 grade B steel pipe in half-oval form, the heating coils are laid out in a serpentine configuration across the bottom third of the tank (TCM 1979).

A safety vent set at 517 kPa (75 psi) is required on top of the rail car. A gauging device, either the rod type or the tape type, is optional. The maximum pressure allowable for the 111A100W1 rail car is 448 kPa (65 psi). Molten sulphur is never transported under pressure.

4.1.1.2 Motor vehicles. Trucks are also used to transport sulphur. Open boxes are typically used to transport formed sulphur. Tank trucks are occasionally used to transport molten sulphur. Similar to railway tank cars, these highway tankers are unloaded through a bottom outlet provided with an inner plug valve (CMI 1980). When compressed air is used for unloading, the standpipe, usually extended down over the back of the tanker, is used (MCA 1959). Because tank trucks are used for hauling molten sulphur relatively

SULPHUR

TYPICAL GONDOLA FOR SULPHUR TRANSPORT

(Reference - CLC 1974, ORER 1983)

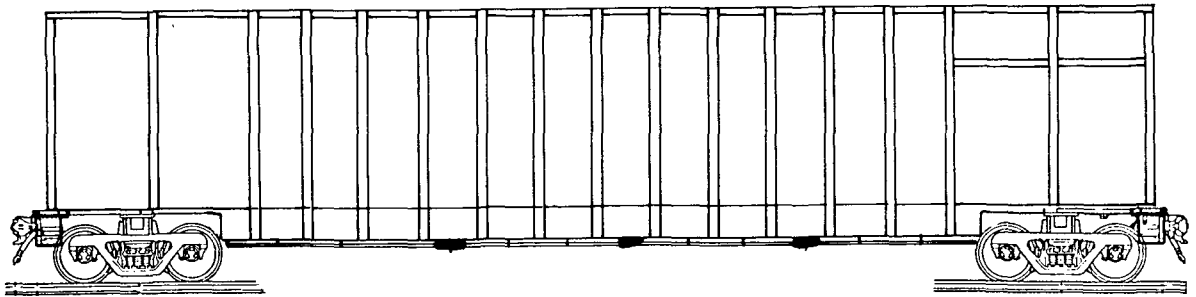


TABLE 2 TYPICAL SPECIFICATIONS FOR SULPHUR GONDOLA (CLC 1974; ORER 1983)

Description		
<u>Overall</u>		
Nominal capacity	125 m ³	(4,400 cu. ft.)
	91 tonnes	(100 tons)
Car weight - (max.)	94,800 kg	(209,000 lb.)
<u>Gondola</u>		
Outside length	17.9 m	(58 ft. 7 in.)
Outside width	3.25 m	(10 ft. 8 in.)
Outside height	3.76 m	(12 ft. 4 in.)
Inside length	14.6 m	(48 ft.)
Inside width	2.97 m	(9 ft. 9 in.)
Inside height	3.43 m	(11 ft. 3 in.)
<u>Approximate Dimensions</u>		
Coupled length	19 m	(63 ft.)
Length over strikers	18 m	(60 ft.)
Length of truck centers	15 m	(48 ft.)
Clearance height	5 m	(15 ft.)
Overall width	3 m	(11 ft.)

short distances, no steaming facilities are usually provided but insulation is required to keep heat losses to a minimum.

Molten sulphur is not transported under pressure. Highway tankers must be pressure tested at 207 kPa (30 psi) minimum to allow for the compressed air pressure of 138 kPa (20 psi) used during top unloading (MCA 1959).

4.2 Off-loading

The off-loading procedure for solid forms of sulphur from both rail and truck is by dumping and thus will not be described further in this section.

4.2.1 Off-loading Equipment and Procedures for Railway Tank Cars. Prior to off-loading, certain precautions must be taken (MCA 1959; Shell 1982; CCPA 1982):

- Ensure that receiving container has sufficient capacity to hold the contents of the tank car.
- For night-time unloading, lights must have an explosion-proof rating.
- Personnel must not enter the car under any circumstances.

SULPHUR

RAILWAY TANK CAR - CLASS 111A100W1

(Reference - TCM 1979, RTDCR 1979)

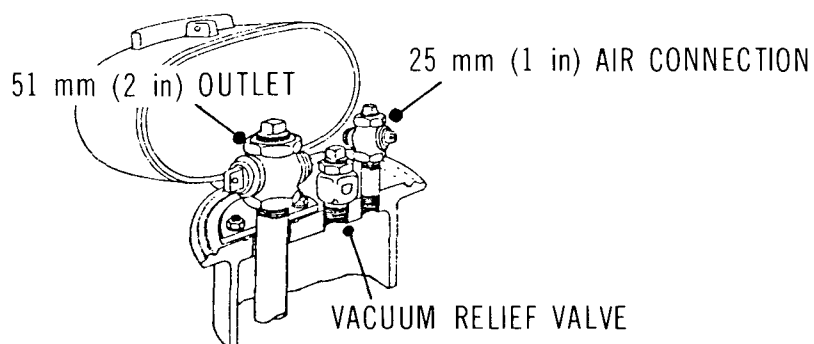
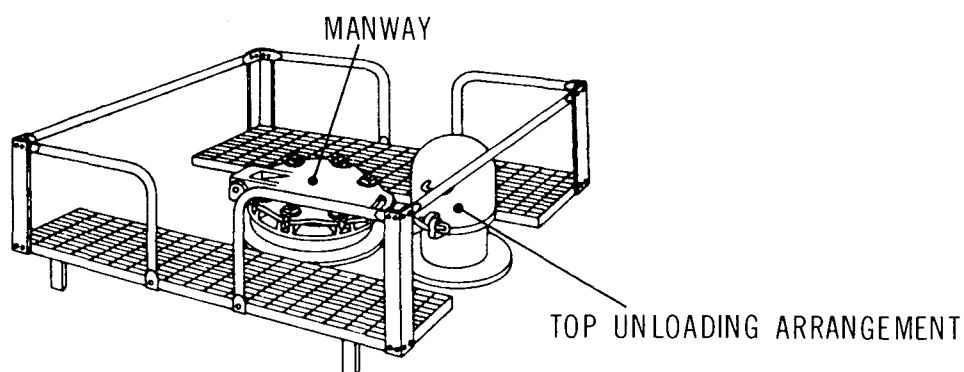
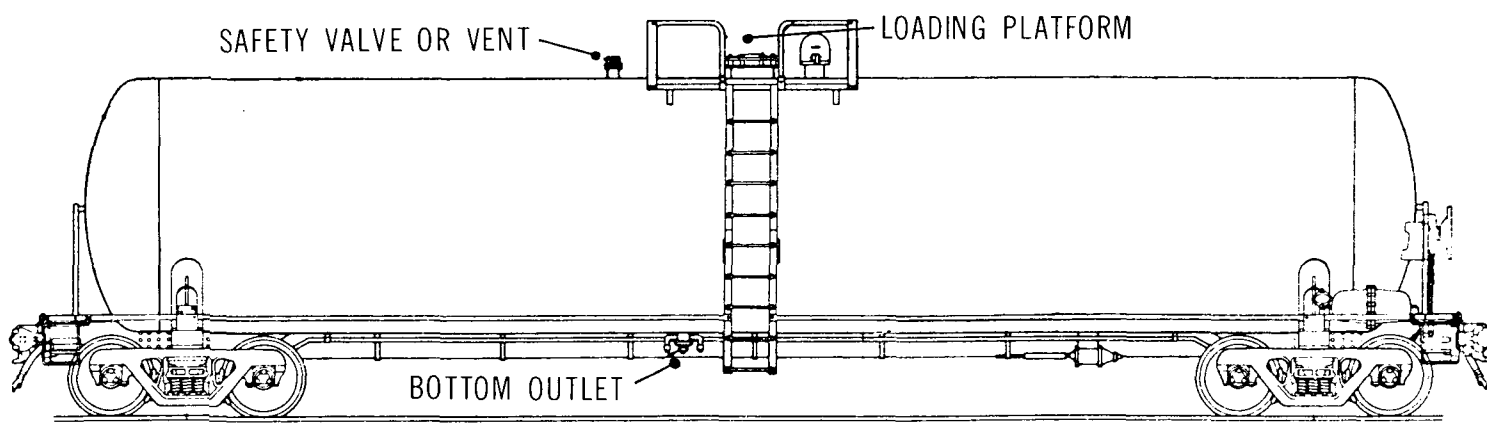
**Detail of top unloading arrangement****Detail of loading platform****Illustration of tank car layout**

