

BROMINE

Safety Handbook



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2014	1		
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INTRODUCTION

This Safety Handbook has been compiled by ICL Industrial Products (ICL-IP) as a part of its continuing commitment to the principles of Product Stewardship, and is intended to provide a guide to the safe handling and use of bromine.

ICL-IP is the industrial chemicals arm of ICL, a major chemical company active in the global markets of performance and specialty chemicals, fertilizers and metallurgy. ICL Industrial Products produces and markets bromine and bromine-based products, phosphorous based products, magnesia products and chlorine-based salts. ICL-IP business units produce and market Flame Retardants; Fire Resistant & Lube Additive Functional Fluids; Drilling Fluids; Space & Soil Fumigation Products; Biocides; Pharmaceutical and Agrochemical Intermediates; Dead Sea Salts. ICL-IP draws on the vast resources of the Dead Sea, one of the world's largest and most concentrated resources of bromine, magnesium and potassium salts. ICL-IP supplies more than a third of the global demand for bromine. The company's economies of scale are unmatched in the industry; its plant by the Dead Sea is the world's largest bromine plant, and is back-integrated to chlorine (bromine production's main raw material) through its own and ICL Group's chlorine sources.

Whether you are a manufacturer, transporter, distributor or end user, we hope that the information contained in this Safety Handbook will prove useful in your handling of bromine. Information is also provided to assist regulatory and transportation authorities in determining whether bromine is being handled or transported properly, and to assist medical personnel in case of an accident involving this product.

Bromine is not a substance to be used casually. It is a hazardous chemical which can be used safely if its properties are understood and the necessary safety precautions are observed. Safety is the personal responsibility of everyone working with bromine. Managers and supervisors should be well versed in the safe handling practices required and enforce their implementation. Operators should be well trained in the use of safety equipment and safety procedures.

Note: The relevant Material Safety Data Sheet should be consulted before undertaking any activities involving bromine.

The handling of bromine is strictly regulated by international agreements and government regulations. As new information is continuously becoming available, anyone handling this substance must keep up-to-date on relevant practices and regulations.

ICL-IP emphasizes the need for the safe handling of bromine, the integrity of the containers and the prominent display of instructions and warnings. For further information on bromine and its formulations, please contact your local office or: Bromine Business Unit, ICL Industrial Products, P.O.B. 180, 8410101 Beer-Sheva, Israel, Tel: +972-8-6594475, website: www.icl-ip.com

We also welcome your comments and input on the content and presentation of this Safety Handbook, which should be sent to the above address.

Although the information and recommendations set forth herein (hereinafter "Information") are presented in good faith and believed to be correct as of the date hereof, ICL-IP makes no representations as to the completeness or accuracy thereof. Information is supplied upon the condition that the person receiving it will make their own determination as to its safety and suitability for their purposes prior to use. In no event will ICL-IP be responsible for damages of any nature whatsoever resulting from the use or reliance upon information in this handbook.

In the event of a discrepancy between the contents of the safety handbook and the updated MSDS, the MSDS will prevail (see ICL-IP website for latest version www.icl-ip.com).

NO REPRESENTATIONS OR WARRANTIES, EITHER EXPRESSED OR IMPLIED OF MERCHANTABILITY, FITNESS FOR A PARTICULAR PURPOSE OR OF ANY OTHER NATURE, ARE MADE HEREUNDER WITH RESPECT TO INFORMATION OR THE PRODUCT TO WHICH THE INFORMATION REFERS.

ICL-IP SUSTAINABILITY POLICY

The managers and employees at ICL-IP are committed to sustaining economic growth without harming our planet or exhausting its resources while improving the quality of life for its current and future inhabitants.

ICL-IP practices Sustainable Development in the knowledge that it makes good business sense and will incorporate sustainability considerations in all operations and business decisions in alignment with a commitment to the global Sustainable Development effort.

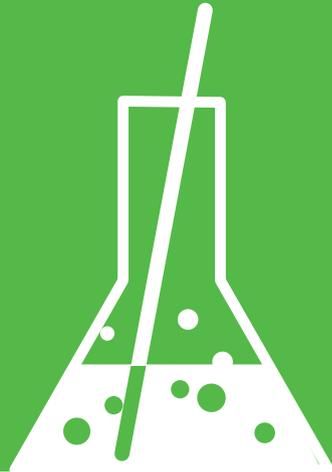
This will be achieved by:

- Maintaining a balance between economic, environmental and social needs of present and future generations
- Developing a companywide culture of Sustainable Development
- Complying with all national and international regulatory requirements including emergency regulatory requirements in cooperation with local emergency authorities
- Implementation of enforcement and risk management plans
- Adoption of Responsible Care and Product Stewardship principles
- Certification of all production facilities to ISO 14001/ OHSAS 18001/ ICL internal "Green Facility" certification
- Transparency and voluntary reporting according to the GRI (Global Reporting Initiative) model
- Focusing R&D on design and development of sustainable products and solutions
- Use of best available and economical technologies (BAT) to ensure conformance to legal requirements and beyond
- Minimizing the corporate environmental footprint including ongoing reduction of greenhouse gas emissions
- Commitment to safety by striving for zero accidents and ensuring a good working environment for employees and contractors
- Encouraging downstream users, transporters and suppliers, to adopt good practices for safe handling of chemicals and to minimize emissions during use and disposal of products and packages
- Promoting programs in support of the community and social involvement
- Upholding the principles of human rights both in and outside the workplace
- Adoption of a Code of Ethics
- Corporate governance according to principles and rules that ensure accountability, fairness, and transparency in relationships between management, the Board, shareholders and other stakeholders
- Educating and training all managers and employees to be fully aware of the Sustainability Policy and to be committed to its implementation
- Supplying resources needed for implementation of this policy

GLOSSARY OF COMMONLY USED ABBREVIATIONS

AAR	American Association of Railroads
ACGIH	American Conference of Governmental Industrial Hygienists
ADR	European Agreement concerning the International Carriage of Dangerous Goods by Road
ANSI	American National Standards Institute
C	Ceiling Limit Value (For TLV)
CAS	Chemical Abstract Service
CERCLA	Comprehensive Environmental Response, Compensation & Liability Act (US)
CFR	Code of Federal Regulations (US)
CHEMTREC	Chemical Transportation Emergency Center (US)
COMAH	Control of Major Accident Hazards Regulations (UK)
COSHH	Control of Substances Hazardous to Health Regulations (UK)
CSC	International Convention for Safe Containers (IMO)
DOT	Dept of Transportation (US)
ICL-IP	ICL Industrial Products
EAC	Emergency Action Code
EPA	Environmental Protection Agency (US)
HSE	Health and Safety Executive (UK)
IATA	International Air Transport Association
IDLH	Immediately Dangerous to Life or Health
IMDG	International Maritime Dangerous Goods code
IMO	International Maritime Organization
ISO	International Standards Organization
MFAG	Medical First Aid Guide (IMO)
MSDS	Material Safety Data Sheet
NFPA	National Fire Protection Association (US)
NIOSH	National Institute of Occupational Safety & Health (US)
OSHA	Occupational Safety and Health Administration (US)
OES	Occupational Exposure Standard (UK)
PEL	Permissible Exposure Limit (US)
PVDF	Polyviniliden fluoride
REL	Recommended Exposure Limit
RID	Regulations concerning the International Carriage of Dangerous Goods by Rail
SCBA	Self-Contained Breathing Apparatus
STEL	Short-term Exposure Limit
TEFC	Totally Enclosed Fan Cooled electric motor
TLV	Threshold Limit Value (ACGIH) (US)

TQ	Threshold Quantity
TWA	Time Weighted Average
UIC	International Union of Railways (Europe)
UL	Underwriters Laboratories (US)
UN	United Nations



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1.1 IDENTIFICATION OF BROMINE

UN number	1744
CAS Number	7726 - 95 - 6
EINECS Number	231-778-1
Empirical Formula	Br ₂
Name	Bromine
Chemical Family	Halogen
Appearance	Heavy red-brown fuming liquid
Odor	Sharp, harsh, irritating

1.2 PHYSICAL PROPERTIES

		Reference*
Boiling Point	58.8°C	2
Freezing Point	-7.3°C	2
Critical Temperature	311°C	14
Critical Pressure	102 atm.	14
Flash Point	None	2
Auto-ignition Temperature	None	2
Decomposition	None	2
Molecular Weight	159.8	2
Liquid Specific Gravity	3.12 g/ml @ 20°C	2
Vapor Density (air=1)	5.5	2
Vapor Specific Gravity @ 760 mm Hg and 0°C	7.1389 g/lit	15
Latent Heat of Vaporization	44.8 cal/g	1
Latent Heat of Fusion	17.4 cal/g	14
Specific Heat, Liquid	0.113 cal/g/°C	15
Specific Heat, Vapor	0.23 cal/g/°C	14
Coefficient of Volumetric Expansion	0.0011 per °C	15
Viscosity, Liquid @ 27°C	0.296 Cs	1
Flammable Limits in Air	Not flammable	2
Solubility, Bromine in Water	35 g/l	2
Solubility, Water in Bromine	34 mg/100g	15
Solubility in Organic Solvents **	Very soluble	2

* See list of references in Appendix B.

** Alcohol, ether, trichloromethane, carbon tetrachloride.

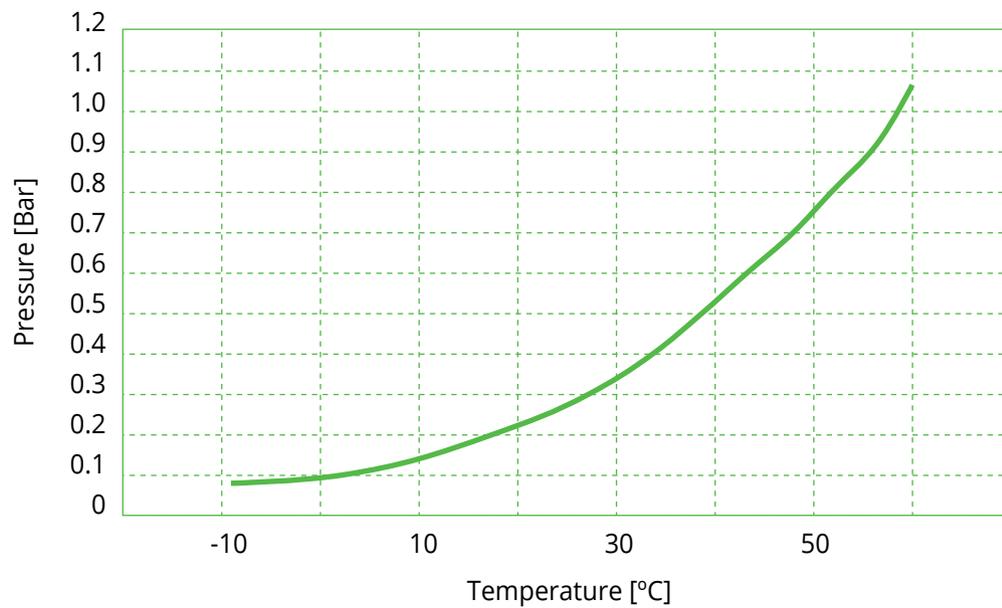


1.3 BROMINE VAPOR PRESSURE CURVE

REFERENCE: CHRIS June 1985 and November 1994 editions

PRESSURE [mm Hg]	PRESSURE [Bar]	TEMPERATURE [°C]
44	0.0587	- 7.3
47	0.0615	- 6.7
50.5	0.0673	- 5.0
54	0.0714	- 3.8
63	0.0826	- 1.1
65.9	0.0879	0
72	0.0953	1.7
83	0.1056	4.4
85.3	0.1137	5.0
95	0.1257	7.2
109	0.1438	10.0
124	0.1641	12.7
138	0.1840	15.0
161	0.2120	18.3
175	0.2306	20.0
182	0.2401	21.1
206	0.2713	23.9
214	0.2853	25.0
232	0.3059	26.7
264	0.3520	30.0
293	0.3862	32.3
329	0.4326	35.0
367	0.4837	37.7
392	0.5226	40.0
472	0.6293	45.0
564	0.7519	50.0
670	0.8932	55.0
760	1.0130	58.8
793	1.0570	60.0
	1.2100	64.7
	10.000	139.8
	20.000	174.0
	60.000	243.5

Bromine Vapor Pressure Curve





1.4 ADDITIONS TO PHYSICAL PROPERTIES

Density of Liquid Bromine

Temperature [°C]	[g/ml]
15	3.140
20	3.123
25	3.106
30	3.088

Viscosity

Temperature [°C]	[mm ² /s] (Cst)
20	0.314
30	0.288
40	0.264
50	0.245

Mutual Solubility

Temperature [°C]	[H ₂ O in Br ₂ [ppm]]	[Br ₂ in H ₂ O [%]]
20	340	3.38
30	435	3.12
40	560	2.88
50	700	2.62

1.5 NEUTRALIZATION OF BROMINE

Liquid phase

Alternative neutralizers

Solid:

Slaked lime, Soda ash.

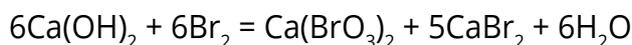
Dissolved:

Soda ash, Sodium hydroxide, Sodium thiosulphate, Sodium sulfite, Sodium bisulfite. Sodium thiosulphate must only be used for small spills (high heat of reaction).

Soda Ash:



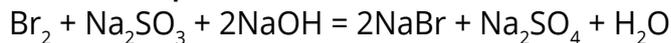
Slaked Lime:



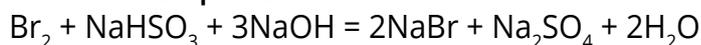
Caustic Soda:



Sodium sulphite:



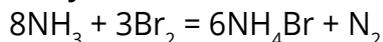
Sodium bisulphite:

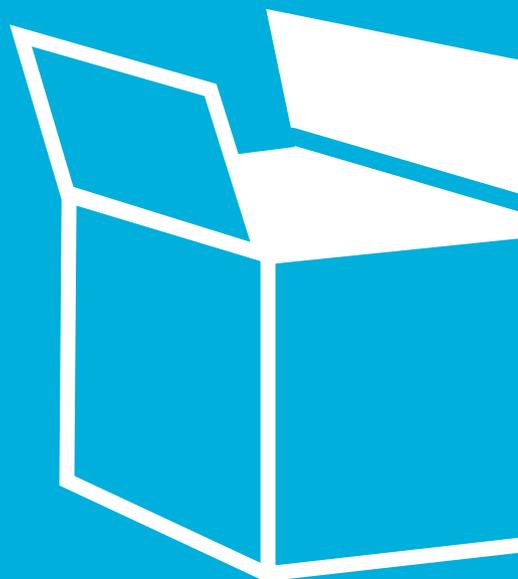


ICL-IP recommends the use of solid slaked lime to neutralize liquid bromine. Absorb the bromine into the material and mix. Add water and continue to mix slowly until all the material has reacted.

Neutralization of gaseous Bromine

Anhydrous Ammonia:



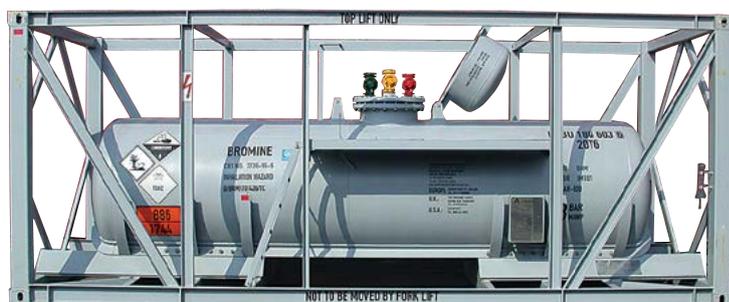


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2.1 GENERAL

Typical Packaging



Bromine Isotank



Bromine Drum



Bromine Goslar



Bromine Goslars in Isoframe



Bromine is supplied as a liquid. Depending on the quantities required by the customer, bromine can be supplied in lead-lined steel drums and/or portable tanks.