TABLE 3 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 111A100W1
(TMC 1979; Shell 1982)

Description		
<u>Overall</u>		
Nominal capacity	50,500 L	(11,000 Imp. gal.)
Car weight - empty	28,600 kg	(63,000 lb.)
Car weight - (max.)	119,000 kg	(263,000 lb.)
<u>Tank</u>		
Material	Steel	
Thickness	11.1 mm	(7/16 in.)
Inside diameter	2.38 m	(94 in.)
Test pressure	689 kPa	(100 psi)
Burst pressure	3,450 kPa	(500 psi)
<u>Approximate Dimensions</u>		
Coupled length	14 m	(45 ft.)
Length over strikers	13 m	(43 ft.)
Length of truck centers	9 m	(28 ft.)
Height to top of grating	3.7 m	(12 ft.)
Overall height	4.3 m	(14 ft.)
Overall width (over grabs)	3.2 m	(127 in.)
Length of grating	2.4 m	(8 ft.)
Width of grating	1.8 m	(6 ft.)
<u>Loading/Unloading Fixtures</u>		
<u>Top Connections</u>		
Siphon tube connection	51 mm	(2 in.)
Manway/fill hole	457 mm	(18 in.)
Air connection	25 mm	(1 in.)
<u>Bottom Unloading</u>		
Bottom outlet	102 mm	(4 in.)
Nipple size	Steam jacketed 51 mm (2 in.)	
<u>Safety Devices</u>		
	Safety vent set at 517 kPa (75 psi)	
<u>Dome</u>		
	None	
<u>Insulation</u>		
	152 mm	(6 in.)
	glass wool	

- Brakes must be set, wheels chocked, derails employed, car grounded, and caution placards displayed.
- Because of the possibility of hydrogen sulphide being present, breathing protection and a doctor should be available.
- A safe operating platform must be provided at the unloading point.

Two means of off-loading are used for molten sulphur rail cars - top off-loading and bottom off-loading. Both means are indicated in Figure 6.

Proceed with top off-loading as follows (MCA 1959; Shell 1982):

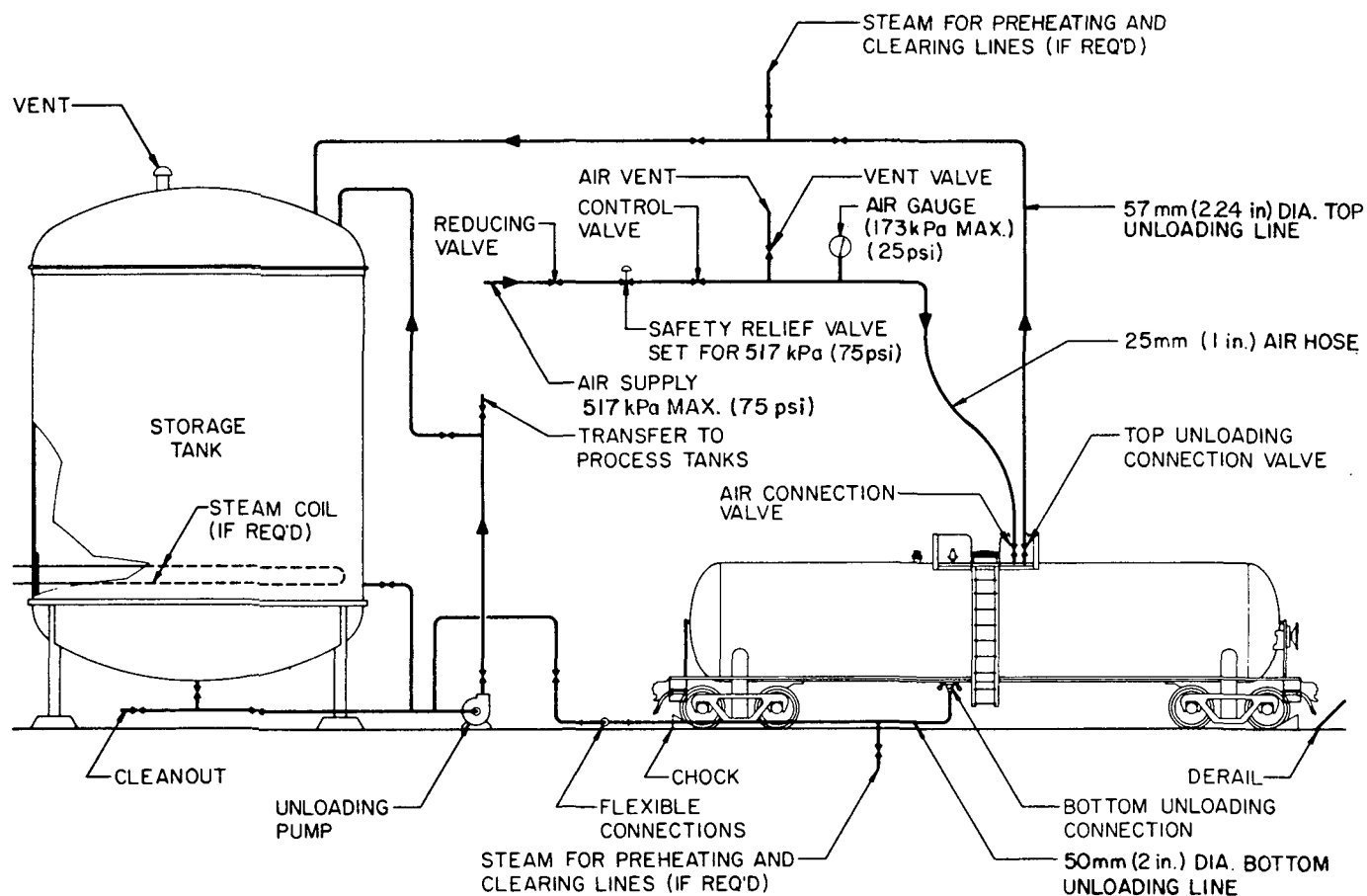
- Ascertain that any pressure buildup within the tank car has been released and that sulphur is completely molten.
- Connect the 51 mm (2 in.) heated unloading line to the discharge outlet.
- Connect the 25 mm (1 in.) air line. Air pressure must be increased to 448-517 kPa (65-75 psi) for unloading. A safety relief valve must be installed in the air line to release at 517 kPa.
- After opening the air supply valve, the unloading connection valve can then be opened to unload the car.
- Once the car is empty, the air supply valve must be closed and the vent valve in the air line opened to allow the line pressure to equalize to atmospheric pressure. Gauge should indicate 101 kPa (14.6 psi).
- Reverse the above procedure to close up the car.

Proceed with bottom off-loading in the following manner using gravity flow, air, or pumping (MCA 1959; Shell 1982):

- Ascertain that any pressure buildup within the car has been released and that sulphur is completely molten.
- In cold weather, apply steam to the bottom unloading connection. Steam coil connection valves (Figure 6) should also be connected to live steam. The steam is regulated to achieve a pressure of 483 kPa (70 psi) to warm the sulphur to 132°C (12 to 20 hours). Before unloading, reduce steam pressure to 276 kPa (40 psi).
- After connecting the unloading line to the 51 mm (2 in.) bottom outlet, open the inside bottom valve by turning the valve rod handle at the top of the car.
- Off-load the car by gravity, air, or pump. The same air pressure precautions must be taken as with top unloading.
- Reverse the above procedure to close up the car.

4.2.2 Off-loading Equipment and Procedures for Tank Motor Vehicles. The unloading of molten sulphur tank trailers is similar to that of tank cars, with the exception that no facilities for steaming are usually provided. The general procedures for tank cars apply equally well to tank trailers.