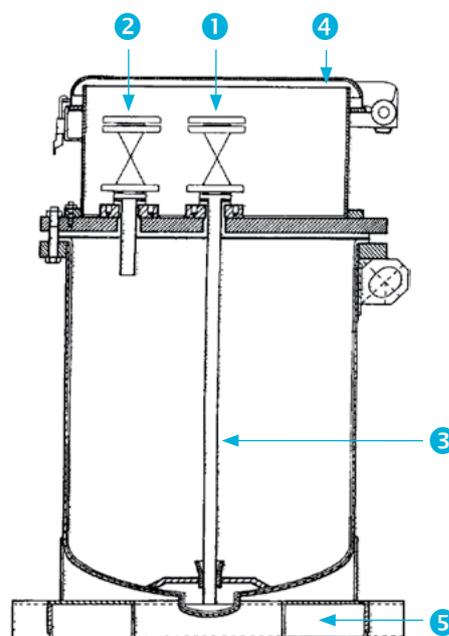
ICL-IP places particular emphasis on the integrity of the packaging and the prominent display of instructions and warnings. Each receptacle undergoes complete inspection after being returned to the ICL-IP production facility and before being refilled.

ICL-IP follows international and national packaging recommendations and regulations. In general these Hazardous Material Regulations (HMR) are based on the Recommendations of the UN Committee of Experts, published in the UN "Orange Book".

Various international professional organizations, as well as national agencies, publish their own regulations, which adopt the "Orange Book" recommendations and add some supplements of their own.

The color of liquid bromine packaging is not regulated. The color of Dead Sea Bromine Group (ICL-IP) packaging is grey.

2.2 DRUMS



Legend:

- ① 1" Diaphragm valve for unloading and filling, painted yellow, with a long dip-pipe
- ② 1" Diaphragm valve for venting and pressurizing, painted red, with a short dip-pipe
- ③ Long dip-pipe
- ④ Manhole covers
- ⑤ Forklift slots

Basic Data:

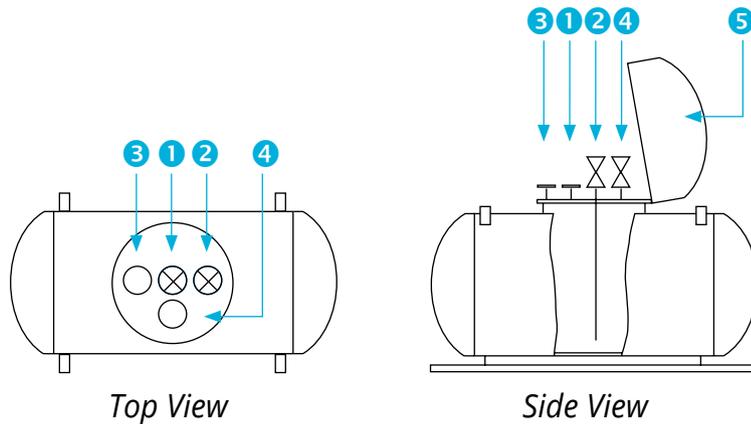
Volume	140 [Liter]
Maximum gross weight	830 [Kg]
Maximum net weight	400 [Kg]
Maximum net allowable pressure	3 [bar]

Built according to UN recommendations as type 1A1 drum for packing group 1.
Approved according to: ADR/RID/IMO

See photograph on page 21



2.3 GOSLARS



Legend:

- ① 1 1/2 " Teflon lined diaphragm valve for unloading and filling, painted yellow, with long dip-pipe
- ② 1 1/2 " Teflon lined diaphragm valve for vent, painted red
- ③ Fusible thermal relief element
- ④ 1 1/2 " Blind flange (not on all tanks)
- ⑤ Manhole cover

Basic Data:

Volume	1,250 [Liter]
Maximum gross weight	5,000 [Kg]
Maximum net weight	3,500 [Kg]
Maximum allowable working pressure	3 [Bar]

See photograph on page 21

2.4 BULK BROMINE PACKAGING

Liquid bromine is shipped in standard Isoframes, as follows:

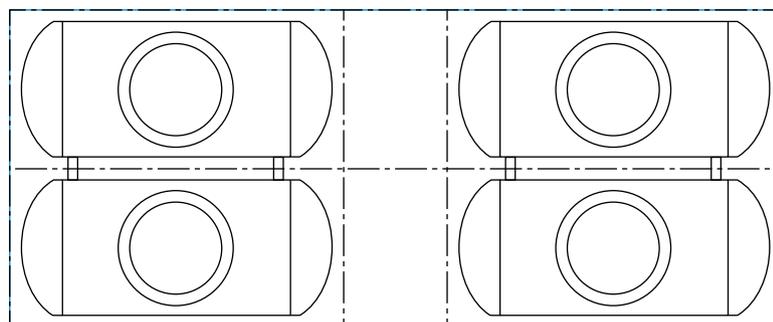
Frame Dimensions: 20 foot X 8 foot X 8 foot

Net Weight	Volume	Working Pressure ***	Bursting Disc Pressure	Safety Valve Setting	Commonly Used Name
[Kg]	[Liter]	Bar/[psig]	Bar/[psig]	Bar/[psig]	
14,000*	5,000*	3/(42)	**	**	Isoframe
15,200	5,300	3/(42)	8.75/(127)	7.5/(108)	Small Isotank
18,000	6,250	3/(42)	8.75/(127)	7.5/(108)	Medium Isotank
23,000	8,000	3/(42)	8.75/(127)	7.5/(108)	Large Isotank

* Four Goslars to an Isoframe (can be supplied with one or two Goslars only, if required)

** Fitted with fusible element

*** Recommended Maximum Working Pressure

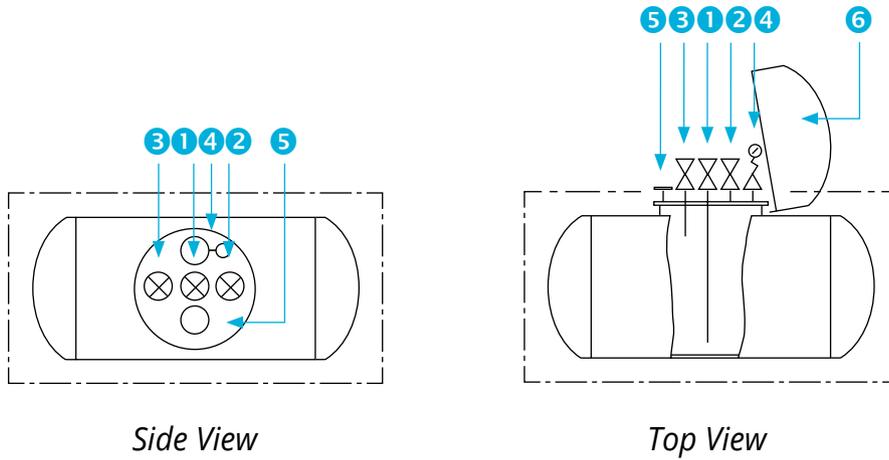


Goslar tank arrangements in isocontainer

See photograph on page 21



Small Isotank



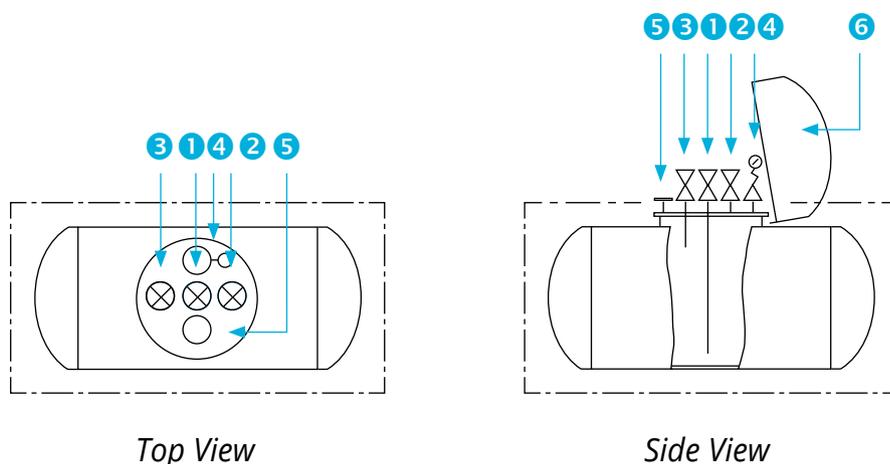
Legend:

- ① 1 1/2 " Teflon lined diaphragm valve for unloading and filling, painted yellow, with long dip-pipe
- ② 1 1/2 " Teflon lined diaphragm valve for vent, painted red
- ③ 1 1/2 " Teflon lined diaphragm valve for pressurizing, painted green
- ④ 1 1/2 " Relief valve, with rupture disc and pressure gauge
(or 2 1/2" Relief valve without fusible element)
- ⑤ Fusible thermal relief element
- ⑥ Manhole cover

Basic Data:

Volume	5,300 [Liter]
Maximum gross weight	21,000 [Kg] (24,000 [Kg])
Maximum net weight	15,200 [Kg]
Maximum allowable working pressure	3 [Bar]

Medium Isotank



Legend:

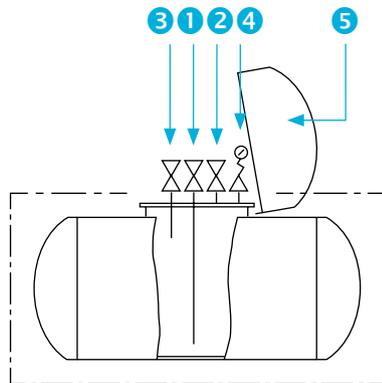
- ① 1 1/2 " Teflon lined diaphragm valve for unloading and filling, painted yellow, with long dip-pipe
- ② 1 1/2 " Teflon lined diaphragm valve for vent, painted red
- ③ 1 1/2 " Teflon lined diaphragm valve for pressurizing painted green
- ④ 1 1/2 " Relief valve, with rupture disc and pressure gauge
(or 2 1/2" Relief valve without fusible element)
- ⑤ Fusible thermal relief element
- ⑥ Manhole cover

Basic Data:

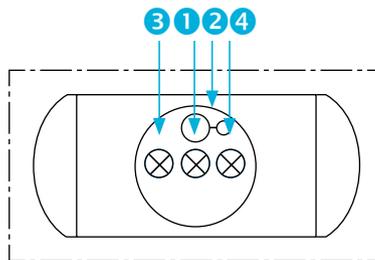
Volume	6,250 [Liter]
Maximum gross weight	24,000 [Kg] and 30,480 [Kg]
Maximum net weight	18,000 [Kg]
Maximum allowable working pressure	3 [Bar]



Large Isotank



Side View



Top View

Legend:

- ① 1 1/2 " Teflon lined diaphragm valve (or ball valve) for unloading and filling, painted yellow, with long dip-pipe
- ② 1 1/2 " Teflon lined diaphragm valve (or ball valve) for vent, painted red
- ③ 1 1/2 " Teflon lined diaphragm valve for pressurizing painted green
- ④ 2 1/2 " Relief valve, with rupture disc and pressure gauge
- ⑤ Manhole cover

Basic Data:

Volume	8,000 [Liter]
Maximum gross weight	30,480 [Kg]
Maximum net weight	23,000 [Kg]
Maximum allowable working pressure	3 [Bar]

2.5 MARKING, LABELING AND PLACARDING

Labels are used for marking:

- Receptacles
- Packages

Placards are used for marking:

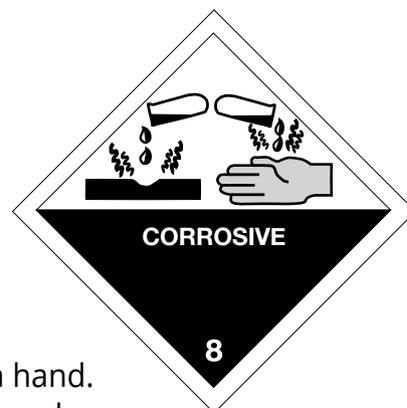
- Transport units
- Transport containers

Diamond-shaped markings

Internationally recognized danger identification

Primary Risk, corrosive substance label:

- Symbol: • Liquid dripping from a test tube onto a plate.
• Liquid dripping from another test tube onto a hand.
- Printing: • Upper triangle, black design on white background.
• Lower triangle, filled black with white border.
• With number "8" in the lower corner.



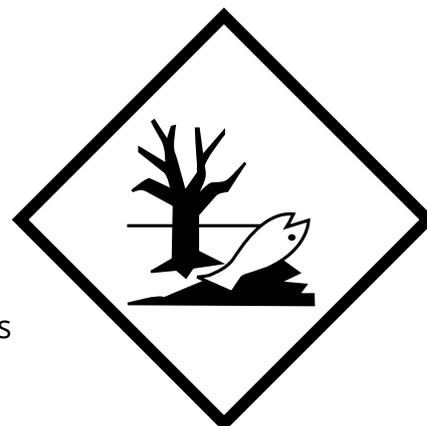
Subsidiary risk, toxic substance label:

- Symbol: • Skull and crossbones.
- Printing: • Black design on white background.
• With number "6" in the lower corner.



Environmentally hazard, toxic substance label:

- Symbol: • fish and tree.
- Printing: • Black design on white background.



United Nations (UN) Orange Book, 17th edition, 2011

Sections 5.2.1 to 5.2.2.2.2

Danger labels for marking receptacles and packages

Size, 100 mm X 100 mm

Section 5.3.1, danger placards for marking transport units

Size, 250 mm X 250 mm



US Department of Transportation (DOT) 49 CFR Regulations, 2010

According to Section 171.12 a label or placard conforming to the IMDG Code regulations may be used, provided that part of the transportation is by sea. Marking requirements for shipments originating and terminating within the United States. The following regulations apply:

General marking requirements

- 172.301 — General requirements for non-bulk packaging.
- 172.302 — General requirements for bulk packaging define the location of the marking on the packaging and its size.

Additional requirements are given by

- 172.304; 172.312 — Non-bulk packaging
- 172.313 — “Inhalation Hazard”
- 172.326 — Portable tanks
- 172.328 — Cargo tanks
- 172.330 — Tank cars
- 172.332 — Identification number on orange panels or hazard warning placards.

Labeling

- 172.400 — General requirements
- 172.402 — Subsidiary hazard labels
- 172.406 — Placement of labels
- 172.407 — Label specifications
- 172.442 — Corrosive label
- 172.430 — Poison (“Toxic” may be used in lieu of “Poison”)

Size of labels: 100 mm (3.9 inches) on each side, with each side having a solid line inner border 5.0 to 6.3 mm (0.2 to 0.25 inches) from the edge.

Placarding

- 172.504 — General requirements
- 172.505 — Subsidiary hazard
- 172.506 — Highway requirements
- 172.508 and 172.510 — Rail requirements
- 172.512 — Freight containers
- 172.519 — General specifications for placards
- 172.558 — Corrosive placard
- 172.554 — Poison placard

Size of placards: 273 mm (10.8 inches) on each side and a solid line inner border 12.7 mm (0.5 inches) from each edge.

Orange panels

United Nations (UN) Orange Book, 17th revised edition, 2011

Section 5.3.2

Requires display of United Nations (UN) number only in the lower half of the danger placard, or an orange panel placed immediately adjacent to the danger placard. Size of the panel: 120 mm high X 300 mm wide.

ADR (Europe), RID (Europe)

The orange panel with the United Nations (UN) number and the Hazard identification number is required by the ADR, Section 5.3.2, and the RID, Section 5.3.2.

The hazard identification number for bromine is 886 indicating that the substance is very corrosive and toxic.