SULPHUR

TANK CAR UNLOADING**NOTE:**

1. FOR TOP OR BOTTOM UNLOADING METHOD SEE TEXT.

4.2.3 Specifications and Materials for Off-loading Equipment. The materials of construction for off-loading system components discussed in this section along with specifications refer to those generally used in molten sulphur service. It is recognized that other materials may be used for the handling of solid sulphur and for particular applications with molten sulphur. The components of a typical off-loading system include pipes and fittings, flexible connections, valves, gaskets, pumps and storage tanks.

Steel is a common material of construction for pipes, valves and pumps in molten sulphur service. PVC pipes and fittings are also acceptable. Swivel joints are commonly used where flexibility is required. If flanged joints are used, they should be welded. Stress relief should be afforded at the weld to lengthen service life. All piping should be tested for leaks using appropriate methods and any leaks carefully sealed. If water is used for leak testing, the piping should be thoroughly dried before use with molten sulphur (CE 1978; MWPP 1978).

Unloading lines, bottom or top, are usually 51 mm (2 in.) diameter, but process piping may be almost any size. Pipe under 25 mm (1 in.), however, is not recommended. Most pipelines and equipment used to handle molten sulphur are heated with steam and insulated. Steam jacketing is a most effective way of controlling the temperature of molten sulphur. Since sulphur is a very poor conductor of heat, it is very difficult to remelt it in piping once the temperature has dropped below 115°C. The outdoor lines must therefore be self-draining. However, if pipelines are drained and allowed to cool, some of the residual sulphur may oxidize and cause corrosion.

For valving, stainless steel 316 plug valves or ball valves will serve adequately (JSSV 1979). Polyvinylidene fluoride resin or chlorinated polyether resin can be used satisfactorily as a gasket material (DCRG 1972). Different types of pumps are used in molten sulphur service, with centrifugal pumps being recommended. Some gear and piston pumps may also be used. The centrifugal pumps should be single-suction, sealless magnetic drive, with wet end material of 316 stainless steel. All pumps must be steam jacketed or steam traced. Due to the relatively high specific gravity of molten sulphur, large horsepower motors are required. When sulphur is stored in pits, sump pumps should be used (CE 1978).

Welded stainless steel storage tanks are commonly used. A sulphur-resistant lining is also acceptable. The storage tank should be well-insulated and provided with heating coils to keep the sulphur in a molten state. Pipelines and storage tanks should be grounded (CE 1978).

4.3 Compatibility with Materials of Construction.

The compatibility of sulphur with materials of construction is indicated in Table 4. The designation "other" listed in Table 4 refers to items where the specific application is not given or is unclear. The unbracketed abbreviations are described in Table 5. The rating system for this report is briefly described below.

- Recommended: This material will perform satisfactorily in the given application.
- Conditional: Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.
- Not Recommended: Material will be severely affected in this application and should not be used.

TABLE 4 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	n.d. ¹	23, to operating limit of material	PE ² (DPPED 1967; MWPP 1978)		
	n.d.	60, to operating limit of material	PVC I (DPPED 1967; MWPP 1978)	PVC II (DPPED 1967)	
	100%	>120, dry, molten	Steel ³ (CE 1978)		
	n.d.	121, molten ⁴	PVDF (DCRG 1972)		
	n.d.	121, molten ⁴	Chlorinated Polyether (DCRG 1972)		
	n.d.	to operating ⁵ limits of materials	ABS (MWPP 1978)		
	100%	>120, dry, molten	Steel, mild Cast Iron (Kirk-Othmer 1979)		
	100%	>120, molten, dry	Steel ³ (CE 1978)		
2. Valves ⁶	n.d.	<130, molten, dry	SS 316 (JSSV 1979)		

TABLE 4 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
2. Valves ⁶ (cont'd)	n.d.	130 to 444.6 molten, dry			SS 316 (JSSV 1979)
	n.d.	n.d., wet		SS 316 (JSSV 1979)	
3. Gaskets	n.d.	n.d. ⁷	PVDF (DCRG 1972)		
	n.d.	n.d. ⁷	Chlorinated Polyether (DCRG 1972)		
4. Pumps	100%	>120, molten, dry	Steel ³ (CE 1978)		
	n.d.	n.d., molten	All Iron (HIS 1969)		
	n.d.	n.d.	SS 304, 316 (HIS 1969)		
5. Storage	100%	129-140 molten, dry	Steel ^{3,8} (Welded) (CE 1978)		
		130, molten	SS 316 ⁹		
	100%	129-140 molten, dry	Steel lined ¹⁰ with concrete (CE 1978)		
6. Others ¹¹	n.d.	20, dry	SS 302, 304, 316, 430 (ASS)	SS 410 (ASS)	
	n.d.	20, wet	SS 316 (ASS)	SS 302, 304, 430 (ASS)	SS 410 (ASS)
	n.d.	20 ¹²	PE, PP, POM, NR, NBR, IIR, EPDM, CR, FPM CSM (GF)	uPVC (GF)	
	n.d.	60 ¹²	PP, POM, NR, NBR,	uPVC PE (GF)	

TABLE 4 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
6. Others (cont'd)			IIR, EPDM, CR, FPM, CSM (GF)		
	n.d.	60, slurry	PVC (TPS 1978)		
		85, slurry ¹³	CPVC (TPS 1978)		
	n.d.	<120, solid moist	Steel alloys of Al, SS (Kirk-Othmer 1979)		
		Molten			NR, SBR, CR, NBR, IIR, CSM, EPDM (GPP)
	n.d.	n.d.	CSM (GPP)	EPDM (GPP)	NR SBR NBR (GPP) IIR (GPP)
	100%	>120, molten, dry			Copper Copper alloys (PB 216658)
	100%	24 to 149	Glass (CDS 1967)		
	100%	204			Glass (CDS 1967)
	100%	To 240, molten ¹²	Ti (PMT) (AMC)		
	n.d.	>120, molten, dry	SS 304, 304L, 321, 347, 316, 316L Ni Monel, Inconel (SFC; GAC)		
	n.d.	n.d., wet	SS 316, 316L Inconel (SFC; GAC)	SS 304, 304L 321, 347 Ni Monel (SFC; GAC)	
	n.d.	high temp.			Ni Ni alloys (CE 1980)

TABLE 4 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
6. Others (cont'd)	n.d.	232-1,010 ¹²	Alon steels (API)		

1. n.d. = No data given.
2. Material given a lower rating at higher temperatures by another reference.
3. Type of steel not stated.
4. Molten assumed, moisture content unknown.
5. Assumed capable of having either solid or molten sulphur.
6. Based on data given for pipes, valves, pumps and storage, one can assume that steel (probably SS 316) is adequate for handling molten, dry sulphur up to about 140°C.
7. Based on data under pipes and fittings; can be used for molten sulphur at 121°C.
8. For large quantities.
9. No reference stated.
10. For small quantities.
11. Many other materials for possible use with sulphur are listed under the "Others" category. No particular application was stated in the reference and specifics must be acquired before use of the material.
12. Moisture content not stated.
13. Slurry liquid not stated.

TABLE 5 MATERIALS OF CONSTRUCTION

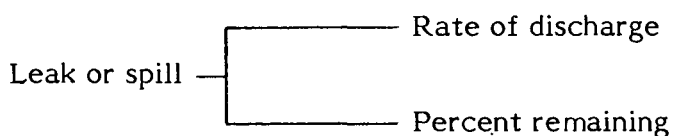
Abbreviation	Material of Construction
ABS	Acrylonitrile Butadiene Styrene
	Bronze
	Chlorinated Polyether
CPVC	Chlorinated Polyvinyl Chloride
CR	Polychloroprene (Neoprene)
CSM	Chlorosulphonated Polyethylene (Hypalon)
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton)
	Glass
	Iron
IIR	Isobutylene/Isoprene (Butyl) Rubber
NBR	Acrylonitrile/Butadiene Rubber (Nitrile, Buna N)
NR	Natural Rubber
PE	Polyethylene
POM	Polyoxymethylene
PP	Polypropylene
PVC (Followed by grade, if any)	Polyvinyl Chloride
PVDF	Polyvinylidene Fluoride
SBR	Styrene/Butadiene (GR-5, Buna N)
SS (Followed by grade)	Stainless Steel
uPVC	Unplasticized Polyvinyl Chloride

5 CONTAMINANT TRANSPORT

5.1 General Summary

Sulphur is transported as a solid in slate, granular or prill forms, and in the liquid state at elevated temperature. When spilled in water, liquid sulphur will sink, thicken, and solidify. There may be occasions where the molten material will form amorphous/plastic sulphur when spilled in very cold water. Large volumes of steam will be produced. When spilled on soil, the molten product will solidify on the surface. Transport of the liquid toward the water table is not an environmental concern. Because sulphur has a low vapour pressure, large-scale dispersion in air is not considered to be a problem. Local problems may occur, however, due to dispersion of powdered material that may have been generated as a result of an accident. A thin coating of sulphur on metal, e.g. equipment, structures, etc., may result in corrosion due to the formation of acids.

Factors considered for a sulphur spill are:



5.2 Leak Nomograms

5.2.1 Introduction. Sulphur is commonly transported in railway tank cars as a non-pressurized liquid at temperatures above 122°C. While the capacities of the tank cars vary widely, one tank car size has been chosen for development of the leak nomograms. It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80,000 L. This size has been chosen for consistency through the EnviroTIPS manuals. It is recognized that the typical tank car for molten sulphur is 50,500 L.

If a tank car loaded with molten sulphur is punctured on the bottom, the contents will drain out by gravity. It is pointed out, however, that tank cars transporting molten sulphur are never heated during transit. A shell of solid sulphur tends to build up around the inside of the car, the thickness depending on the transit time and the outside air temperature. Rate of drainage would depend on the severity of the puncture and the outside temperature. It is conceivable that molten sulphur would solidify at the puncture and seal off the drainage completely (SUDIC 1983). The following leak nomograms are prepared for worst case situations, namely where all the sulphur leaks out. The aim of the nomograms is to provide a simple means to obtain the time history of the conditions in the

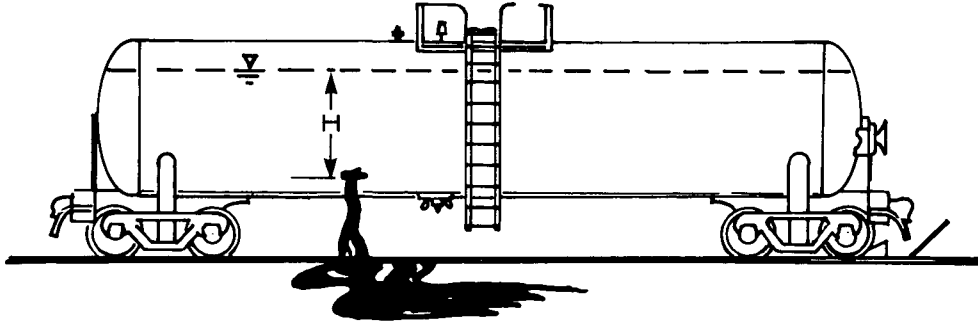


FIGURE 7 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

tank car and the discharge rate of the liquid. Because liquid sulphur is not highly volatile and the tank cars are not pressurized, no leak nomograms have been prepared for vapour release from a puncture in the top of the tank.

The rate of outflow (q) from a puncture hole in the bottom of the tank car is defined by the standard orifice equation (Streeter 1971). The discharge rate (q) is a function of the hole size (A) and shape, the height of the fluid above the puncture hole (H), and a coefficient of discharge (C_d). For the purposes of nomogram preparation, a constant discharge coefficient of 0.8 has been assumed.

5.2.2 Nomograms.

5.2.2.1 Figure 8: Percent remaining versus time. Figure 8 provides a means of estimating the percent of liquid remaining in the standard tank car after the time of puncture, for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The standard tank car (2.75 m ϕ x 13.4 m long) is assumed to be initially full (at $t=0$) with a volume of about 80,000 L of molten sulphur. The amount remaining at any time (t) is not only a function of the discharge rate over time, but also of the size and shape of the tank car.

5.2.2.2 Figure 9: Discharge rate versus time. Figure 9 provides a means of estimating the instantaneous discharge rate (L/s) at any time (t) after the time of puncture, for a number of equivalent hole diameters. The nomogram is only applicable to the standard tank car size with an initial volume of 80,000 L.

FIGURE 8

SULPHUR

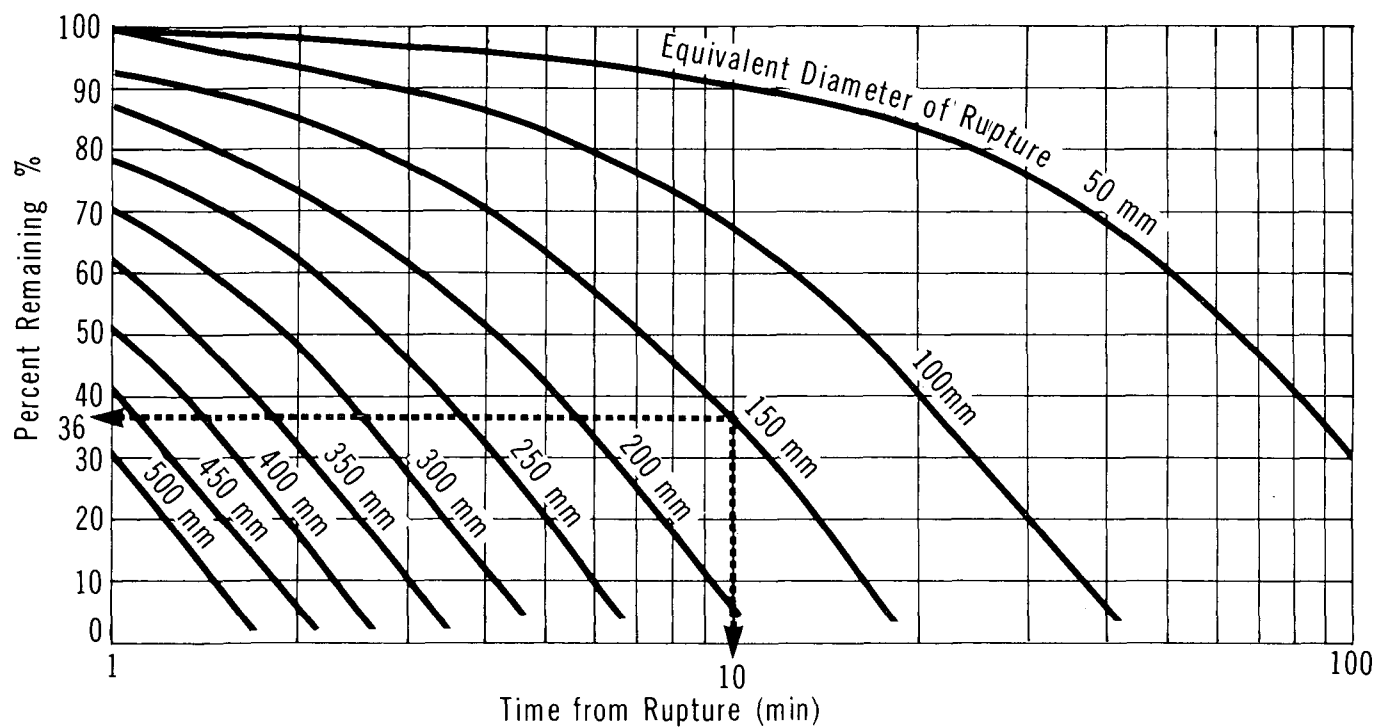
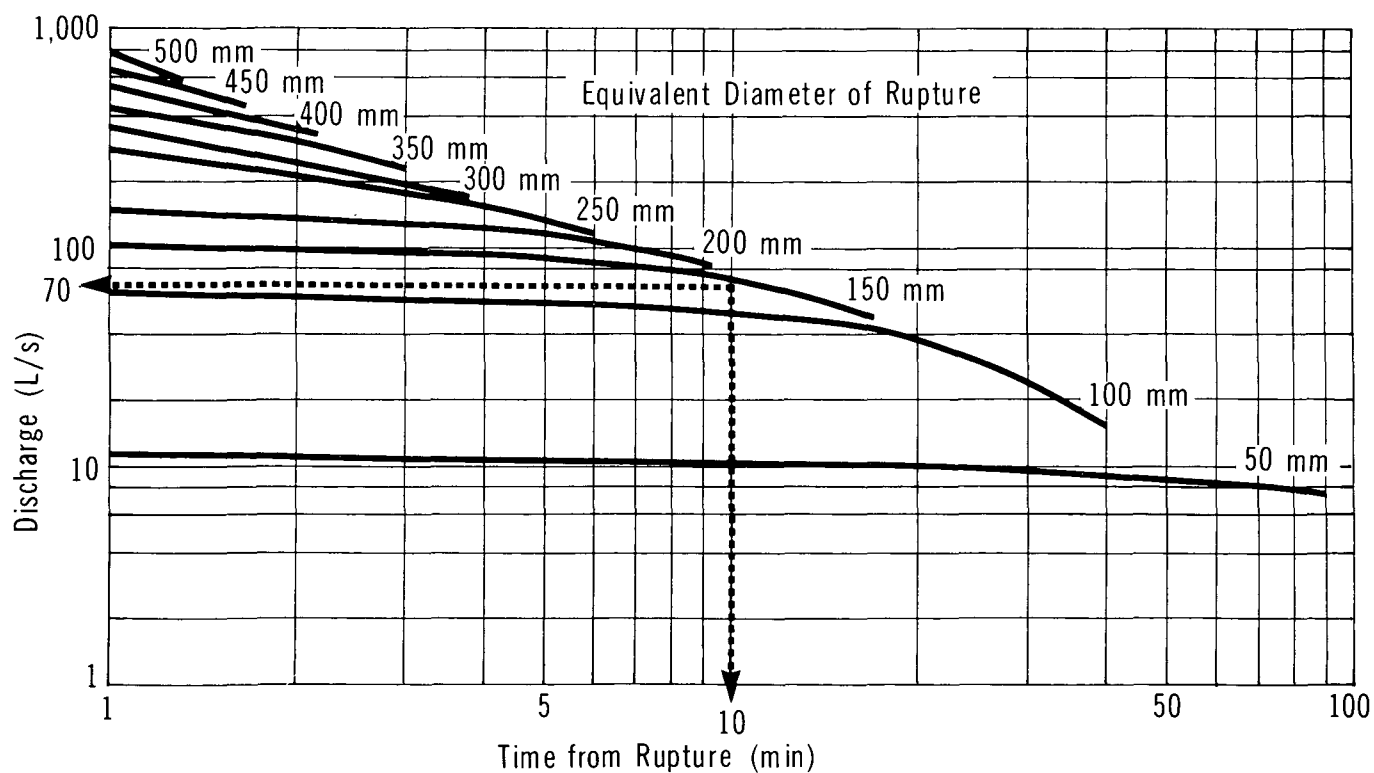
PERCENT REMAINING
VS TIME