United Kingdom

The United Kingdom requires the United Nations (UN) number and the Hazchem (Hazardous Chemical) Emergency Action Code, which for bromine is: 2XE

These characters indicate the following emergency action:

- 2** Use fine water spray for extinguishing a fire.
- X** Precautions to be taken in case of a fire or spill:
 - Contain, avoid spillages from entering drains or water courses.
 - Wear full protective clothing including breathing apparatus.
- E** Evacuation of people from the neighborhood of an accident should be considered.





Marking of packaging

United Nations (UN) Orange Book — 17th revised edition, 2011

Section 6.1 for packaging

Applies to packaging for the transport of substances in classes 3 to 9 having a capacity not over 450 liters.

Section 6.7 applies to portable tanks and multimodal tank containers.

International Maritime Dangerous Goods (IMDG) Code, 2012.

Section 6.7 and section 6.8

Applies to portable tanks and road vehicles for dangerous substances.

Marking requirements are essentially in agreement with the United Nations (UN) Orange book recommendations.

US Department of Transportation (DOT), 2013

The required markings are indicated in the tank specification.

Code of Federal Regulations, 49 CFR 178.255-14.

Every tank should have a permanent plate attached showing nominal capacity, tare weight and date of manufacture.

ADR (Europe), 2013

Section 5.3.1

Applies to tank-containers, portable tanks and vehicles.

RID (Europe), 2013

These regulations are similar to the European Agreement Concerning the Carriage of Dangerous Goods by Road (ADR).

2.6 TESTING, INSPECTION AND MAINTENANCE

Before Shipment

After filling has been completed, each packaging unit is pressurized to 3 bar for ten hours. If there are no observable leaks or drop in pressure, the tank is released for shipment.

A visual external inspection is made according to a checklist that includes markings, valves, manhole and cover, and paint condition.

Annual test

Each bromine Isotank is checked annually in accordance with the regulations. This test includes:

- Checking ancillary equipment including valves, safety valve, platform and ladder.
- Thorough external examination including corrosion, dents or mechanical damage, missing or loose bolts, required markings, and checking that the framework and supports are in satisfactory condition.
- Inspection of the internal lead lining for pitting, corrosion, distortion, or other defects.
- Leak-proof test.
- This examination is witnessed by an inspector of an internationally authorized expert body.

5 Year Inspection

- Execution of inspection and testing in accordance with the annual test described above.
- Hydraulic pressure test.

Maintenance

ICL-IP has a large Isotank maintenance division.

Each Isotank returned by a customer is checked thoroughly, and any unit failing to meet ICL-IP's requirements is referred to the workshop for maintenance.

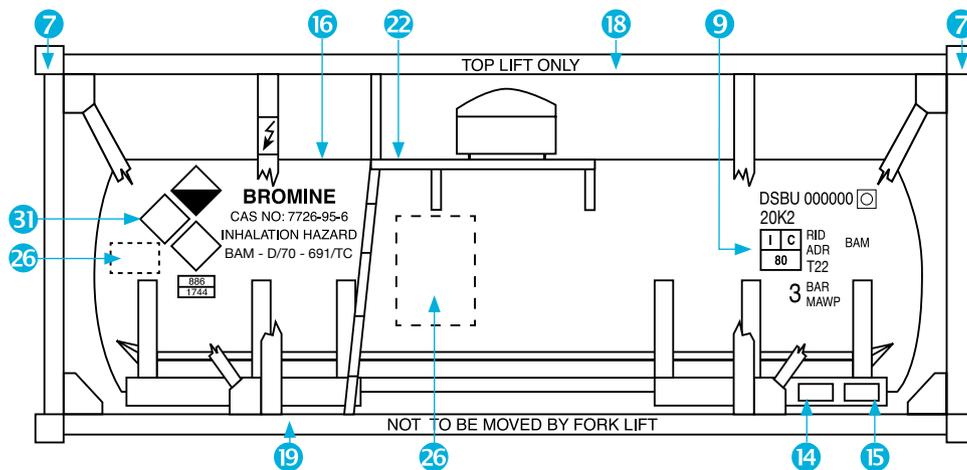
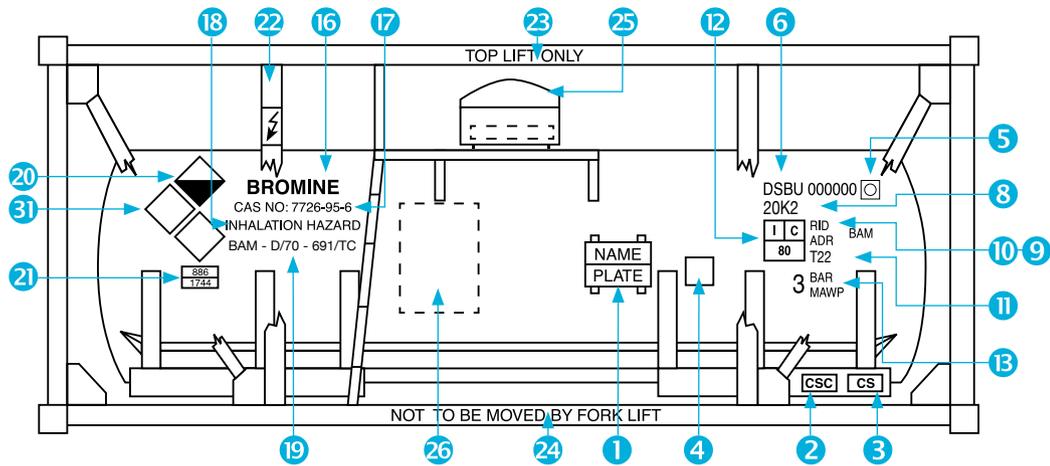


2.7 SAMPLE MARKING OF BROMINE ISOTANKS

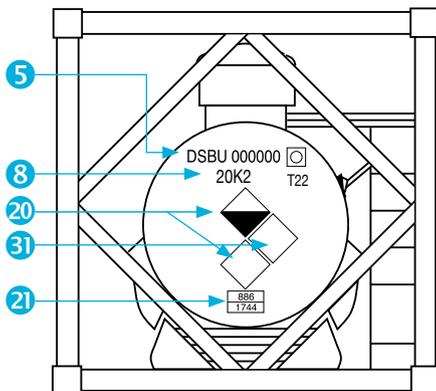
Legend:

- ① Manufacturer's nameplate
- ② International Convention of Safe Containers (CSC) safety approval plate
- ③ Customs seal
- ④ Tank inspection stamp
- ⑤ Isotank number on tank
- ⑥ Letter owner code "DSBU" and owner identification number
- ⑦ Isotank number on frame
- ⑧ International Standards Organization (ISO) Identification
 - 2 Letter Country Code — NL
 - 2 Digit Container Size Code — 20
 - 2 Digit Container Type Code — 76
- ⑨ International Union of Railways (UIC) Registration
- ⑩ Design standards,
 - Federal Institute of Material Testing, Germany (BAM)
 - European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR)
 - Regulations Concerning the International Carriage of Dangerous Goods by Rail (RID)
- ⑪ Department of Transportation (DOT), Tank Specification, Marking, IM — 101
- ⑫ United States Railroad Regulations AAR-600 — Impact Approved
- ⑬ Maximum Allowable Working Pressure 3 BAR
- ⑭ Isotank size and ICL-IP Number
- ⑮ Date of next test
- ⑯ Name of substance, BROMINE
- ⑰ Chemical Abstract Service (CAS) Number, 7726-95-6
- ⑱ "INHALATION HAZARD"
- ⑲ Federal Institute of Material Testing, Germany (BAM) Approval number
- ⑳ Hazard diamond placard marking:
 - Corrosive — (Model 8) with number "8" in bottom corner
 - Toxic — (Model 6.1) with number "6" in bottom corner
- ㉑ ADR Orange placard:
 - United Nations (UN) number — 1744
 - Hazard number — 886
- ㉒ Ladder location marking
- ㉓ "TOP LIFT ONLY"
- ㉔ "NOT TO BE MOVED BY FORK LIFT"
- ㉕ Valve identification markings
- ㉖ Shipper's emergency response instructions
- ㉗ Gross shipping weight
- ㉘ Tare weight
- ㉙ Maximum net weight
- ㉚ Maximum payload volume
- ㉛ Marine Pollutant

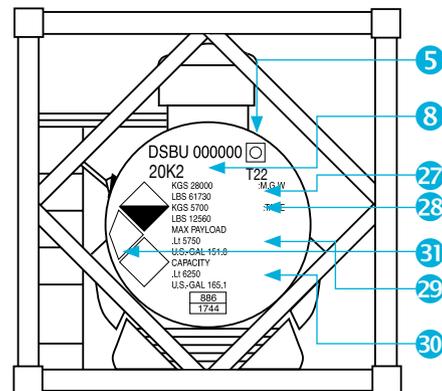
Side Views



End View



Right



Left



3. TRANSPORTATION

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The following is a summary of the main international regulations and requirements regarding the transportation of bromine. Furthermore, the shipper should ensure that the transport of bromine conforms to all relevant local regulations.

3.1 PACKAGING AND TRANSPORTATION

United Nations (Orange Book)

There has been considerable harmonization between the Orange Book and the various international regulations. These model regulations have been adopted in the various regulations, agreements and codes specified in this section. Many of the sections are numbered in the same way and much of the text is identical.

US Department of Transportation Regulations (DOT)

(As reflected by the changes published in the Federal Register, 1 October 2010)

49 CFR 173.24

There will be no identifiable release of bromine to the environment.

There will be no residue adhering to the outside of the package during transport.

UN portable tanks manufactured outside the United States may be filled, offered and transported in the United States, see 49 CFR 173.24 (d) Tanks must conform to 49 CFR 178.275.

Table of Hazardous Materials: 49 CFR 172.101

Packaging

Non-bulk packaging — 49 CFR 173.226 Materials poisonous by inhalation

Bulk packaging — 49 CFR 173.249 Bromine

Special provisions:

- (1) This material is poisonous by inhalation in hazard zone A
- (B9) Bottom outlets are not authorized
- (B85) Cargo tank must be marked with the name of the lading as per 172.302 (b)
- (N34) No aluminum construction materials are permitted
- (N43) Nickel or Monel drums are permitted
- (T22) UN portable tanks - minimum test pressure to be 10 bar; pressure relief devices are determined by 178.275(g)(3). Each tank must have a minimum shell thickness of 10 mm.
- (TP2) Degree of filling formula
- (TP10) Lead lining must be at least 5 mm, and tested annually
- (TP13) Self-contained breathing apparatus must be provided when transported by sea



Other requirements for stowage as per 49 CFR 176.84:
As per IMDG Code below

Emergency response information 49 CFR 172.602
Emergency response telephone number must be entered on the shipping papers 49 CFR 172.604

DOT Emergency Response Guidebook, 2012
Guide number 154

DOT training requirements are specified in 49 CFR 172.704

A label or placard conforming to the UN recommendations may be used.

DOT Corrosive and poison inhalation placards:

- Sections 49 CFR 172.555 and 172.558
- For marking vehicles
- Size: 273 mm x 273 mm (10.8» x 10.8»)

Details of the placard holder are shown in Appendix C of section 172

IMDGC International Maritime Dangerous Goods Code

Packing and Stowage Regulations
Dangerous Goods List, Chapter 3.2
Stowage, Chapter 7.1 General stowage provisions

Bromine is in stowage category D and has to be transported ON DECK only with the following recommendations:

- Keep as cool as reasonably practical
- Clear of living quarters
- Segregate as for class 5.1, but “separated from” classes 4.1, 5.1 and 7.

Segregation Table, chapter 7.2

“Separated from”

Explosives
Flammable gases, liquids and solids
Organic peroxides
Oxidizing substances
Infectious substances
Radioactive materials
Corrosive substances

For bromine, the emergency schedule is:
F-A General Fire Schedule
S-B Spillage schedule for corrosive substances

The Medical First Aid Guide (MFAG) is also contained in the supplement and is for use in accidents involving dangerous goods.

ADR (EUROPE)

European Agreement concerning the international carriage of dangerous goods by Road.

Bromine is listed in Section 3.2.1 Table A — Dangerous goods list

Section 2.2

Bromine is classified as “CT1”
Corrosive substance, toxic — Liquid.

Section 2.1.1.3

Packing group I — Substances presenting high danger

Section 3.5.12— Code “E0” - Bromine is not permitted as excepted quantities.

Packing — section 4.1.4

P804 Combination packagings (glass inner packaging individually placed in a metal receptacle with cushioning and absorbent material). The metal receptacles will be further packed in a box together with absorbent material (sufficient to absorb the entire contents of the glass bottles).
The combination packaging shall have a maximum gross weight of 25 Kg.



Mixed packing instruction MP2 section 4.1.10 — Shall not be packed together with other goods

Portable tanks Section 4.2.5.2

(T22) Minimum test pressure to be 10 bar; pressure relief devices are determined by Section 7.3.2. Each tank must have a minimum shell thickness of 10 mm.

Special provisions Section 4.2.5.3

(TP2) Degree of filling formula

(TP10) Lead lining must be at least 5 mm thick, and tested annually

Section 4.3 Tank-containers

Section 4.3.5 Special provisions:

TU14 Closures of tanks to be protected with locked caps during carriage

TU33 Tanks filled to not less than 88% and not more than 92% of capacity, or to 2,86 kg per liter of capacity

TC5 Lead lining not less than 5 mm thick

TE 21 The closures shall be protected by lockable caps

TT2 Condition of lining to be inspected every year

TM3 Tank shall have plate with shipping name and maximum permissible load

TM5 Tank shall have date of most recent inspection

Section 9.1.1.2 Vehicle for tank carriage

Bromine to be transported in "AT" vehicle designed for dangerous goods

Transport category 1.

Section 7.5.11 Loading, unloading and handling

CV13 A vehicle may not be re-used after a leakage until it has been thoroughly cleaned and decontaminated

CV28 Not to be loaded or stacked in immediate proximity to foodstuffs or animal feeds

Instructions in writing – Actions in the event of an accident or emergency, paragraph 5.4.3.

Hazard identification number for labeling transport units, paragraph 5.3.2.3.

Hazard Identification Number, No. 886

Highly corrosive substance, toxic

Retention of dangerous goods transport information, paragraph 5.4.4

The consignor and the carrier shall retain a copy of the Dangerous goods transportation documentation for a minimum period of three months.

RID (EUROPE)

Regulations concerning the international carriage of dangerous goods by Rail.

These regulations are similar to the ADR agreement

IATA — International Air Transport Association Regulations

- Section 4.2, List of Dangerous Goods
Forbidden to be carried on passenger or cargo aircraft.
- Section 4.4, Remark A2, Special provisions
This applies to small quantities such as samples. These bromine items may be carried on passenger or cargo aircraft with written prior approval of the country of origin. In addition, for passenger aircraft, written prior approval of countries of transit, overflight and destination, are required. Authorization must indicate quantity, packing and labeling requirements.



3.2 DRIVERS' LOADING CHECKLIST

The following is a suggested checklist, based on European Agreement concerning the Carriage of Dangerous Goods by Road (ADR) regulations and good practice. The shipper should also ensure that all local regulations are complied with.

Marking and Placarding

- Vehicle is marked clearly in front and rear with the UN No.(1744)
- Hazard Identification Number 886
- Hazard Placard no. 8
- Corrosive Substances, and Subsidiary Hazard Placard no. 6, Toxic. Vehicles are marked on the sides and rear, containers on both sides and at each end.

Fire fighting equipment

- One fire extinguisher with a minimum capacity of two Kg. dry powder for fighting a fire in the engine or cab.
- Two portable dry powder fire extinguishers with a minimum capacity of six Kg. dry powder or equivalent, checked within the past year.