FIGURE 9

SULPHUR

DISCHARGE RATE
VS TIME

5.2.3 Sample Calculations.

i) Problem A

The standard tank car (2.75 m \varnothing x 13.4 m long) filled with molten sulphur has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80,000 L remains after 10 minutes?

Solution to Problem A

- . Use Figure 8
- . With $t=10$ min and $d=150$ mm, the amount remaining is about 36 percent or 28,800 L

ii) Problem B

With the same conditions as Problem A, what is the instantaneous discharge rate from the tank 10 minutes after the accident?

Solution to Problem B

- . Use Figure 9
- . With $t=10$ min and $d=150$ mm, the instantaneous discharge rate (q) = 70 L/s

5.3 Dispersion in the Air

Since solid sulphur is nonvolatile and liquid sulphur will solidify fairly rapidly, there is no significant potential for large-scale dispersion in air. Local dusting may occur from storage piles or from powder generated at the spill site.

5.4 Behaviour with Water

Sulphur is transported in solid form or as a liquid at an elevated temperature. When spilled into water, molten sulphur in most cases will sink, thicken, and solidify. This insoluble material may not represent a significant source of water pollution in the short term; however, long-term effects should be considered. (See Sections 6.2.3, 6.5, 6.6, 9.1.3 and 9.1.4 for more discussion on the behaviour of sulphur with water and soil.) No nomograms have been prepared to describe its behaviour in water.

5.5 Subsurface Behaviour: Penetration into Soil

A spill of either molten or solid sulphur does not represent a significant source of groundwater pollution in the short term. See comments in Section 5.4 regarding the potential for long-term problems.

When spilled onto soil, molten sulphur will solidify prior to any significant movement into the soil. In solid form, sulphur is insoluble and cannot be transported downward to the groundwater table. The formation of acidic products from the reaction of sulphur and water may increase the potential for a long-term problem. Traces of hydrogen sulphide represent the only aqueous phase contaminant likely to be detected. Because of these considerations, soil penetration nomograms have not been prepared.

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water (WQS 1979). Drinking water limits for sulphur have not been set, although there are regulations governing its predominant oxidation and reduction products: sulphate and sulphide. The maximum acceptable sulphate level is 500 mg/L for drinking water and 1,000 mg/L for livestock; the objective is a level of 150 mg/L. The maximum acceptable sulphide level is 0.05 mg/L for drinking water. Sulphide in aerated water of normal pH rapidly oxidizes to sulphate.

6.1.2 Air. There are no quality standards set for sulphur. Standards of 830 and 30 $\mu\text{g}/\text{m}^3$ have been set for its possible reaction or combustion products, sulphur dioxide and hydrogen sulphide, respectively (Ontario E.P. Act 1971).

6.2 Aquatic Toxicology

6.2.1 U.S. Toxicity Rating. Sulphur has been assigned a TL_m 96 (4-day median lethal toxicity rating) of over 1,000 mg/L (RTECS 1979).

6.2.2 Measured Toxicities.

6.2.2.1 Freshwater toxicology.

Conc. (ppm)	Time (hours)	Species	Result	Water Conditions	Reference
<u>Fish Kill Data</u>					
16,000	5	Goldfish	100% mortality	colloidal sulphur in turbid water	NRCC 1977*
10 to 80	not specified	Goldfish	theoretical threshold		NRCC 1977
10,000	96	Mosquito fish	TL_m	turbid water	NRCC 1977
1,600	3.5 to 5.25	Goldfish	fatal	colloidal sulphur in tap water	NRCC 1977

* Dates of actual experiments range from 1922 to 1957.

No references were found dealing with the physiological effects of sulphur on aquatic invertebrates or microorganisms.

6.2.3 Aquatic Studies. Some general comments regarding both molten and solid sulphur spills are provided in this section. Molten sulphur, if spilled into water, will sink, thicken and solidify. Some bottom-related damage may occur as indicated below. A solid sulphur spill resulting in a colloidal suspension may cause problems similar to those caused by other suspended solids. These suspended solids may kill fish and shellfish by causing abrasive injuries or clogging the gills and respiratory passages. The sulphur that settles may blanket the bottom and kill eggs, young and food organisms, as well as destroy spawning beds. Thickened/solidified molten sulphur will probably cover the bottom in a much thicker layer and be more localized. Indirectly, the colloidal sulphur may be harmful to aquatic life by reducing light penetration sufficiently to reduce photosynthesis. Sulphur in colloidal suspension has been found to be toxic to fish at levels from 1,600 to 10,000 $\mu\text{g/L}$ over several hours (PB 216658).

It is conceivable that other problems could occur due to a sulphur spill into the aquatic environment. Molten sulphur, for example, may contain significant amounts of hydrogen sulphide gas which would be released into the water. In addition, sulphur dispersed as a colloid will slowly oxidize, forming SO_2 and acidic conditions. These pollutants are toxic to aquatic life; the degree of the problems caused will depend on the conditions at the spill site and the nature of the aquatic system.

Sulphur reaches local watercourses, in limited amounts, by dusting of solid sulphur (slate form) during transportation and handling at ports; from runoff from storage areas; and from accidental spills (NRCC 1977).

6.3 Toxicity to Other Biota

6.3.1 Livestock.

Intake by Ingestion (g)	Species	Result	Reference
170 to 227	Cattle	death	NRCC 1977
227 to 397	Horses	death	NRCC 1977
2% sulphur (in diet)	Chicks	harmful	NRCC 1977
45	Sheep	colicky pains, depressed, unwilling to stand, 35% mortality	NRCC 1977
Herbage in mining areas	Lambs	copper deficiency diseases	Gough 1980

Toxicity to animals is due to super-purgation and to partial conversion of sulphur into hydrogen sulphide by bacteria of the alimentary tract (NRCC 1977).

6.3.2 Plants.

Conc.	Species	Result	Reference
0.118 to 0.154% (total S in dry matter)	Fir needles (1 yr old)	needles became heavier with increasing distance from source; fir growth rate decreased with decreasing needle weight	Zawada 1981
200 to 250 kg/ha/yr (S fungicide)	Cotton and soybean ecosystem	health declines	Jones 1980
740 to 3,420 ppm (S content of needles)	Scots pine (1 to 3 yr old needles)	visible injuries on needles, i.e. erosion of waxes	Lehtio 1980
700 to 4,250 ppm (S content of needles)	Norway spruce (1 to 3 yr old needles)	visible injuries on needles	Lehtio 1980

6.3.3 Insects.

Conc.	Species	Result	Reference
10 g/hive	Honeybees	lethal; reproduction ceased and bees gradually died out	Skrypnik 1980
5 g/hive	Honeybees	not toxic	Skrypnik 1980

6.3.4 General - Animal and Plant Life. Sulphur is essential for animal and plant life and is present in all tissues. Sulphur and its compounds, unlike many pollutants, occur naturally and participate in widespread cycling processes throughout the environment. The feeding of excess sulphur to ruminants can give rise to problems in that it may be converted to hydrogen sulphide in the rumen and poison the animal. A deficiency of sulphur, on the other hand, inhibits protein synthesis and induces general malaise. It is also known that excess amounts of certain sulphur compounds are toxic to plants. Compared with other major nutrients, however, knowledge is lacking on its dynamics in the soil-plant-animal system and on its nutritional and physiological roles in agriculture and forest growth (NRCC 1977).

6.4 Other Air and Land Toxicity

Natural sources of sulphur discharged to the atmosphere are derived from the hydrogen sulphide and other sulphur compounds released during the biological decay of vegetation and other organic matter on land and in the ocean, and from windblown sea salt and particulate matter. It has been calculated that annual global biogenic sulphur emissions are $62-110 \times 10^6$ metric tonnes from land and $58-170 \times 10^6$ metric tonnes from the sea. Sulphur derived from sea spray is $39-45 \times 10^6$ metric tonnes per year (NRCC 1977).

6.5 Degradation

6.5.1 Aquatic Environment. Sulphur is readily oxidized in an aerobic environment. Under aerated water, fresh or salt, the sediment in lakes will generally be found to lose sulphur to the water as sulphate (NRCC 1977; Sweeney 1980). Elemental sulphur may be produced through the utilization of hydrogen sulphide in water by the bacteriological attack of a number of species of thiobacilli. The rate of sulphur oxidation is a function of the physical form of the sulphur present (NRCC 1977).

6.5.2 Persistence in the Environment. Sulphur can slowly oxidize to sulphur dioxide in the presence of moisture (OHM-TADS 1981).

6.6 Long-term Fate and Effects

There is no potential for accumulation or food chain concentration (OHM-TADS 1981).

6.7 Soil

6.7.1 Soil Degradation of Material. The chemical forms of sulphur in soil are presently recognized as 1) organic, 2) water-soluble sulphate, 3) absorbed sulphate, 4) insoluble sulphate (e.g., barium sulphate), 5) insoluble sulphate co-precipitated with calcium carbonate, and 6) inorganic sulphur compounds of lower oxidation states than sulphate. In general, then, it can be considered to be present in the soil system in either an organic or inorganic form. In well-aerated soils, inorganic sulphur is present as sulphate, the form principally absorbed by plant roots. Waterlogged or poorly aerated mineral and organic soils contain reduced forms of sulphur. These latter compounds are unavailable to plants and may attain concentrations that are harmful to plant growth. Sulphur may be oxidized to sulphur dioxide or sulphates or reduced, depending on soil conditions (NRCC 1977).

6.7.2 Effects on Soil Biota. Gaseous sulphur compounds have been found to affect selected groups of soil and epigeal (living on soil surface) fauna. An increase in pollution resulted in a declining density of soil fauna; it eliminated earthworms and decreased the spider population; however, the number of ants increased with advancing environmental degradation (Puszkas 1979).

Studies have shown that high sulphur residues in soil greatly reduce carrot and bean production (Pimental 1971).

Certain plants, such as beech and oak seedlings and lichen, may be used as air pollution indicators of sulphur and heavy metals (Mankovska 1981; Peterson 1977).

7 HUMAN HEALTH

Elemental sulphur is thought to be virtually nontoxic. Chronic inhalation, however, can cause irritation of the mucous membranes. It is described in the literature as a nuisance dust (Sax 1979). Repeated contact may induce an allergic response (GE 1979). The primary human health hazards associated with elemental sulphur are burns resulting from contact with the molten material, residual hydrogen sulphide resulting from hydrocarbon impurities in the production process, sulphur dioxide resulting from combustion, and explosion resulting from the ignition of the dust or vapour.

The toxicological data summarized here have been extracted from published papers and reliable standard reference sources and are representative of information in the literature.

7.1 Recommended Exposure Limits

No recommended occupational exposure limits specifically for sulphur were found in the literature. Sulphur has been described as a nuisance dust (Sax 1979), but is not included in the class of nuisance particulates designated by USA-ACGIH. (A TLV® of 10 mg/m³ for total dust and 5 mg/m³ for respirable dust has been established by USA-ACGIH for nuisance particulates (TLV 1983).)

7.2 Irritation Data

7.2.1 Skin Contact. Sulphur dust can be irritating to the skin, inner surfaces of the eyelids, and the mucous membranes of the respiratory passages. It may enhance the development of skin pore blockages (Strauss 1978). Molten sulphur can cause serious skin burns.

No information on the effects to the skin of exposure to levels of elemental sulphur was found in the literature.

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
8 ppm	Irritation	RTECS 1979

7.3 Threshold Perception Properties

No data.

7.4 Long-term Studies

7.4.1 Inhalation. No information pertaining to systemic poisoning from breathing sulphur dust was found in the literature.

7.4.2 Ingestion. No information pertaining to systemic poisoning from ingesting elemental sulphur was found in the literature, although metabolic acidosis has been observed after ingestion (Blum 1977). (Metabolic acidosis is bio-reduction to acid within the body by metabolic activity.)

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their sources indicated.

7.5.1 Inhalation.

1. Irritation of respiratory passages.
2. Sneezing, coughing.

7.5.2 Ingestion.

1. Metabolic acidosis (Blum 1977).

7.5.3 Skin Contact.

1. Irritation of the skin.
2. Repeated contact may induce allergic response (GE 1979).
3. Molten sulphur will cause serious burns.

7.5.4 Eye Contact.

1. Mechanical irritation on inner surface of eyelid (GE 1979).
2. Watering of the affected eye(s).

7.6 Human Toxicity to Decay or Combustion Products

The principal residual of the sulphur production process is hydrogen sulphide (H_2S), while the principal combustion product is sulphur dioxide (SO_2). Both gases are toxic and are described below.