Equipment required for each member of the vehicle crew:

- Approved portable lamps
- A warning vest
- Protective gloves
- Eye protection (goggles)
- Emergency escape mask

Equipment required to be carried on board the vehicle:

- Wheel chocks
- Two self-standing warning signs
- Eye rinsing liquid

Additional equipment:

- Shovel
- Drain seal
- Collecting container
- Self-contained breathing apparatus (SCBA)

Driver and Vehicle

- Hazardous transport unit should not consist of more than one trailer.
- Vehicle has valid license for hazardous materials (Hazmat license). The validity of the license shall expire not later than one year after inspection date.
- Driver and assistant driver have valid licenses to operate hazardous material vehicles (Hazmat license).
- The vehicle is not carrying any materials incompatible with bromine at the same time (explosives, flammables, radioactive materials, organic peroxides and oxidizing substances, infectious substances, or strong bases and metals).
- Bromine will be kept apart from foodstuffs and animal feed.

Shipping papers include:

- Product name: Bromine
- UN Identification Number: 1744
- Permit to transport bromine
- Quantity being shipped
- All papers concerning the transport of the hazardous material are kept in a holder on the inside of the door on the driver's side of the vehicle.
- Driver has approved route to destination with specified stops. No alternative routes will be used or unauthorized stops made.
- Vehicle has a full fuel tank before loading bromine.
- Containers have been fastened with all the twist lock corner fittings.

3.3 DRIVERS' ROAD REMINDERS

The driver and assistant driver of any vehicle transporting bromine should comply with the following requirements:

Supervision of vehicles (Section 8.4)

Parking the hazardous goods transport unit should be under one of the following conditions:

- Supervised parking lot, attendant aware of the nature of the load, and how to contact the driver.
- Vehicle parking lot where unit is not likely to suffer damage.
- Open space separated from public highway and public dwellings, where public does not normally pass or assemble.

Miscellaneous requirements (Section 8.3)

- No passengers are allowed.
- The crew shall know how to use fire-fighting appliances.
- The driver or driver's assistant may not open a package containing bromine.
- The portable lighting apparatus used shall not exhibit any metal surface liable to produce sparks.
- No smoking is permitted around the transport unit or in the vicinity of the vehicle during handling operations and inside the vehicle.
- The engine is to be shut off during all handling operations unless required to drive pumps, hoist, etc.
- Parking brakes are to be applied whenever parked. Trailers without braking devices shall be restrained from moving by applying at least one wheel chock.



4. USER GUIDE

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4.1 SAFETY AND ENGINEERING SERVICES

ICL-IP can supply safety and engineering services to existing and prospective customers.

ICL-IP is committed, via our product stewardship program, to training and advising any personnel involved in handling or storing our products along the logistic supply chain. We also carry out audits on storage locations and transportation operations with a view to improving safety awareness. Emergency plans and procedures are checked to ensure mitigation of incidents involving bromine.



4.2 GENERAL SITE RECOMMENDATIONS

Since bromine is a regulated hazardous material, storage and operating areas should be carefully supervised. Local regulations must be reviewed and implemented.

This guide is indicative of precautions to be taken at a bromine installation. The storage areas can be supplier distribution warehouses, third party distribution warehouses or user storage areas.

Storage should be located in an area designated for ports or industry and should have a valid permit for storing hazardous goods.

- Any site where bromine is stored or used should be away from populated areas and located so that prevailing winds will not blow bromine vapors towards inhabited areas, offices, workshops, or other employee concentration areas.
- The site should be more than 25 meters from a public road or main rail line to minimize the risk of damage in case of an accident.
- Areas in which liquid bromine or bromine vapors can accumulate should be minimized, such as pits or confined spaces.
- Corrosion and toxic hazard signs should be prominently displayed.
- Where freezing temperatures can be expected, bromine tanks should be stored at temperatures above -7°C (see page 55).
- The site should preferably be near a fire station and an accident and emergency hospital (no more than 30 minutes drive).

Bromine Storage Facilities

The following is a general guide for choosing and supervising a storage area, especially for storage of quantities of 10 tons or more. Note that all local laws and regulations and codes must be strictly followed; the precautions listed below are in addition to those specified in local codes.

- The amount of bromine in storage should be kept to a minimum. Separation distance between the storage area and the site boundary will be determined by local regulations.
- Minimize the dispersal of bromine vapors by locating the storage area on low ground. Low curbs or walls (called dikes), 200 mm high, should enclose the storage area to protect the area from external flooding and to minimize the dispersal of bromine vapors. The minimum diked volume should be equivalent to the largest storage tank plus 10%.
- The diked area should not have a sewer connection. Provide an adequate size sump for collecting bromine spills and pump away collected rainwater and fire-fighting water. Fire-fighting water should be prevented from contaminating water sources.
- Outside shaded or detached storage areas are preferred. A detached storage area is either an outside shaded area or a separate building containing no incompatible materials and located away from all other structures.
- In the case of detached storage the building construction should be fire resistant and provisions made for potential fire-fighting activities, according to relevant local and national codes, and in consultation with local fire-fighting professionals. The fire-fighting installation should include provision for an adequate supply of water.
- Drainage should be adequate to prevent flooding of any point on the site and particularly flooding of outside storage areas or around the entrances to, or emergency exits from, warehouses.
- Fire extinguishers and hydrants should be distributed around the area. Fire-fighting water run-off should be prevented from polluting water sources.
- Provisions should be made for quickly closing off storm water drains to prevent entry of chemicals in the event of a major loss of containment of one or more of the chemicals on site.



- Floors should be of impervious construction, preferably concrete.
- Bromine isotanks should be stored no closer than 10 meters from human or animal foodstuffs. Explosives and flammable materials should not be stored close to bromine.
- Full bromine isotanks may be stacked 2 high in such a manner that each receptacle can be inspected without having to move other receptacles. Empty isotanks may be stacked 3 high.
- The concrete surface under the isotank storage positions should have a slope of at least 2% running to a drain channel located at the side of the storage area.
- There should be a strengthened approach way for emergency vehicles on two sides of the installation.
- External storage areas should be concreted. The concrete should be of adequate thickness to withstand the use of lifting equipment and capable of bearing the point loading from the stock.
- Storage bays should be clearly marked and either remote from vehicle access routes or protected from vehicular impact by walls or crash barriers. The storage arrangement should comply with relevant regulations and/or guidelines on minimum separation distances from site boundaries, occupied premises etc.
- Piping between 20 mm (1/2") and 110 mm (4") diameter should be solid PVDF (polyviniliden fluoride) pipe, stress relieved, with plain ends for fusion socket welding connection PN-16, as per DIN 8077. 160 mm (6") and 225 mm (8") diameters should be according to PN 10, for butt welding connection. Flanges should have a backing ring fabricated from carbon steel, drilled to ANSI 150 pounds rating, painted with epoxy 240 micron. Flange gaskets should be a PTFE sandwich, 3 mm thick with a non-asbestos filler. Teflon lined flanged plug or diaphragm valves are preferred. Hoses should be PTFE with stainless steel braid covering and carbon steel flanges. Screwed fittings are not used.
- Electrical installation:
Junction boxes and light fittings should be dust and vapor tight.
Cast iron, epoxy-based coated or non-metallic materials are suitable.
Do not use aluminum or aluminum alloys unless suitably coated.
Use Totally Enclosed Fan Cooled (TEFC) motors of cast iron or steel construction and epoxy-based coating.

- Provide lightning protection.
- There should be sufficient bromine storage tank capacity or an empty isotank to accommodate the transfer of bromine from a leaking container.

Safety and Security

- Any area where bromine is used or stored should be enclosed so that unauthorized persons and animals are prevented from entering the area. Adequate lighting should be provided to allow sufficient night surveillance. Surveillance should be provided 24 hours a day.
- The site should be surrounded by a full perimeter fence preferably topped with barbed wire.
- Entrance to the site should be controlled preferably by a logging in/logging out system for all site employees and visitors at a manned gatehouse.
- The site speed limit(s) should be clearly displayed.
- Traffic flow on site should be organized with vehicle routes, designated parking areas and loading/unloading areas clearly marked.
- Provide clearly marked personnel escape routes without obstructions including adequately sized doors and windows
- Locate facilities upwind of offices, eating, showering and changing rooms, remote from the area where bromine is handled or stored. Provide an adequate supply of clean water for washing and showers. Provide a smoking area remote from the operating area.
- A telephone should be provided which is freely available and readily accessible for the reporting of accidents or emergency situations. The emergency telephone numbers should include the fire department, ambulance service, emergency response team, hospital and police.
- A wind sock should be clearly visible from all points on the site and replaced as required. This is required for indicating wind strength and direction.
- Emergency respirator equipment cabinets should be installed not more than 30 meters or ten seconds walking distance from any location in the storage area.



- Non-freeze safety showers and eyewash fountains shall be provided, clearly marked, well lit and with unobstructed access. They should be installed close to the bromine storage area and not more than 30 meters or ten seconds walking distance from any location in the storage area. Provide alternative sources of water supply.
- The arrangement of the first aid room and the first aid supplies required should be discussed with the local emergency medical services.
- Signs should be posted prominently at the site entrance and throughout the installation with area maps showing access routes, hydrant locations, emergency showers, location of emergency equipment and emergency telephone numbers.

Handling Bromine

All management and operating personnel involved in the use or handling of bromine should undergo safety training, in addition to specific task training.

Only experienced well-trained operators should be allowed to receive and unload bromine receptacles.

The management should ensure that emergency response plans have been made and coordinated with the emergency response local authorities.

Precautions should be taken from the moment the shipment of bromine arrives at the site gate. All handling of bromine should be carried out with a high standard of housekeeping and personal hygiene.

- Ensure that road vehicles cannot be moved during a transfer operation.
- Respirators, rubber gauntlets, boots and full body covering clothing should be worn while unloading containers containing bromine.
- If there are any signs of spills, take appropriate action as indicated in section 5, Emergency Response.
- At no time should the bromine receptacles be handled roughly. The valve protection hood and blind flanges are removed only when ready to use the bromine.
- No open flame heating is allowed in an unloading area.

Handling Bromine Spills

In case of a bromine spill, water can be used to prevent the dispersion of bromine vapors. The bromine will sink below the water and the overlaying water will prevent the bromine from vaporizing.

Provide neutralizing agents in sufficient quantities and in suitable containers, as follows:

For liquid bromine spills:

- Bagged slaked lime $[\text{Ca}(\text{OH})_2]$ or bagged soda ash (Na_2CO_3) .

For Bromine vapor leaks:

- Ammonia vapor only. Do not use liquid ammonia on bromine spills or leaks as the reaction can be violent.

For minor spills and leaks:

- Sodium thiosulphate solution of the following proportions:

Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$)	90 kg
Water	200 liter
Soda ash (Na_2CO_3)	2.5 kg

This solution is stable for about four to six weeks.

Ascertain a source of supply of additional neutralizing material, which can be called on in a major emergency. About 20 tons of bagged slaked lime $\text{Ca}(\text{OH})_2$ or bagged soda ash (Na_2CO_3) should be available.

As bromine is toxic, no worker should be alone in an area where bromine exposure can take place.

Code of Federal Regulations, 29 CFR 1910.134 (e)(3)(i).

- Should bromine start to freeze inside the isotank, it should be allowed to thaw slowly either by placing the container inside a building, waiting until the temperature rises, or by using a hot air cannon. Under no circumstances should live steam be used because there would be a danger of pressurizing the isotank to the point where either the fusible element or the rupture disc is actuated.



Sample Checklist for a Bromine Handling Facility

	Yes	No
Away from populated areas		
At least 25 meters from public road or railway		
Corrosive and toxic hazard signs displayed		
Minimum amount is being stored		
Area surrounded by curb or dike with no sewer connection		
Sump for collecting spills		
Outside or detached storage		
Fire resistant building construction		
Fire-fighting hydrants and extinguishers		
Impervious floor		
Prevent freezing temperatures		
Separate from flammables and consumable articles		
Isotanks stacked 2 high if full or 3 high if empty		
Reinforced road for emergency vehicles		
Minimize pits and confined spaces		
Ensure correct piping specification		
No aluminum electrical fittings		
Dust and vapor tight electrical fittings		
TEFC electric motors		
Sufficient storage for transfer from leaking tank		
Area enclosed and secure		
Clearly marked escape routes		
Remote eating, changing and smoking areas		
Emergency telephone		
Wind sock		
Emergency equipment cabinets, showers and eye-wash		
First aid room		
Signs and area map at site entrance		
Safety training		
Emergency plan		
Good housekeeping and personal hygiene		
Prevent vehicles from moving during handling operations		
Personal protection equipment used when unloading or handling		

4.3 MATERIALS OF CONSTRUCTION - RECOMMENDATIONS

ICL-IP supplies “dry bromine” liquid, which has a water content of less than 30 ppm. The following materials can be used for handling bromine in liquid form at temperatures up to 58°C. Note that bromine should be stored under dry nitrogen or dry air to prevent moisture being absorbed, and to prevent corrosion.

- Glass or glass-lined piping and vessels have excellent corrosion resistance to wet or dry bromine. Glass fittings must be well supported and protected.
- Lead-lined vessels (as in ICL-IP Isotanks) are recommended for bromine service, provided that the water content is less than 700 ppm.
- Nickel and Nickel alloys (Hastelloy B and C, Monel 400) are suitable for dry bromine.
- The fluorinated polymers such as PVDF, PTFE and Fluoroelastomer such as VITON are highly resistant to bromine and can be used as piping materials and linings, and in gasket or sealing applications.

Mild steel and stainless steel are NOT recommended for bromine service.



4.4 PROCESS SAFETY MANAGEMENT REGULATIONS

United States

- Facilities handling HIGHLY HAZARDOUS CHEMICALS over a threshold quantity (29 CFR 1910.119): For bromine the threshold quantity is 1500 lbs (682 kg).

The management is required to prepare EMERGENCY ACTION PLANS to minimize the consequences of a hazardous release of this toxic material. This written emergency action plan describes the measures taken to prevent any release and the activities of the workers and community services in the event of a release. Workers, including contractor workers, are to be given adequate training and refresher courses to implement this emergency action plan.

Compliance audits are to be made before starting up a facility and after changes have been made in a facility or its operation procedures. Deficiencies and the corrections made are to be documented to ensure that the facility can be put into safe operation. Changes may have to be reflected in emergency action plans. A compliance audit is to be repeated every three years.

All incidents, which result in a release of hazardous materials or could have resulted in the release, are to be investigated. The results of the investigation and corrective actions recommended and taken are to be documented.

- Toxic Chemical Release Reporting (40 CFR 372)
A facility manufacturing, importing or processing 25,000 pounds per year of bromine, must report its operations.
- CERCLA (40 CFR 302)
Bromine is not listed.

Europe & UK

Directive 82/501/ EEC (COMAH)

This directive is aimed to prevent and limit the consequences of major accidents involving a dangerous substance.

The qualifying quantities for bromine are as follows:

For the purpose of notification and drawing up a major accident prevention policy — 20 tonnes.

For the purpose of producing a safety report, preparing emergency plans and reporting of accidents — 100 tonnes.

4.5 EXPOSURE LIMITS

Exposure limit values go under different names in the various standards, countries, time periods and populations.

4.5.1 OCCUPATIONAL EXPOSURE LIMITS

Occupational exposure limit for Bromine is specified as TLV-TWA, Time Weighted Average, for an 8-hour work shift of a 40-hour work week (ACGIH) and TLV-STEL, Short Term Exposure Limit for fifteen minutes, should occur no more than 4-times per workday, and there should be 60-minutes between successive exposures in this range.

Some of the limits are called TLV, Threshold Limit Values (ACGIH), REL, Recommended Exposure Limit (NIOSH) or OEL, Occupational Exposure Limits (UK - HSE - COSHH).

In the following table are representative Threshold Limit Values (TLV):

USA	
ACGIH, Time Weighted Average (TWA)	0.1 ppm
Short Term Exposure Limit (STEL)	0.2 ppm
OSHA 29 CFR 1 910.1000, Table Z-1 limits for air contaminants, lists the following:	
Bromine	0.1 ppm (0.7 mg/m ³)
EUROPE	
EU Directive 2006/15/EC	TWA-0.1 ppm (0.7 mg/m ³)
UNITED KINGDOM	
EH 40/2005 Occupational exposure limits	
OES/LTEL	0.1 ppm (0.7 mg/m ³)
OES/STEL	0.2 ppm (1.3 mg/m ³)



4.5.2 EMERGENCY RESPONSE EXPOSURE LIMITS

The following are common terms for emergency planning and response: ERPG (AIHA,USA) are Emergency Response Planning Guideline value for planning exposure limits for the civilian population that includes children, the elderly and disabled persons. NIOSH (OSHA ,USA) Immediately Dangerous to Life or Health (IDLH). US Department of Energy DOE Protective Action Criteria PAC values

The following table shows the Emergency Response Values:

NIOSH (OSHA ,USA)	
Immediately Dangerous to Life or Health (IDLH)	3.0 ppm
ERPG (AIHA)	
for Bromine:	
ERPG1	0.1 ppm
ERPG2	0.5 ppm
ERPG3	5.0 ppm
* DOE O 151.1C(HSS-Office of Health Safety and Security) PAC:	
PAC1	0.033 ppm
PAC2	0.24 ppm
PAC3	8.5 ppm

* adopted from Table 2: Protective Action Criteria PAC Rev.27 based on applicable 60-minutes AEGL, ERPG or TEEL February 2012 DOE.HSS

4.6 DETECTION METHODS

Introduction

While bromine appears to give adequate warning of its presence by color, during daylight, and odor, there is an uncertainty over the odor threshold value.

To be on the safe side, detection instruments for detecting bromine should be used to determine the bromine concentration in a workplace. It may be difficult to detect a specific bromine leak if the atmosphere is contaminated with another halogen or halogen compound such as Freon, etc.

There are a variety of sampling techniques and types of equipment for determining the concentration of bromine in the air. The technique and/or equipment chosen will depend on the type of monitoring system needed to meet a specific regulatory requirement. Types of sampling techniques include time weighted average (TWA) exposure, continuous monitoring, or point-in-time exposure measurements.

4.6.1 Detector Tubes

The detector tube method is an officially approved analysis method. Detector tubes should meet one of the standards issued by competent authorities.

Detector tubes will indicate bromine presence when the correct disposable tube is used. Some vendors do not list a specific bromine detector tube but indicate that bromine reacts with approximately the same sensitivity and a similar discoloration, as chlorine in a chlorine detector tube.

Used and date-expired tubes should be neutralized before disposal, in accordance with the manufacturer's instructions.

Long-term detector tubes are also available which will average bromine vapors over an 8 hour period.

A possible erroneous indication of the presence of bromine caused by the interference of other gases, such as free halogens, hydrogen halides, or other halogenated hydrocarbons, must be taken into account.



The apparatus is simple, hand pump operated. The method can be slightly cumbersome under the stress conditions of a leak or a spill.

Suppliers of detector tubes are, for example:

- Draeger (Germany)
- Kitagawa (Japan)
- RAE Systems (USA)
- MSA (USA)

4.6.2 Electronic gas sensors

Electronic gas sensors have been developed for the detection of halogen gases including bromine. As in the other methods described above, there is the possibility of an erroneous indication of bromine caused by the interference from other halogens.

If a continuous or a portable electronic monitor is required, the PID (photo-ionization detector) type instruments and technology can be used. Suppliers of portable electronic monitors are for, example RAE Systems (USA), Draeger (Germany), and Bionics Instrument Company (Japan), would be suitable instruments. However, contact should be made with the supplier in order to receive expert advice on the type of instrument that can be used.

4.6.3 Ammonia Solution

Use of aqueous ammonia solution (2-5%)

It is possible to detect leakages of bromine vapors by spraying small quantities of aqueous solution (2-5% in water) especially for leak detection under the manhole cover of the isotank around valve gauges and relief elements.

If bromine is present, white fumes will be evolved as the result of a chemical reaction between bromine and ammonia.

4.7 PROTECTIVE EQUIPMENT FOR OPERATING PERSONNEL

As bromine is corrosive and toxic, no worker should be alone in an area where there is potential exposure to bromine.

The protective equipment required for workers, under routine operating conditions, should allow the worker to escape the hazardous area, if there should be a release of hazardous material.

Protective equipment for operating personnel should be issued on a personal basis. For routine operations, full body, washable work clothes with rubber gauntlets, boots and aprons should be worn. A safety helmet should be worn, where required, or some other head covering.

Goggles should be worn if there is a possibility of a liquid splash. Otherwise, a full-face shield should be worn.

The clothing should be laundered, under supervision, by the employer and not at home. All clothing exposed to bromine should be thoroughly washed before reusing.

A gas mask with an appropriate bromine filter has to be available for escape purposes. Color coding of gas mask filters differs under different regulations.

Personal protective equipment of polyvinyl chloride (PVC) will be attacked by liquid bromine but can be used in a bromine vapor atmosphere. Equipment of Viton is suitable for all bromine exposures but may be heavy.

Emergency response personnel responding to large spills must wear a fully encapsulated suit. A self-contained breathing apparatus (SCBA) must be worn under the suit where it will be protected from the corrosive bromine vapors.

4.8 RESPIRATORY PROTECTION

Air purifying respirators can be used in Europe but are no longer approved for respiratory protection in the USA. NIOSH only allow “nonoxidizable sorbents” i.e. not charcoal. As filter manufacturers use activated charcoal as a sorbent, they will not supply these filters for protection against bromine vapors. Hence in the USA a supplied air respirator will be required.

Under routine operating conditions at most bromine facilities, a gas mask does not need to be worn at all times.

However, each person working in an area where bromine is being handled should be trained in the use of respirators in case hazardous fumes are released.

When there is an uncontrolled exposure of bromine, a full-face gas mask with a new, unused inorganic vapor canister (type B) or a universal canister (type ABEK) should be used to escape the area.

The gas mask should not be used in an area with oxygen content of less than 19.5%.

The face piece should be full-face made of neoprene or other non-natural or nonbutyl rubber elastomer. Eyeglasses cannot be worn with regular face pieces. Special face pieces or face adapter kits can be supplied for use with special eyeglass frames.

Color coding of canisters:

- European Standard, EN 141,
Inorganic vapors: Type B, Color coded **grey**, or universal canister A2B2E2K1-P2. Smaller size cartridges, such as the chin type, should not be used for bromine. These cartridges are too limited in their length of service life and vapor concentration limitation to be used for bromine.

If respirators are used, it should be emphasized that filter life is limited, even at low bromine concentrations (no more than 20 minutes continuous use).

A self-contained breathing apparatus should be worn to re-enter an area where there is a bromine release.

Respirators should be stored in a clean sanitary cupboard, conveniently located. Whenever possible, respirators should be individually assigned for hygienic reasons and to assure good fit. After each use, they should be inspected, cleaned and disinfected. Once a month, even if the respirator has not been used, the respirator should be inspected, cleaned and disinfected. A record should be kept of the date of the inspections, and what was found at that time.

The breathing air cylinders of the self-contained breathing apparatus should be tested and maintained in accordance with local pressure vessel regulations.

A new operator should receive training in respirator use, and fitting the face piece before starting his assignment. A record should be kept of the training and fitting dates.

Bromine vapors can seep through punctured ear drums while wearing a respirator. Protection is possible with lubricated earplugs, but hearing can be affected.

Contact lenses must not be worn with a respirator.

Canisters should not be used after expiration date.

Respirator Regulations

A respirator protection program is required in the U.S. (29 CFR 1910.134(c)), and is recommended for other locations:

- Written standard operating procedures governing the selection and use of respirators shall be established.
- Written procedures shall be prepared, covering safe use of respirators in dangerous atmospheres that might be encountered in normal operations or in emergencies.
- Training shall provide an opportunity to handle the respirator, have it fitted properly, test its face-piece-to-face seal, and wear it in normal air and in a test atmosphere.
- A record shall be kept of inspection dates and findings, for respirators maintained for emergency use.
- There shall be an annual inspection and evaluation to determine the effectiveness of the respiratory program including respirator condition and correct gas mask face-piece fitting.



4.9 ISOTANK EMPTYING PROCEDURES

When connecting, disconnecting or inspecting the receptacle flanges, a full-face gas mask should be worn together with other protective equipment such as polyvinyl chloride (PVC) gauntlets and apron. Another worker should observe the activity from a safe remote location to call for assistance, should it become necessary.

Some cleaning substances can have a violent, even explosive reaction with bromine, for example, acetone. Cleaning bromine-spotted receptacles should not be done with quick drying organic solvents.

At all times that bromine receptacles are not in use, the valves should be closed and the gaskets and blind flanges should be replaced. The valve dome cover should be closed and pinned to prevent accidental opening.

Ensure that road or rail vehicles cannot be moved during a transfer operation.

An elevated unloading platform can be provided which will give protected access to isotank unloading valves during the unloading operation.

Provide handling devices to assist in the manipulation of unloading arms or hoses.

Bromine tanks can be unloaded under pressure, by vacuum, or with unloading pumps.

ICL-IP has issued the accompanying two cards, "Recommended Procedure for Bromine Unloading" using either a 2 Valve system (see page 70) or a 3 Valve system (see page 70). The user should follow the instructions appropriate to the installation having either two or three connecting lines (see page 72).

If the installation has three connecting lines, one for the transfer of the liquid bromine, one for use as a pressurizing connection and one to be used as a vent connection, then the three isotank valves are connected as indicated.

The vent connections and the pressurizing valve with its piping should be bromine resistant to prevent corrosion by diffusion of bromine back into the pressurizing or venting systems.

The pressurizing medium can be dry air (dewpoint below -40°C) or dry nitrogen. Excessive padding pressure should be avoided. A recommended padding pressure is 2 bar. Under no circumstances should the padding pressure exceed 3 bar, which is the maximum allowable working pressure indicated on the isotank.

The use of nitrogen as the padding medium may lead to frothing when the gas comes out of solution. At 1 bar gauge nitrogen pressure, approximately one volume of nitrogen gas dissolves in one volume of liquid bromine.

For unloading under vacuum, the liquid bromine unloading line and the bromine receiving tank are put under vacuum. Then the bromine is siphoned over. This alleviates the necessity of pressurizing and its possible dangers.

A sight glass in the liquid bromine unloading line is helpful to observe that liquid flow is taking place. No flow indication is a sign that the unloading has been completed or that there is some difficulty that has to be corrected.

Bromine Vent Scrubbing Tower (bromine absorber)

A system should be installed to prevent bromine vapors from being dispersed into the atmosphere, such as a bromine absorption recovery tower or a scrubbing system.

The stack of a bromine scrubbing system should be high enough to prevent air stream inversion during adverse weather conditions. Three meters above adjacent buildings should be sufficient.

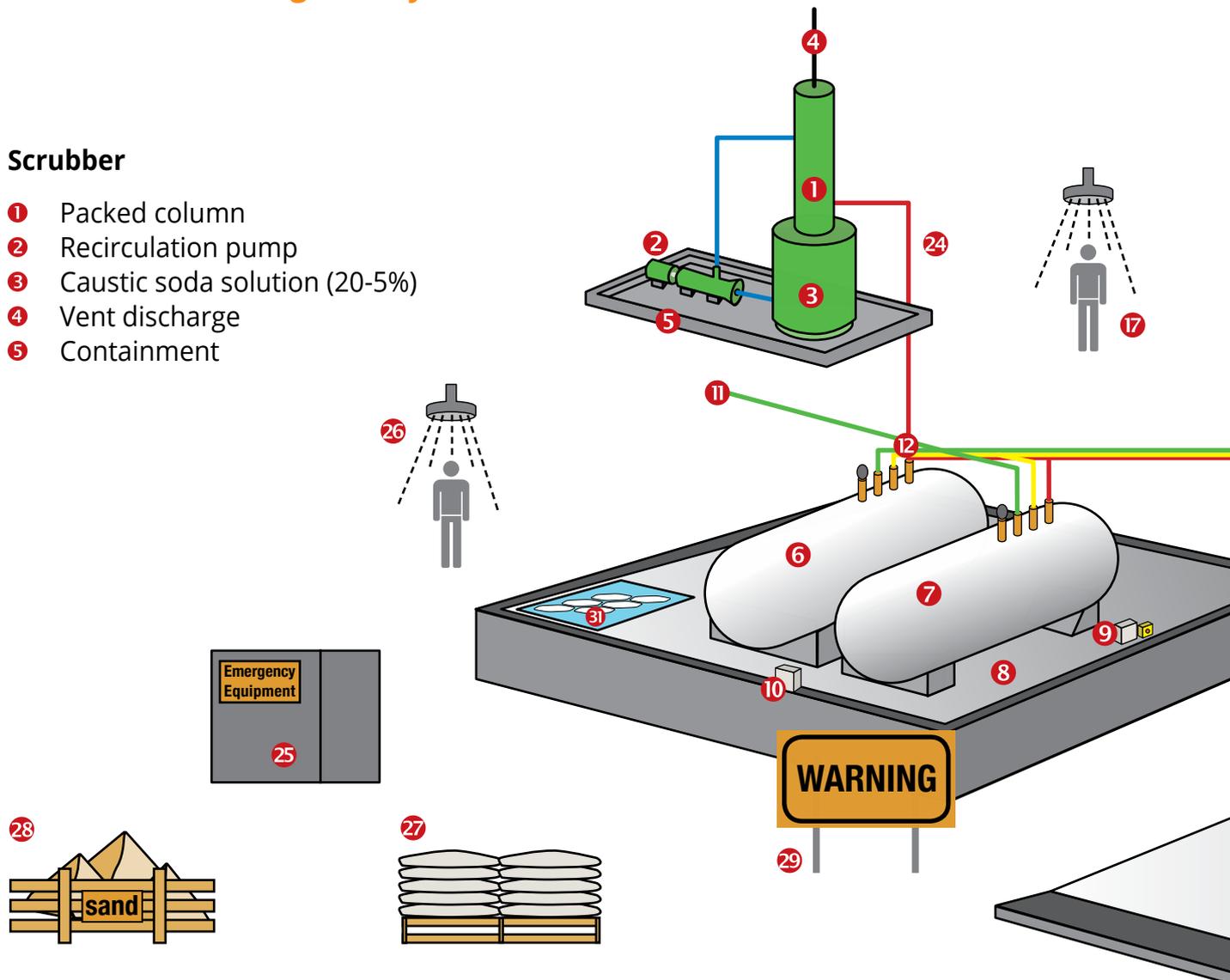
The vent is always directed to the caustic soda vent scrubbing tower.

The concentration of the caustic soda solution in the scrubbing system should be maintained between 15% to 5%. The initial concentration should never exceed 15% as sodium bromate can be formed, crystallize under heat and clog the system. To be effective, the final concentration of the scrubbing liquor should not be less than 5%.