7.6.1 Hydrogen Sulphide and Sulphur Dioxide. Hydrogen sulphide is a colourless gas with an offensive odour which, in high concentrations, acts as a systemic poison causing unconsciousness and death through respiratory paralysis. In lower concentrations, hydrogen sulphide causes corneal damage, headaches, nausea and other such symptoms. The TLV® for hydrogen sulphide is 10 ppm (8 h - TWA); the STEL is 15 ppm (TLV 1983).

Sulphur dioxide is a colourless gas with a strong, suffocating odour which causes irritation of the mucous membranes and bronchoconstriction. The TLV® for sulphur dioxide is 2 ppm (8 h - TWA); the STEL is 5 ppm (TLV 1983).

Hydrogen sulphide is particularly dangerous in that it paralyses the olfactory glands; after exposure to the gas for a period of time, a worker may believe that the gas is no longer present.

[illegible]

8.1 Compatibility of Sulphur with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	DECOMPOSITION	FORMATION OF TOXIC FUMES	PRESSURIZATION OF VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Calcium		x	x								Calcium burns in sulphur vapour. Vapour reaction begins at about 480°C. When mixed with solid and ignited, reacts explosively	Bretherick 1979
Calcium Carbide		x									Becomes incandescent with sulphur vapour at 500°C	NFPA 1978
Calcium Phosphide		x									Incandescent at 300°C	NFPA 1978
Calcium Hypochlorite			x	x							When mixed with damp S ₈ , produces a brilliant crimson flash with scattering of molten sulphur. Explosive when heated in a closed vessel	NFPA 1978
Charcoal (freshly calcined or lampblack)			x								With powdered sulphur, spontaneously flammable	Bretherick 1979

8.1 Compatibility of Sulphur with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF VIOLENT POLYMERIZATION	FORMATION OF FLAMMABLE GASES	DECOMPOSITION OF GREATER TOXICITY	FORMATION OF TOXIC FUMES	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Chlorine Dioxide	x	x										Spontaneously flammable and may produce an explosion	NFPA 1978
Chlorine Monoxide			x					x				Mere contact	NFPA 1978
Chlorine Trifluoride		x											NFPA 1978
Chromic Anhydride		x	x									Ignites when heated and may explode	NFPA 1978
Chromium Trioxide		x	x									Ignites when heated and may explode	NFPA 1978
Chromyl Chloride		x										Ignites spontaneously with dry sulphur	NFPA 1978
Diethyl Ether			x									When mixed with residue from evaporated, wet peroxidized ether	Bretherick 1979
Fluorine		x											Bretherick 1979
Indium	x											At ordinary temperature when heated, incandesces	NFPA 1978

8.1 Compatibility of Sulphur with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	DECOMPOSITION	FORMATION OF TOXIC FUMES	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Iodine Penta- fluoride	x									Spontaneously, usually with incandescence	NFPA 1978
Iodine Pentoxide			x							Explosive when warmed	NFPA 1978
Lead Chlorate		x								Ignites at about 63°C to 67°C	NFPA 1978
Lead Chlorite			x								NFPA 1978
Lead Dioxide			x								NFPA 1978
Lithium			x					x		Very violent when either is molten	NFPA 1978
Lithium Carbide		x								Burns in sulphur vapour	NFPA 1978
Mercuric Nitrate			x								NFPA 1978
Mercuric Oxide			x					x		Violent explosion when heated in retort	NFPA 1978
Mercurous Oxide		x								Mixture of polymerized materials ignites from light impact	NFPA 1978
Nitrogen Dioxide		x								Sulphur burns vigorously in nitrogen dioxide	NFPA 1978

8.1 Compatibility of Sulphur with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Phosphorus (Yellow)		x	x									When warmed	Bretherick 1979
Phosphorus (red)	x								x			Ignition of intimate mixture	Bretherick 1979
Phosphorus (III) Oxide									x			Violent reaction in large amounts	Bretherick 1979
Potassium Nitride		x			x							Evolves ammonia and hydrogen sulphide in contact with water, when heated from highly flammable mixture	Bretherick 1979
Potassium Perchlorate			x									Can be exploded by a moderately strong impact	NFPA 1978
Potassium Permanganate			x									Explosive on heating with powdered sulphur	NFPA 1978
Rubidium Acetylide		x										Burns with molten sulphur	Bretherick 1979
Selenium Carbide	x											Incandescences with vapour	NFPA 1978
Silver Nitrate			x									Explodes on impact	NFPA 1978

8.1 Compatibility of Sulphur with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	DECOMPOSITION	FORMATION OF TOXIC FUMES	PRESSURIZATION OF VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Silver Oxide		x									Ignites upon grinding	NFPA 1978
Sodium			x					x				NFPA 1978
Sodium Chlorite			x								If moistened	NFPA 1978
Sodium Hydride								x			With vapour	Bretherick 1979
Strontium Carbide	x										Incandesces at 500°C with a vapour	NFPA 1978
Tetraphenyllead			x									Bretherick 1979
Thallic Oxide			x								When ground	NFPA 1978
Thorium								x				NFPA 1978
Thorium Carbide	x										Incandesces when heated to 500°C	NFPA 1978
Tin	x							x				NFPA 1978
Uranium	x										Incandescent with boiling sulphur	NFPA 1978
Uranium Carbide		x									Ignites at about 500°C	Bretherick 1979
Zinc			x								Explosive when warmed	NFPA 1978

8.1 Compatibility of Sulphur with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF VIOLENT POLYMERIZATION	FORMATION OF FLAMMABLE GASES	DECOMPOSITION OF GREATER TOXICITY	FORMATION OF TOXIC FUMES	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
<u>CHEMICAL GROUPS</u>													
Bromates			x									When mixed with finely divided sulphur will explode with heat, percussion and sometimes light friction (Ba, Ca, Mg, K, Na, or Zn only)	NFPA 1978
Chlorates		x										Liberates oxygen and heat explosively (Ba, Ca, Mg, K, Na or Zn only)	NFPA 1978
Hydrocarbons		x			x	x						With molten sulphur only, generates hydrogen sulphide and carbon disulphide which may accumulate in explosive concentrations	NFPA 1978

8.1 Compatibility of Sulphur with Other Chemicals and Chemical Groups (Cont'd)

[illegible]

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged - in so doing, it is recognized that there may be some discrepancies between different sources of information. It is recognized that countermeasures are dependent on the situation, and thus what may appear to be conflicting information may in fact be correct for different situations. These procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire/Explosion Concerns. Sulphur is a combustible solid which releases toxic sulphur dioxide gas while burning. Molten sulphur can react with hydrocarbons and other organic materials to produce toxic hydrogen sulphide and carbon disulphide which may accumulate to explosive concentrations (NFPA 1978). It can react exothermically, as an oxidizing agent, with carbides and metals. It can be dangerously explosive when intimately mixed with oxidizing agents such as nitrates and chlorates (GE 1979). Sulphur dust is a moderate explosion hazard when dispersed in air.

9.1.2 Fire Extinguishing Agents. Use water spray to cool containers involved in a fire (ERG 1980). Avoid straight streams of water which will scatter molten sulphur and dust (NFPA 1978).

Small fires: Dry chemical, sand, water spray or foam.
Large fires: Water spray, fog or foam.

Move containers from fire area if this can be done without risk. For massive fire in cargo area, use unmanned hose holder or monitor hose (ERG 1980).

9.1.3 Spill Actions.

9.1.3.1 General. Stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition. Avoid skin contact with molten material or inhalation of dust or fumes (GE 1979).

9.1.3.2 Spills on land. When spilled in a molten form, contain if possible by forming mechanical or chemical barriers and let it solidify. Shovel solid sulphur, whether solidified from molten state or spilled in solid form, into containers with covers (avoid dusting) for recovery or disposal (ERG 1980; GE 1979; EPA 670/2-75-042).

9.1.3.3 Spills in water. When spilled in a molten form, contain if possible by using natural deep water pockets, and sand bag barriers to trap material at the bottom. Remove trapped material with suction hoses (EPA 670/2-75-042). Generally, when molten sulphur is spilled into water, it will sink, thicken, and solidify. There may be occasions when the molten material will form amorphous plastic sulphur, e.g. when spilled into very cold water (SUDIC 1983). If removal is not possible, let the material solidify and apply a cover material, preferably inert and basic (limestone), to the spill area until recovery procedures begin. This will reduce the possible formation and release of sulphuric acid in the water (CG-D-56-78).