Bromine Offloading Facility

Scrubber

- ① Packed column
- ② Recirculation pump
- ③ Caustic soda solution (20-5%)
- ④ Vent discharge
- ⑤ Containment

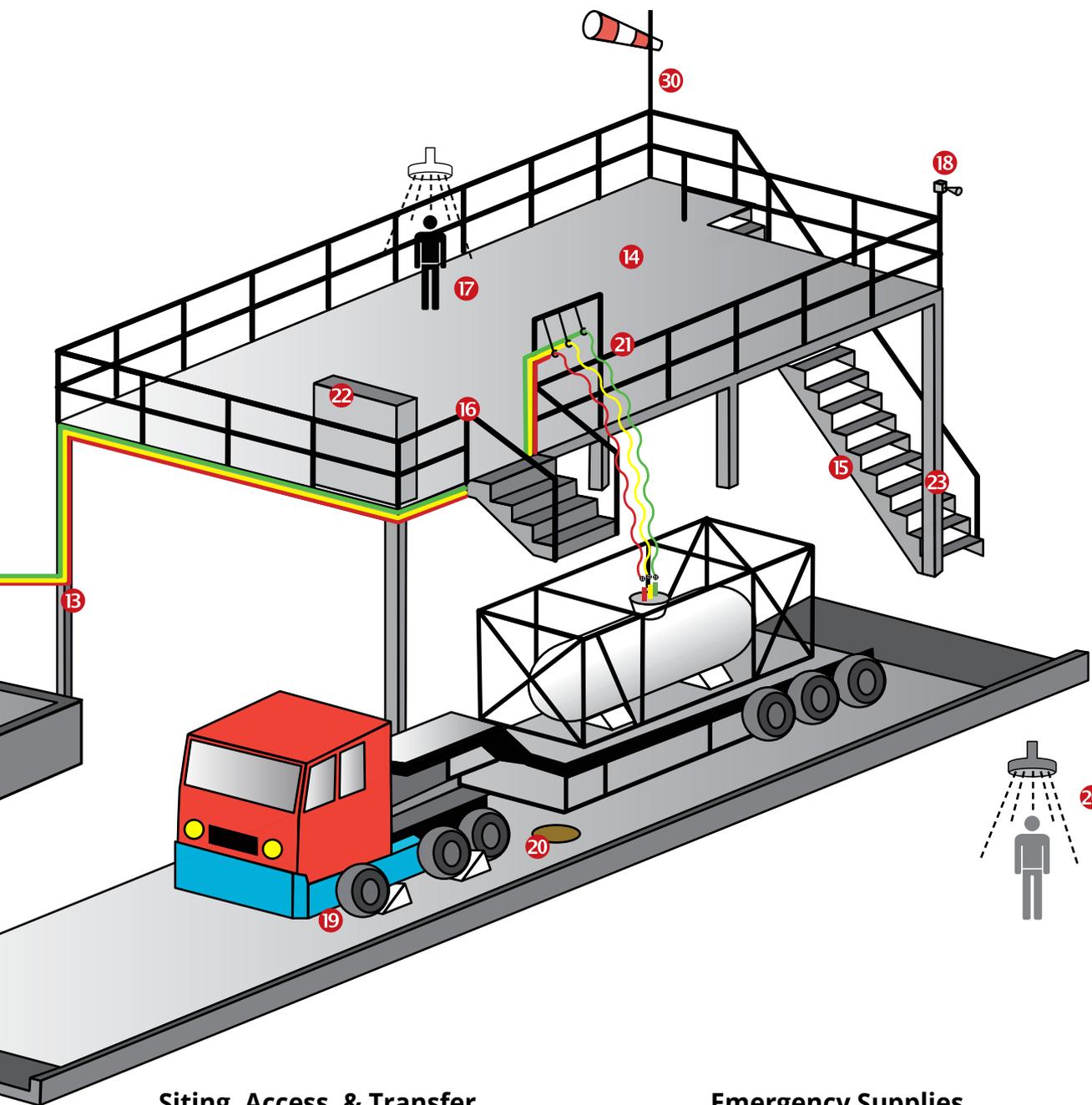


Storage Tanks

- ⑥ Storage tank
- ⑦ Back-up storage tank
- ⑧ Secondary containment
- ⑨ Weight indicators
- ⑩ Halogen Detection
- ⑪ Dry air/nitrogen supply
- ⑫ High level indicator with alarm
- ⑬ Emergency stop button

Access Platform

- ⑭ Elevated offload platform with easy access
- ⑮ Multiple escape routes
- ⑯ Handrail
- ⑰ Eyewash and shower station
- ⑱ Alarm horn



Siting, Access, & Transfer

- 19 Chocked Wheels
- 20 Secondary Containment
- 21 Transfer lines supported
- 22 Control Panel
- 23 Alarm button
- 24 Vacuum to scrubber

Emergency Supplies

- 25 Emergency Response Personal Protective Equipment (including SCBA)
- 26 Eyewash and safety shower
 - Unobstructed path
 - Upwind option
- 27 Neutralizing agents
- 28 Diking materials
- 29 Warning signs
- 30 Wind sock
- 31 Optional Emergency Pond



INSTRUCTION CARD

Recommended Procedure for Bromine Unloading (Two Valve System)

General

The following instructions are written for people who are familiar with the physical and chemical properties of bromine as well as first aid instructions (see Material Safety Data sheet and this Handbook.)

In case expert advice is needed, please contact our agent.

FIGURE 1 - SIDE VIEW OF RECOMMENDED UNLOADING HOOK-UP

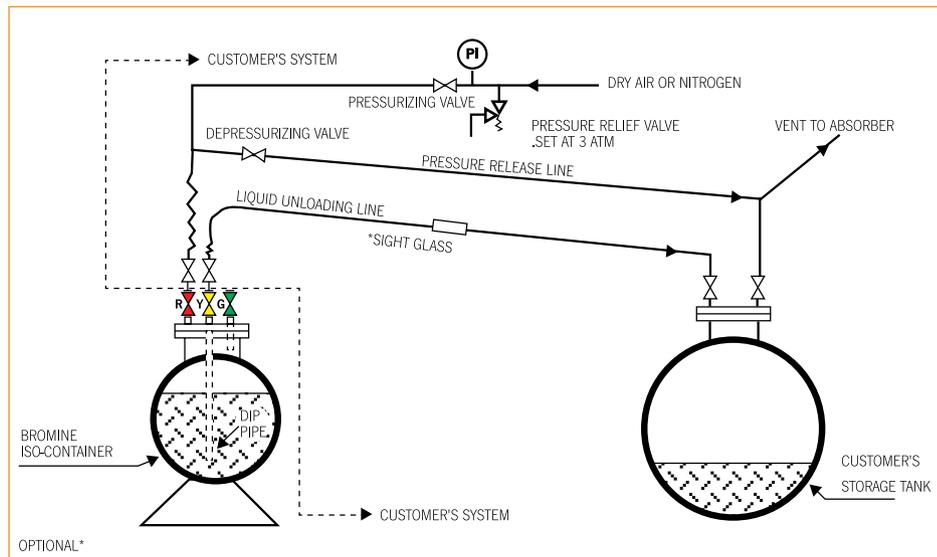
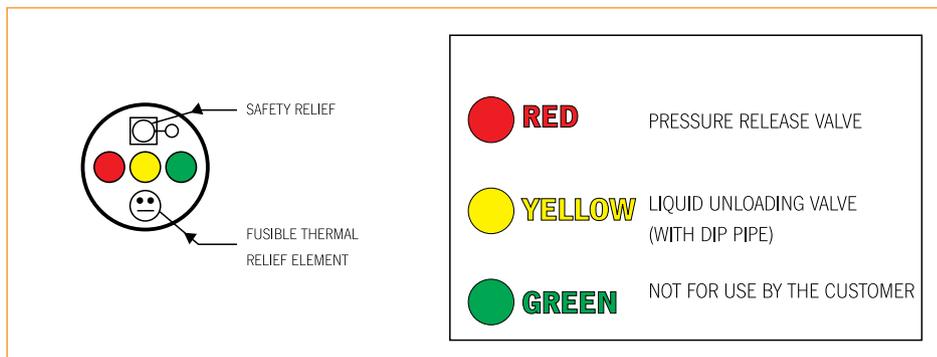


FIGURE 2 - PLAN VIEW OF VALVES ON THE ISO-CONTAINER (with the dome cover open)



The information herein is believed to be correct and is given in good faith, but no warranty, expressed or implied, is made with respect to the procedure described or its application.

RECOMMENDED UNLOADING PROCEDURE (Two Valve System)

(See figures 1 and 2 for typical piping set-up and Iso-container valve arrangement.)

1. Wear recommended personal protective equipment.
2. Make sure the absorber unit is working and capable of handling vented bromine fumes.
3. **BE SURE THAT DRY AIR (DEW POINT -40°C) OR DRY NITROGEN** is available in ample supply and its pressure is controlled below 3 atm. gauge.
4. Check that all the Iso-container valves are closed and blind flanges are in place.
5. Remove the blind flange above the red valve.
6. Connect your pressure release line to the red valve outlet. Use a new rubber gasket (use limit - 24 hours) to ensure tight connection.
7. Open the red valve slowly and then the depressurizing valve, to release any pressure which might have developed in the Iso-container.
8. Remove the blind flange above the yellow valve.
9. Connect your unloading line to the yellow valve outlet. Use a new rubber gasket (use limit - 24 hours) to ensure tight connection.
10. Open the yellow valve and all the valves in your liquid unloading line.
11. Close the depressurizing valve.
12. Open the pressurizing valve, at first slowly (to check for bromine leaks), then fully, to start bromine unloading. Use only enough pressure to lift the bromine to the high point in the unloading system (1 atm. pressure will lift bromine about 3.3 meters).

NEVER EXCEED 3 ATM. PRESSURE.

13. When air/nitrogen blows through the unloading line into your storage tank, the Iso-container is empty.
14. Close the pressurizing valve.
15. Close the yellow valve and then all the other valves in your liquid unloading line.
16. Slowly open the depressurizing valve to release the air/nitrogen pressure on the Iso-container to your absorber unit. Wait 5 minutes.
17. Close the red valve and then the depressurizing valve.
18. Cautiously disconnect your liquid unloading line from the yellow valve of the Iso-container. Replace its blind flange, tightening all the bolts. Do not forget to reinstall the proper gasket.
19. Disconnect your pressure release line from the red valve of the Iso-container. Replace its blind flange, tightening all the bolts. Do not forget to reinstall the proper gasket.
20. If there has been a bromine spillage, wash it off the Iso-container with plenty of water to prevent corrosion. Small bromine spills on the ground may be neutralized with a clear soda ash or a sodium thiosulphate solution. Then dispose of it in a manner approved by the local authorities.
21. Close the cover dome and pin it securely.



INSTRUCTION CARD

Recommended Procedure for Bromine Unloading (Three Valve System)

General

The following instructions are written for people who are familiar with the physical and chemical properties of bromine as well as first aid instructions (see Material Safety Data sheet and this Handbook.)

In case expert advice is needed, please contact our agent.

FIGURE 1 - SIDE VIEW OF RECOMMENDED UNLOADING HOOK-UP

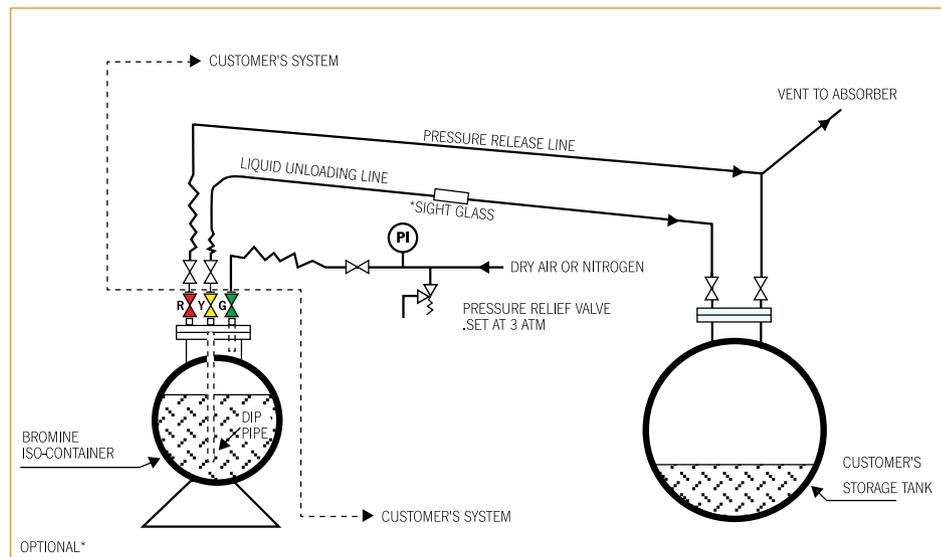
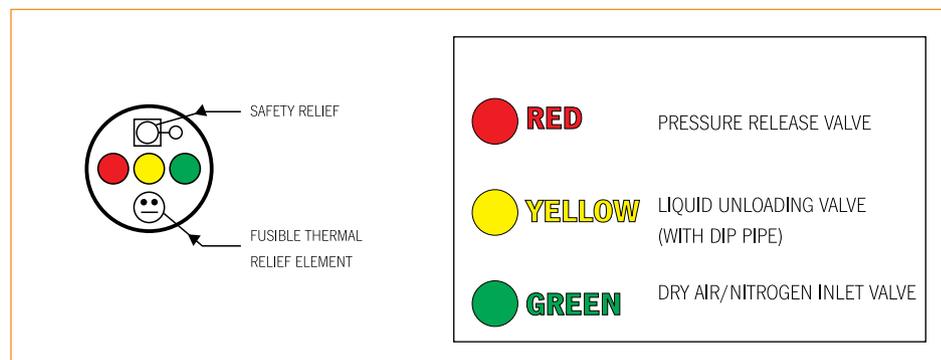


FIGURE 2 - PLAN VIEW OF VALVES ON THE ISO-CONTAINER (with the dome cover open)



The information herein is believed to be correct and is given in good faith, but no warranty, expressed or implied, is made with respect to the procedure described or its application.

RECOMMENDED UNLOADING PROCEDURE (Three Valve System)

(See figures 1 and 2 for typical piping set-up and Iso-container valve arrangement.)

1. Wear recommended personal protective equipment.
2. Make sure the absorber unit is working and capable of handling vented bromine fumes.
3. **BE SURE THAT DRY AIR (DEW POINT -40 ° C) OR DRY NITROGEN** is available in ample supply and its pressure is controlled below 3 atm. gauge.
4. Check that all the Iso-container valves are closed and blind flanges are in place.
5. Remove the blind flange above the red valve.
6. Connect your pressure release line to the red valve outlet. Use a new rubber gasket (use limit - 24 hours) to ensure tight connection.
7. Open the red valve slowly, to release any pressure which might have developed in the Iso-container.
8. Remove the blind flange above the yellow valve.
9. Connect your unloading line to the yellow valve outlet. Use a new rubber gasket (use limit - 24 hours) to ensure tight connection.
10. Open the yellow valve and all the valves in your liquid unloading line.
11. Close the red valve.
12. Remove the blind flange above the green valve.
13. Connect your pressurizing line to the green valve outlet. Use a new rubber gasket (use limit - 24 hours) to ensure tight connection.
14. Open the green valve, at first slowly (to check for bromine leaks), then fully, to start bromine unloading. Use only enough pressure to lift the bromine to the high point in the unloading system (1 atm. pressure will lift bromine about 3.3 meters).
15. **NEVER EXCEED 3 ATM. PRESSURE.**
15. When air/nitrogen blows through the unloading line into your storage tank, the Iso-container is empty.
16. Close the green valve.
17. Close the yellow valve and then all the other valves in your liquid unloading line.
18. Slowly open the red valve to release the air/nitrogen pressure on the Iso-container to your absorber unit. Wait 5 minutes.
19. Close the red valve.
20. Cautiously disconnect your liquid unloading line from the yellow valve of the Iso-container. Replace its blind flange, tightening all the bolts. Do not forget to reinstall the proper gasket.
21. Disconnect your pressure release line from the red valve of the Iso-container. Replace its blind flange, tightening all the bolts. Do not forget to reinstall the proper gasket.
22. If there has been a bromine spillage, wash it off the Iso-container with plenty of water to prevent corrosion. Small bromine spills on the ground may be neutralized with a clear soda ash or a sodium thiosulphate solution. Then dispose of it in a manner approved by the local authorities.
23. Close the cover dome and pin it securely.



4.10 ISOTANK TROUBLE SHOOTING

The following sections deal with minor valve and flange leaks only. Only experienced maintenance personnel should handle other leaks from the body of the tank.

Details of the relevant isotank parts may be seen at the end of this section.

Preparations

Suspected bromine leaks should be dealt with promptly. They can only get worse. They will never get better.

Prepare sufficient neutralizing material, conveniently located, either bagged or as a slurry. A sodium thiosulphate solution can be prepared in small quantities. In larger quantities, calcium hydroxide (slaked lime) slurry or 20% soda ash (sodium carbonate) slurry can be prepared.

Maintenance personnel should be experienced workers, familiar with the properties and potential hazards of bromine.

Keep upwind of the bromine leak area.

Have an observer at a safe distance from the repair activity to call for outside assistance if necessary.

Wear full body protective clothing, rubber gauntlets, boots, and apron.

Wear a self-contained breathing apparatus, a supplied air respirator, or a full face gas mask with a new canister.

Small vapor leaks may be detected by spraying with aqueous ammonia solution.

Leaking from above a valve

- a. Make sure valve is properly closed by turning the handwheel clockwise.
- b. Check the condition of the gasket under the valve blind flange.
Replace if torn or damaged.
- c. Tighten the valve blind flange bolts.

Leaking valve bonnet or body gasket

- a. Dismantle the blind flange from the red vent valve (for pressure relief). Relieve any pressure in the vessel by opening the red vent valve, slowly and cautiously.
- b. Open the leaking valve by turning the handwheel counter clockwise, then tighten the four nuts connecting the bonnet to the valve body.
- c. Close the leaking valve and the red vent valve. Check for leakage.
- d. If the leak has not stopped, repeat step "a". Then replace the faulty valve with the gasket and blind flange, which had been above the faulty valve. Ensure tight connection.

Leaking from below a valve

- a. Tighten the nuts of the studs on the vessel flange under the valve.
- b. If the leak continues, dismantle the blind flange from the red vent valve (for pressure relief). Relieve any pressure in the vessel by opening the red vent valve, slowly and cautiously.
- c. Remove the leaking valve and check the flanges. They should be smooth and without deep scratches. If necessary, carefully smooth out any scratches. Check the Teflon envelope gaskets and replace if torn or damaged.
- d. Reinstall the valve, close it, then close the red vent valve. Check for leakage. If there is no leakage, replace the blind flange over the valve. Ensure tight connection.
- e. If the leak has not stopped, then remove and replace the valve again but replace it upside down. Check for leakage. If there is no leakage, replace the blind flange over the valve. Ensure tight connection.
- f. If the leak has not stopped, repeat step "b". Then replace the faulty valve with the gasket and blind flange which had been above the faulty valve. Ensure tight connection.



Leaking dip pipe

- a. Tighten the nuts of the studs, connecting the dip pipe flange and valve.
- b. If a leak continues, dismantle the blind flange from the red vent valve (for pressure relief).
Relieve any pressure in the vessel by opening the red vent valve, slowly and cautiously.
- c. Caution:
 - Wear full body protective clothes including boots.
 - Remove valve and dip pipe.
 - Remember that the dip pipe may be wet with liquid bromine.
- d. Check the flange faces. They should be smooth and without deep scratches. If necessary, smooth out any scratches.
Check the Teflon envelope gaskets and replace, if torn or damaged.
- e. Reinstall the dip pipe and valve, close the red vent valve. Check for leakage. If there is no leakage, replace the blind flange over the valve.
Ensure tight connection.
- f. If the leak has not stopped, repeat step “b”. Then, once more remove the valve and dip pipe.
Remember that the dip pipe may be wet with liquid bromine. Install the gasket and blind flange directly to the container outlet, or replace the dip pipe.

Replacement of the dip pipe

If the leakage of the dip pipe next to the tank body continues, or if bromine flow does not start, the dip pipe needs to be replaced, as follows:

- a. Relieve any pressure in the receptacle by opening the red vent valve.
- b. Remove the existing yellow valve and the faulty dip pipe from the isotank.
- c. Disassemble the yellow valve from the dip pipe.
- d. Install the new dip pipe into the tank using new gaskets. Tighten all connecting bolts.
- e. Reinstall the yellow valve onto the dip pipe using new gaskets and tightening all bolts.

REMEMBER:

The old dip pipe might be wet with liquid bromine. Observe all safety precautions.

In any case of leakage, even if the steps taken were effective, notify one of the addresses appearing on the container, as soon as possible, giving as many details as possible.

If the leak persists, contact the nearest emergency response team and remove the isotank to an open area.

Leaking between dip pipe flange and valve

- a. Tighten the nuts of the studs connecting the dip pipe flange and valve.
- b. If the leak continues, dismantle the blind flange from the red vent valve (for pressure relief).
Relieve any pressure in the vessel by opening the red vent valve, slowly and cautiously.
- c. Remove the valve and check the flanges. They should be smooth and without deep scratches. If necessary, carefully smooth out any scratches.
Check the Teflon envelope gaskets and replace if torn or damaged.
- d. Reinstall the valve, close it, then close the red vent valve. Check for leakage. If there is no leakage, replace the blind flange over the valve.
Ensure tight connection.
- e. If the leak has not stopped, repeat step “b”. Then remove the faulty valve and install the gasket and blind flange in place of the faulty valve.
Ensure tight connection.

Leaking from under the manhole cover flange

Tighten the nuts of the manhole cover. If necessary, use a two meter long pipe on the spanner arm to increase the torque.



Leaking from under safety valve

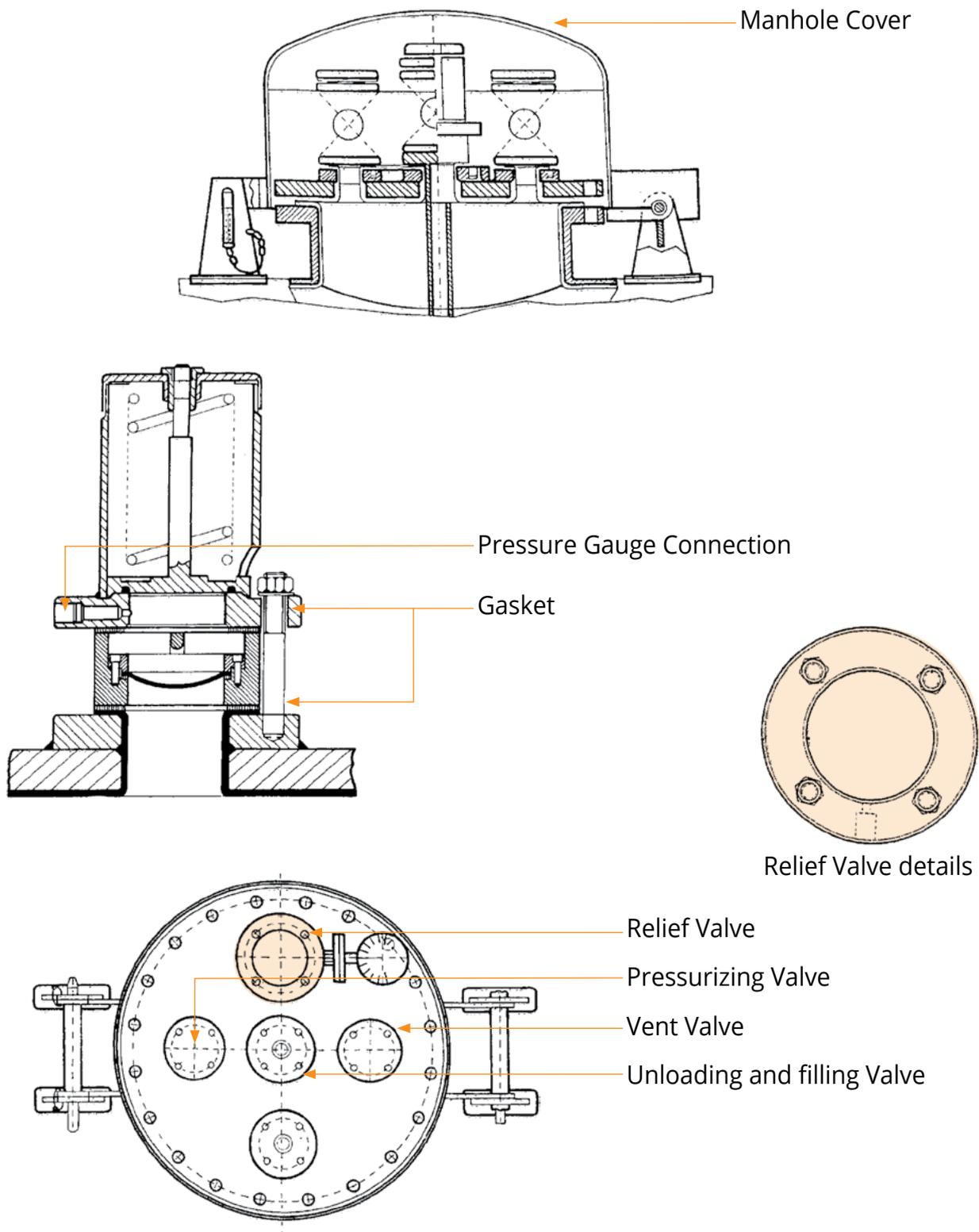
- a. Tighten the nuts of the studs on the vessel flange under the valve.
- b. If the leak continues, dismantle the blind flange from the red vent valve (for pressure relief).
Relieve any pressure in the vessel by opening the red vent valve, slowly and cautiously.
- c. Remove the valve and check the flanges. They should be smooth and without deep scratches. If necessary, carefully smooth out any scratches.
Check the Teflon envelope gaskets and replace if torn or damaged.
- d. Reinstall the valve, close the red vent valve.
Ensure tight connection. Check for leakage.
- e. If the leak has not stopped, repeat step "b". Then remove the faulty valve again.
Install a sheet of lead in place of the safety valve.
Ensure tight connection.

Vapors leaking from under the fusible element (when installed)

- a. Tighten the bolts connecting the fusible element to the tank outlet.
- b. If the leak continues, dismantle the blind flange from the red vent valve (for pressure relief).
Relieve any pressure in the vessel by opening the red vent valve, slowly and cautiously.
- c. Remove the leaking fusible element. Install in place of the fusible element, the blind flange from above the red vent valve.

Under no circumstances should damaged parts be reused. They should be returned to the Sdom plant for evaluation and rejection.

Isotank Manhole details





5. EMERGENCY RESPONSE

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5.1 FACILITY EMERGENCY ACTION PLANNING

USA – OSHA (29 CFR 1910.119n and 29 CFR 1910.120q)

Emergency Action plans must be established and submitted to state and local authorities for any facility where Threshold Quantities (TQ) of hazardous substances are handled.

For bromine (UN 1744), the threshold quantity is 1500 lbs. (682 kg.)

A Facility Emergency Coordinator is to be appointed to the local Emergency Planning Committee. The plan has to be reviewed and audited every three years.

When there is a release of a hazardous material, the Emergency Planning Committee is to be advised of the following information (a transportation related release may be notified to the 911 emergency operator):

- That the released material, bromine, is corrosive and toxic.
- The quantity released, the time of the release and its duration.
- The media into which the release occurred.
- An indication of the health risks and sources for medical advice.
- Precautions to be taken by the local community, preferably as established in a previously prepared emergency plan.
- Names and phone numbers for receiving further information on the material.

The Emergency Planning Committee is to be given the following follow-up information:

- Actions that were taken to contain the release.
- Any acute or chronic health problems that were the result of the release.
- Medical advice that was given to the exposed individuals.

The European Economic Community has issued regulations on Major Accident Hazards, Directive 82/501/EEC, with the latest amendments

Storage and process sites having an inventory of 20 tons or more of bromine must prepare documents identifying the major accident hazards at their sites, including what steps have been taken to prevent and limit the consequences of major accidents. Information, training and equipment are to be prepared for these sites.

Sites with an inventory of 100 tons or more of bromine must prepare emergency plans and report accidents involving bromine.



5.2 TRANSPORT EMERGENCY RESPONSE

The driver of a vehicle involved in an accident while transporting a hazardous material should immediately leave the vehicle, taking with him the shipping papers, and take reasonable measures to extinguish any small fires.

The driver should call for help, and furnish the following information about the hazardous material involved:

- UN number: 1744 (Bromine).
- Hazard Class Placard.
- Hazardous response markings (e.g. EAC Code, NFPA diamond numbers).
- Quantity of hazardous material involved.
- Emergency contact phone number.

The first responder, which is generally the local fire department, should:

- Protect persons, property and environment.
- Contain the release from a safe distance.
- Not get involved in stopping the release.
- Ensure that a qualified responder has been called.

The qualified responder trained in accordance with the hazardous Waste Operations & Emergency Response (HAZWOPER) regulations, is called by the shipper of the hazardous material or by the first responder if the shipper has not acted.

A Hazardous Materials Technician is qualified to stop the release.

A Hazardous Materials Specialist provides support to responders with information and procedures on the hazardous materials, but he is not authorized to become actively involved in response action.

The emergency response telephone number should be clearly identified as "EMERGENCY CONTACT" on labels and shipping papers.

- | | |
|--|-----------------|
| • USA: CHEMTREC | 1-800-424-9300 |
| National Response Center | 1-800-424-8802 |
| ICL-IP AMERICA | 1-304-675-1150 |
| • UK: National Chemical Emergency Center "CARECHEM 24" | 44-1865-407333 |
| • EUROPE: ICL-IP Terneuzen B.V. | 31-1156-89000 |
| • ICL-IP, Israel | 972-8-6544475/6 |
| • JAPAN: | |
| East Japan Area: Kyogoku unyu shoji Co. | 81-44-322-2678 |
| West Japan Area: Rissyo Transport Co. | 81-6-6478-1702 |
| Kyushu Area: Seagate Corp. | 81-93-331-2166 |
| • CHINA: | |
| NRCC: | 86 21 2315 7500 |
| | 86-532-83889090 |

5.3 HAZARD IDENTIFICATION

ADR — Hazard Identification Number

Bromine	UN 1744
Hazard identification number	No. 886
Highly Corrosive	88
Class (Corrosive)	6.1

EAC — Emergency Action Code

The UK CDG Road — Carriage of Dangerous Goods regulations require the display of this code number in the UK.

The Emergency Action Code for Bromine is:

2 X E

- 2** Use fine water spray for extinguishing a fire.
- X** Precautions to be taken in case of a fire or spill:
 - Contain, avoid spillage from entering drains or water courses.
 - Wear full protective clothing including breathing apparatus.
- E** Evacuation of people from the neighborhood of an accident should be considered.

NFPA Hazard Identification: Bromine

Health hazard — 3

Serious. Materials that under emergency conditions can cause serious or permanent injury.

Areas should be entered only when wearing self-contained breathing apparatus and special protective clothing.

Flammability hazard — 0

Bromine does not burn.

Reactivity Hazard — 0

Materials that are normally stable even under fire conditions.

Oxidizer (OX - special hazard)

Strong oxidizer. Heat of reaction may ignite combustibles on contact.

May accelerate combustion reactions.



5.4 RISK AND SAFETY PHRASES

Bromine is listed in Annex I of European Council Directive 67/548/EEC, relating to the classification, packaging and labeling of dangerous substances.

The classification for bromine under the Directive is:

Very Toxic
Corrosive

The following Risk and Safety phrases are assigned for bromine:

Risk Phrases:

- R26 Very toxic by inhalation
- R35 Causes severe burns
- R50 Very toxic to aquatic organisms

Safety Phrases:

- S7/9 Keep container tightly closed and in well-ventilated place.
- S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
- S45 In case of accident or if you feel unwell, seek medical advice immediately (show the label when possible).
- S61 Avoid release to the environment. Refer to special instructions/ Safety data sheets.

5.5 GLOBALLY HARMONIZED SYSTEM (GHS)

Regulation (EC) No 1272/2008 (CLP Regulation) on classification, labeling and packaging of substances and mixtures, the Globally Harmonized System (GHS) implementation in the EU, entered into force on 20 January 2009.

As of 1 December 2010, substances must be classified, labeled and packaged according to CLP.

As of 1 June 2015, mixtures must be classified, labeled and packaged according to CLP.