9.1.4 Cleanup and Treatment.

9.1.4.1 Spills in water. Use mechanical dredges or lifts to remove immobilized masses of sulphur and precipitate from the bottom (EPA 670/2-75-042).

9.1.5 Disposal. Waste sulphur must never be discharged directly into sewers or surface waters. The combustion of sulphur is not a recommended disposal technique, since sulphur dioxide is produced. The contaminated material can be recovered or it can be mixed with three (3) parts by weight of calcium carbonate and buried in a secure landfill. The calcium carbonate will neutralize any sulphuric acid that might be generated (GE 1979).

9.1.6 Protective Measures. For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spilled material is known to be sulphur, the following worst case protective measures are recommended:

- Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode should be worn to avoid over-exposure (from known or suspected effects) and for firefighting purposes. Under certain conditions where fire is not involved and the presence of hydrogen sulphide is not detected, normal dust protection will suffice (Ashland MSDS).
- Response personnel should be provided with and required to use chemical splash or dust-proof goggles, face shields (20 cm minimum), heat-resistant gloves and clothing (Ashland MSDS). Non-heat-resistant gloves may be adequate for non-fire situations or where the spilled sulphur is in a form other than molten.

- Clean work clothes should always be used. Do not use clothing which is impregnated with sulphur dust (GE 1979).
- The following chemical suit materials are recommended for protection against sulphur (EE-20): butyl and neoprene (excellent resistance).
- Eye wash stations and washing facilities should be readily available where exposure to sulphur dust may occur (GE 1979).

9.1.7 Special Precautions. Store in a cool, ventilated area away from sources of heat and ignition and away from oxidizing agents and reactive chemicals. Guard against conditions or actions that could disperse sulphur dust in air. Provide grounding, humidification, etc., when handling powdered sulphur to prevent static sparks from electrical charges which may develop. Use nonsparking tools (GE 1979).

10 PREVIOUS SPILL EXPERIENCE

This section contains information on previous spill experiences which will be useful to readers in understanding spill response and countermeasures. Only those which meet the criteria are included; thus, the number of experiences is not an indication of the problems or frequency of spillage. As technology in spill control advances, this section will be updated in future manual revisions to include the most useful information.

10.1 Train Derailment (Personal Communication SUDIC 1982)

A derailment occurred in which 30 of 80 hopper cars carrying approximately 6,000 tonnes of solid sulphur sustained damage and several began burning. Five cars were found to be burning out of control. Firefighters arrived at the site and applied water spray to the burning cars. Soil was used to smother small sulphur fires on the ground. Water bombers were called and applied a water-diammonium phosphate mixture to the larger fires. The plume from the fire was monitored and observations indicated that it was drifting towards a populated area. The area was evacuated immediately. After the fire was extinguished, the contaminated (spilled) sulphur was removed and deposited at an industrial waste site. Soil samples were taken to determine soil damage, if any, and to monitor pH levels.

The following observations on this spill response can be made:

- Although any conventional firefighting technique can be used, water fog works better than spray since water does not wet the sulphur surface and runs off without soaking in. Foam, in turn, is better than fog.
- Because sulphur burns with a nearly invisible flame, it is difficult to tell when a fire is completely extinguished. Firefighters should remain on-scene during cleanup to ensure that the fire is out and to take action if the sulphur is reignited.
- Sulphur has a low heat of combustion so that fumes (sulphur dioxide), rather than heat, are generally the major firefighting hazard. Response personnel must use SCBA and protective clothing.
- Monitoring the fume plume is necessary for evacuation preparedness.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows.

Methods have been documented here for analyses of samples from air, water and soil in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they did not require highly specialized laboratory equipment, no additional methods were sought.

If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well. Depending on the situation, monitoring for sulphur dioxide and hydrogen sulphide may also be necessary. Consult the EnviroTips manuals specific to these for procedures.

11.1 Detection of Sulphur in Air, Water and Soil

Since sulphur is not volatile, is insoluble in water and is heavier than water, sulphur contamination of the air or water in the event of a spill would only be expected in a localized area. Visual inspection of the spill site will determine if sulphur has been spilled. Sulphur is a pale yellow, odourless, solid (may be slates, granules or prills) or a yellow to orange-brown liquid (molten). It may be identified by an ignition test. When heated in a crucible, sulphur ignites at a low temperature and burns with a pale blue flame, forming acrid sulphur dioxide gas (Welcher 1955).

11.2 Quantitative Method for the Detection of Elemental Sulphur in Soil or Sediments

After a sulphur spill has been removed, the soil or sediment may be analyzed for traces of sulphur that may remain (Hesse 1972). The following method may be used for concentrations of 20 to 140 ppm sulphur in soil if a 5 g sample of dried soil is used. This range may be extended by varying the sample size.

A representative sample of soil or sediment is collected. It is dried in vacuo over phosphorus pentoxide and in the presence of alkaline pyrogallol. The latter is prepared, as required, by mixing 40 percent aqueous potassium hydroxide with 25 percent aqueous pyrogallol solution in the ratio of 4:1. The dry sample is ground in an agate mortar, and a suitable aliquot is weighed into a centrifuge tube. Acetone, 25 mL, is added and the sample is shaken for 5 minutes. It is centrifuged at 400 rev/s for 15 minutes. A suitable aliquot of the clear supernatant is placed in a 100 mL volumetric flask containing about 80 mL of water, with gentle shaking during the process. Colloidal sulphur begins to form immediately. The volume is brought up to 100 mL with water. It is mixed and allowed to stand for 3 hours before the optical density is measured at 420 nm using a suitable photometer. Standard sulphur solutions are used to prepare a standard curve. These standards should cover the range 0-10 $\mu\text{g}/\text{cm}^3$ sulphur and are prepared from recrystallized sulphur and pure, redistilled acetone.

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EnviroTIPS
Common Abbreviations

BOD	biological oxygen demand	MMAD	mass median aerodynamic diameter
b.p.	boiling point	MMD	mass median diameter
CC	closed cup	m.p.	melting point
cm	centimetre	MW	molecular weight
CMD	count median diameter	N	newton
COD	chemical oxygen demand	NAS	National Academy of Sciences
conc.	concentration	NFPA	National Fire Protection Association
c.t.	critical temperature	NIOSH	National Institute for Occupational Safety and Health
eV	electron volt		
g	gram		
ha	hectare		
Hg	mercury		
IDLH	immediately dangerous to life and health		
Imp. gal.	imperial gallon	nm	nanometre
in.	inch	o	ortho
J	joule	OC	open cup
kg	kilogram	p	para
kJ	kilojoule	P _c	critical pressure
km	kilometre	PEL	permissible exposure level
kPa	kilopascal	pH	measure of acidity/alkalinity
kt	kilotonne	ppb	parts per billion
L	litre	ppm	parts per million
lb.	pound	P _s	standard pressure
LC ₅₀	lethal concentration fifty	psi	pounds per square inch
LC _{LO}	lethal concentration low	s	second
LD ₅₀	lethal dose fifty	STEL	short-term exposure limit
LD _{LO}	lethal dose low	STIL	short-term inhalation limit
LEL	lower explosive limit	T _c	critical temperature
LFL	lower flammability limit	TC _{LO}	toxic concentration low
m	metre	T _d	decomposition temperature
m	meta	TD _{LO}	toxic dose low
M	molar	TL _m	median tolerance limit
MAC	maximum acceptable concentration	TLV	Threshold Limit Value
max	maximum	T _s	standard temperature
mg	milligram	TWA	time weighted average
MIC	maximum immision concentration	UEL	upper explosive limit
min	minute or minimum	UFL	upper flammability limit
mm	millimetre	VMD	volume mean diameter
		v/v	volume per volume
		w/w	weight per weight
μg	microgram		
μm	micrometre		
°Be	degrees Baumé (density)		