Label Elements

Symbols



Signal word

Danger

Hazard statements

H330

Fatal if inhaled

H314

Causes severe skin burns and eye damage

H400

Very toxic to aquatic life

Precautionary statements

P260

Do not breathe fume/gas/mist/vapors/spray.

P284 + P280

Wear respiratory protection/protective gloves/protective clothing/eye protection/face protection.

P304 + P340

IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.

P301 + P330 + P331

IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.

P303 + P361 + P353

IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower.

P305 + P351 + P338

IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

P310

Immediately call a POISON CENTER or doctor/physician.



5.6 FIRE-FIGHTING

It is very important that bromine receptacles should not remain in a fire zone. The heat can lead to release of poisonous and corrosive fumes of bromine. Although not combustible itself, bromine liquid will react with combustible materials and may cause them to ignite.

Bromine itself is not a flammable substance, but if a bromine drum or tank becomes involved in a fire, the vapor pressure increases rapidly and might lead to the rupture of the receptacle. Therefore, if possible, the bromine receptacles should be removed from the fire, and if not possible, they should be cooled by water sprays until the fire itself is extinguished.

A fire in an area containing bromine should be extinguished with the most appropriate means available.

If there is a bromine spill at the same time as a fire, the safety procedure for spills should be immediately implemented:

- Have all non-essential personnel leave the area immediately.
- Provide self-contained breathing apparatus for the fire fighters.
- Wear impervious and chemical resistant clothing.
Note: This clothing may not be suitable for fire-fighting.
- Protect water sources from being contaminated by fire-fighting water or spilled bromine which has not been neutralized.

After the fire, all bromine containers should be carefully inspected for leaks or any physical damage. The supplier should be immediately informed of any unusual conditions found.

On the road

If a vehicle carrying bromine catches fire and no bromine leak is detectable, the driver should move the vehicle to an open area, remove shipping and other emergency response documents (MSDS) from the vehicle and make reasonable efforts to extinguish any small fires. He should then:

- Notify the local police and the fire department.
- Warn other drivers and pedestrians of the danger.
- Notify the nearest bromine handling facility.
- Stay at a safe distance until the incident has been declared resolved by the responder in charge on the scene.

If the driver cannot reasonably extinguish the fire and/or a bromine leak is evident, "Spills and Leaks," On The Road procedure (Section 5.6) should be followed immediately.

5.7 SPILLS AND LEAKS

Bromine has been shipped for many years with very few accidents. This is due to the care taken in packaging and handling this material.

Only trained, suitably protected personnel should respond to a bromine emergency. See section 4.7 of this handbook for the personal protective equipment recommended for emergency response personnel.

If there should be an uncontrolled bromine spill or leak, immediately call the fire department, giving them the maximum information. The competent authorities should be informed of the spill in accordance with local regulations.

Twenty-four hour telephone advice is available in most countries for bromine road transport emergencies, as noted in section 5.2 above.

The reddish-brown vapors and the harsh irritating odor very quickly indicate a bromine spill or leak.

All non-essential personnel should be kept out of the spill area. The spill area should be entered wearing a self-contained breathing apparatus. Impervious, fully encapsulated and chemically inert clothing should be worn.

Note: This clothing may not be suitable for fire fighting.

There is generally no need for an evacuation alarm in case of a bromine spill. However, nearby residents should be advised to stay indoors and to keep all windows closed.

Prevent the spilled liquid bromine from penetrating a water source or sewer system unless it has been neutralized.

A bromine spill should be contained and neutralized. Earth dams are sometimes convenient for containing the spill.

The neutralized spilled liquid can be flushed into drains with copious amounts of water, or can be absorbed in inert absorbent materials such as sand, earth or vermiculite.

The contaminated absorbent material can then be carefully shoveled into an open-head drum for eventual authorized disposal.



The remains on the spill area and neutralized spilled liquid can be flushed into drains with copious amounts of water, with the approval of local authorities.

Bromine may persist in pits, hollows, depressions, sewers, and confined spaces.

Certain fire-fighting foams have varying effectiveness in reducing the evaporation of bromine.

The foams do not neutralize the bromine and are not instead of neutralization materials.

Water spray can be used to knock down bromine vapors. When spraying water and when a bromine puddle is drenched with the water, there may be a temporary increase in bromine vapor emission. Bromine vapors can be neutralized with ammonia vapors. Anhydrous ammonia or aqueous ammonia should not be used to neutralize liquid bromine, as the reaction is violent. Ammonia vapors should be released in the direction of the bromine vapor until a white cloud (ammonium bromide) is formed.

On the road

The driver of a vehicle leaking bromine should try to get the vehicle to an unpopulated area, put on his escape gas mask, take with him all the shipping documents, and get to a safe spot upwind and higher than the vehicle.

From this safe spot, he should warn oncoming traffic and pedestrians and call for help. People not properly equipped should be kept out of the area.

In any bromine road transport emergency, call the EMERGENCY CONTACT that should be clearly marked on the shipping papers and labels.

Properly protected and trained responders should attempt to stop the leak, using emergency repair materials (i.e. wooden cones, lead wool, etc.), or by freezing the bromine at the escape opening.

If the bromine is leaking out from between flanges, the responders should follow the troubleshooting recommendations in section 4.10. To contain a bromine spill on the ground, earth or sandbag dams should be built around the spill and the contained bromine neutralized with dry soda ash or a slaked lime $\text{Ca}(\text{OH})_2$ water slurry.

Evacuation Guidelines

Spill Danger Zones

(Based on ERG 2013 — Emergency Response Guidebook)

UN number: 1744

Small spill — up to about 200 liters

Immediately isolate in all directions: 60 meters

Protect persons downwind during the:

Day 300 meters

Night 1100 meters

Large spill — over about 200 liters

Immediately isolate in all directions: 185 meters

Protect persons downwind during the:

Day 1600 meters

Night 4000 meters



5.8 EMERGENCY REPAIRS

Empty, clean, dry, covered receptacles (overpacks) should be available for leaking bromine drums and for collecting spilled bromine or contaminated absorbent materials.

The emergency response team of the bromine user should have at their disposal those tools and parts which will allow them to deal quickly and efficiently with any bromine incident. The equipment should include: personal protective equipment, specific and general tools, repair parts, first aid kit, fire-fighting hoses, nozzles and extinguishers, some maintenance equipment and neutralizing materials.

The personal protective equipment can include:

- Hard hats
- Face shields
- Full face masks
- Self Contained Breathing Apparatus (SCBA)
- Spare air bottles
- Tyvek safety suits
- Neoprene gloves
- Leather gloves
- PVC boots
- Wool blanket
- Safety goggles
- Work clothes
- Bromine gas filters
- PVC safety suits
- Viton safety suit
- PVC gloves
- Heat resistant gloves
- Safety shoes
- Eye wash bottles

The toolbox should include general tools, as well as tools specifically required for bromine receptacles, such as wrenches for the manhole flange, and valve bolts.

Repair parts can include:

- Spare valves
- Spare studs — nuts
- Blind flanges
- Caps
- Teflon pipe thread tape
- 5 mm lead sheet
- Spare gaskets
- Spare dip pipe
- Pipe plugs
- Teflon sheet
- Wood cone plugs

Other useful equipment: (for major bromine users)

- Compass
- Binoculars
- Detector tube set
- Chemical candles
- Barrier columns/tapes
- Spare cables
- Electric welding set
- Flood lights
- Medical guide sheets
- Spare fuel cans
- Approved flashlights
- Wind anemometer
- Road maps
- Detector tubes
- Air sealing cushions
- Electricity generator
- Air compressor
- Polyvinylidene fluoride (PVDF) diaphragm pump
- Stretcher
- Tent
- Material Safety Data Sheets (MSDS)



5.9 EXPOSURE TO BROMINE

When a person who has been exposed to bromine vapors is sent to a hospital, information should be pinned to the person's clothing stating that he was exposed to bromine. If possible, the MSDS should be sent with the patient.

Liquid bromine rapidly attacks the skin and other tissues, producing irritation and burns which heal very slowly. Even comparatively low concentrations of vapor are highly irritating and painful to the respiratory tract.

Acute exposure:

Eye contact:

Corrosive.

Symptoms include redness, pain and blurred vision.

Direct contact may result in serious corneal burns. May cause temporary or even permanent eye damage. Lachrimation occurs at less than 1 ppm.

Skin contact:

Corrosive.

Symptoms include redness, pain and edema. Direct contact may result in serious skin burns.

Inhalation:

Corrosive to mucous membranes and upper respiratory tract.

Symptoms include sore throat, dizziness, headache, nosebleed, coughing, shortness of breath and nasal irritation. May cause delayed pulmonary edema.

Ingestion:

Corrosive by ingestion.

Symptoms include sore throat, abdominal pain, vomiting and diarrhea. May cause severe burns to the mucous membranes of the mouth, esophagus and stomach.

First Aid

Eye contact:

Holding the eyelids apart, flush eyes at once with copious flowing water for at least 20 minutes. Get medical attention immediately.

Skin contact:

It is highly important to wash immediately, with water, any contaminated skin or eyes and get medical attention.

Flood skin with water, directing a stream of water under the clothing while they are being removed. Wash skin with mild soap and plenty of water for at least 15 minutes. Get medical attention immediately.

NO DECONTAMINATION OTHER THAN WATER SHOULD BE USED ON HUMANS.

Treat contaminated clothing with 10% sodium bicarbonate and wash them before re-use.

Inhalation:

Remove person to fresh air. Keep him quiet and warm. Apply artificial respiration if necessary, and get medical attention immediately.

Ingestion:

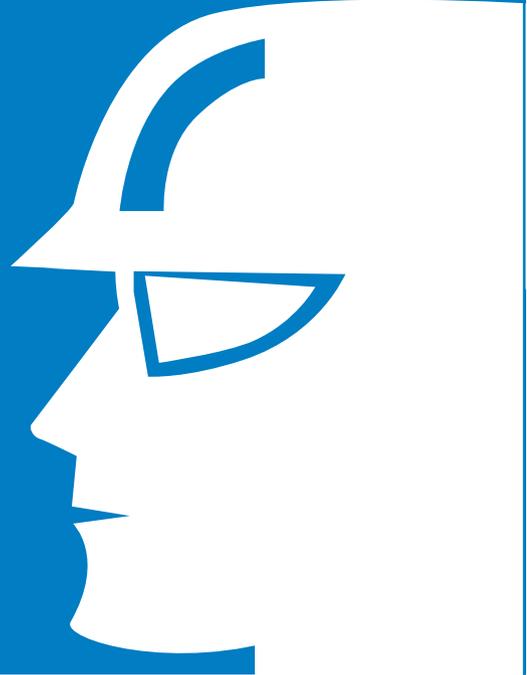
If no respiratory compromise is present, wash mouth with water.

DO NOT INDUCE VOMITING. Get medical attention immediately.

Note: Never give an unconscious person anything to drink.

Recommended Antidote

There is no specific antidote for bromine. Treatment is symptomatic and supportive.



6. OPERATORS GUIDE

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6.1 OPERATOR HEALTH MONITORING

Workers regularly exposed to possible bromine vapors should be given routine medical check-ups. This applies to personnel of operations where bromine is used, stored, filled, or unloaded.

(US Code of Federal Regulations, 29 CFR 1910.120 f)

There are no regulations or standards indicating a medical test, which would show an overexposure to bromine.

It is recommended that complete medical records be kept for each person working in a facility where there is potential exposure to bromine vapors.

A sample medical record is provided on the following page.



MEDICAL RECORD FOR EMPLOYEE EXPOSED

Name: _____ Date of birth: _____

Address: _____

Occupation: _____ Date start employment: _____

Previous history of following disorders Yes / No

(Provide details if necessary)

Skin diseases _____

Lung diseases _____

Liver diseases _____

Kidney diseases _____

Psychiatric _____

Neurologic _____

MEDICAL EXAMINATIONS

Date	Test	Remarks
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

SICK LEAVE

From	To	Reasons
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

6.2 OPERATOR/DRIVER SAFETY TRAINING

The installation management should be aware of the potential dangers of bromine. Management personnel should undergo training in bromine specific safety inspections and safety auditing.

Workers involved with bromine must have special safety training regarding the precautions to observe in accordance with local regulations. This applies to personnel of operations where bromine is used, stored, filled or unloaded.

The safety training for handling bromine has to include both theoretical classroom courses and practical hands-on and observation exercises, appropriate to the level of likely exposure of the individual worker to bromine. Records should be kept of each person's participation in initial training and refresher courses.

The theoretical classroom training should be at least three days.

Some of the subjects to be covered should be:

- The main types of hazards
- Packaging details
- Labeling and marking to indicate hazards
- Precautions during loading and unloading
- Environmental protection
- First aid
- Fire-fighting
- Selection and use of personal protection equipment
- Respiratory protection
- Emergency procedures

Refresher training courses should be taken, at least every two or three years, and should include new technical and substance-related developments. The refresher course should be for at least one full day.

The following are some regulations which can be used for guidance in establishing a safety training program for operators and drivers

- **The restructured ADR agreement**, July 2013 chapter 8.2 covers driver training requirements and is helpful in planning operator training programs.
- The following **USA CFR** sections give the training details for handling hazardous materials as a driver, operator or emergency responder:

Driver Training	DOT	49CFR177.816
Operator Training	OSHA	29CFR1910.119g
Responder Training	OSHA	29CFR1910.120

APPENDIX

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APPENDIX A:

Bromine Specifications

BROMINE ASSAY %	99.98	MIN
IODINE (ppm)	1	MAX
CHLORINE (ppm)	60	MAX
HEAVY METALS (ppm)	1	MAX
RESIDUE AFTER EVAPORATION (ppm)	30	MAX
S.G. 20°C [g/cc]	3.12	MIN
SULPHUR COMPOUNDS (ppm)	30	MAX
MOISTURE (ppm)	30	MAX
TOTAL ORGANIC MATTER (ppm)	30	MAX
Fe (ppm)	1	MAX

APPENDIX B:

REFERENCES

1. Dead Sea Bromine Group
ICL Industrial Products
(www.ICL-IP.com)
2. Dead Sea Bromine Group
MATERIAL SAFETY DATA SHEET for Bromine
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3. UNITED NATIONS TRANSPORT OF DANGEROUS GOODS (ORANGE BOOK)
17th revised edition 2011
4. INTERNATIONAL MARITIME DANGEROUS GOODS (IMDG) CODE, 2012
(www.imo.org)
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OF DANGEROUS GOODS BY ROAD (ADR), 1 July 2013 (Restructured)
(www.unece.org/trans/danger/danger.htm)
(Also, corresponding document for carriage of dangerous goods by rail — RID)
6. US CODE OF FEDERAL REGULATIONS (Issued annually)
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7. International Air Transportation Association
DANGEROUS GOODS REGULATIONS 42nd Edition, January 2001
(www.iata.org)
8. AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL
HYGIENISTS (ACGIH)
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9. HEALTH AND SAFETY EXECUTIVE, MERSEYSIDE, ENGLAND
OCCUPATIONAL EXPOSURE LIMITS, 2002
Guidance Note EH 40/02
10. US CHEMICAL HAZARDS RESPONSE INFORMATION SYSTEM (CHRIS)
HAZARDOUS CHEMICAL DATA, U.S. COAST GUARD,
DEPARTMENT OF TRANSPORTATION (DOT), November 1992
11. NATIONAL FIRE PROTECTION ASSOCIATION (NFPA)
Hazardous Chemical Data, NFPA 49
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EMERGENCY RESPONSE GUIDE BOOK, 2012 Edition
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13. NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH (NIOSH)
POCKET GUIDE TO CHEMICAL HAZARDS, Publication 97 — 140, June 1997
(www.cdc.gov)
14. BROMINE AND ITS COMPOUNDS
Z. E. Jolles, 1966
15. BROMINE IN BULK QUANTITIES
Guidelines for Safe Storage and Handling,
Chemical Industries Association, London, 1989

Note: The internet websites are given for reference only, as their contents are continually changing.

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