Bromine Safety Handbook

MARCH 18,2019

India Bromine Platform

Contents

1.0 INTRODUCTION

1.1 India Bromine Platform

The India Bromine Platform (IBP) was launched in June 2019 as a cross-industry initiative between – The International Bromine Council (BSEF), the Indian Chemical Council (ICC) and India's bromine producers and suppliers, with the goal to foster the bromine ecosystem in India. The IBP has among its members, the leading bromine producers and suppliers of India, with the ICC, India's leading chemical industry body, playing the role of a catalyst and host to enhance collaboration of various stakeholders in this effort.

1.2 Bromine

Bromine is a member of the halogen group of elements along with chlorine, iodine and fluorine. It is a heavy, reddish-brown liquid that gives off a red vapor at room temperature. It is the only non-metallic element that is liquid at room temperature.

Bromine serves as a starting material for a variety of products that are the building blocks for highly complex organic molecules that meet specific performance, environmental, and quality requirements. Bromine is utilized in many applications including flame retardants, agrochemicals, pharmaceuticals, fine chemicals, high performance rubber, polymers, biocides and energy storage, as well as in chemicals used by the oil and gas industries in completion fluids, and inorganic bromides for mercury control.

1.3 Bromine Safety Handbook

Bromine as a liquid or as a vapour is highly irritating to skin, mucous membranes, eyes and respiratory tract. Being a powerful oxidizing agent, it also constitutes a fire hazard. Exposure even at low concentrations may result in inflammatory reactions in the eyes and respiratory passages.

This document is a compilation of good practices on the safety of personnel engaged in industries where bromine is produced, stored, handled or used. The information contained in this document is aligned with the Indian Standard Code for Safety of Bromine (IS 6953) as well as international practices for safe bromine handling.

2.0 BROMINE (BR_2) - PRODUCT DESCRIPTION

2.1 Identification of Bromine

Bromine (Br2) [7726-95-6] is the only nonmetallic element that is liquid at ordinary temperatures and pressures. It has a dark, amber-red color and an intensely irritating odor. The name is derived from the Greek (bromos), meaning "stench." There are two stable isotopes, 79Br, and 81Br, present in nearly equal proportions such that the atomic weight is 79.904. The atomic number is 35. Within rather wide limits the liquid and vapor are diatomic (Br2).

UN number	1744
CAS Number	7726 - 95 - 6
EINECS Number	231-778-1
Empirical Formula	Br2

Name	Bromine
Chemical Family	Halogen
Appearance	Heavy red-brown fuming liquid
Odor	Sharp, harsh, irritating

2.2 Physical Properties

Melting point/range	-7.3 ^{o}C
Boiling point/range	58.8 ^{o}C
Critical temperature	315 °C
Critical Pressure	102 atm.
Flash Point	None
Auto-ignition temperature	Not self-ignitable
Decomposition	None
Molecular Weight	159.8
Liquid Specific Gravity	3.12 g/ml @ 20°C
Vapour density	5.5 at 15 °C
Solubility in water	3.3 g/100 ml at 20 ^{o}C
Vapour Pressure	175 mmHg (20 ^{o}C)
Evaporation rate	High
Relative Density	3.119
Density	3.14 g/cm3 (15 °C)
Partition coefficient	Log Pow – 1.3 (estimated)
pH	Not Applicable
Flammability (liquids)	Does not sustain combustion
Explosive properties	Not explosive
Oxidizing properties	Oxidizer

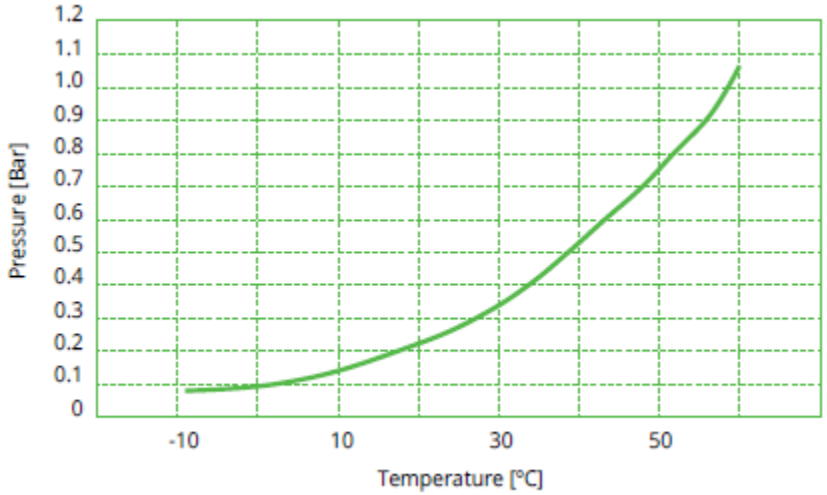
Solubility: Soluble in alcohol, ether, chloroform and carbon disulphide, slightly soluble in water

Reactivity: Anhydrous bromine is less reactive than wet bromine with many of the elements and metals. It is a powerful oxidizing agent particularly in presence of water. It reacts vigorously with reducing agents and with many organic compounds, such as phenols, amines, hydrocarbons, ketones, acids of aliphatic and aromatic series

Bromine Vapor Pressure Curve

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



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_2O in Br_2 [ppm]]	[Br_2 in H_2O [%]]
20	340	3.38
30	435	3.12
40	560	2.88

3.0 PACKAGING AND STORAGE

3.1 Typical Packaging

The majority of the bromine supplied in India is packaged in ISO tanks or glass bottles. This handbook covers good practices related to both types of packaging.

3.2 Glass Bottles

Glass bottles are ideal for laboratory or other small scale uses. Bromine can be discharged from the bottle through pouring, siphoning, or with the use of pumps.

Store bottles in their case in a cool dry location away from direct sunlight and protected from the weather. Storage temperatures must not fall below -7 °C (20 °F), the freezing point of bromine

3.3 Plastic and Wooden Crates

Bromine bottles are packed in Wooden and Plastic Crates of 18 Kg each for storage and transport.

Plastic Crate

Wooden Crate

Storage Area

Filled Bromine bottles in Plastic or Wooden crates are required to be kept under shed to protect from Direct sunlight while ensuring proper ventilation.

Plastic and Wooden Crate Details

Description	Plastic Crate	Wooden Crate
Length (mm)	400	445
Height (mm)	270	290
Width (mm)	285	285
Holes in top for venting	4 No	In Piece (Open)
Weight of Crate (Kg)	2.2	6.5
Weight of Empty 1 Ltr glass bottle (gm)	0.55	0.55
Total capacity of bottles per Crate	6	6
Net Weight of Bromine in Bottle(kg)	3	3
Weight of Saw Dust	0	5
Gross Weight of one filled bottle crate	23.5	32.8

Merits and Demerits of Plastic Crates

Merits:	**Demerits:**
Bromine is filled in glass bottles and kept in crate. There are all possibilities of breakage of filled glass bottles. • Spilled bromine remains content in PP Plastic crate. • Identification in market is easy to handle recycled material. • Foam Installation at bottom and top to absorb shocks during transit / shifting	• Spilled bromine vapours remain content in crate only • Material of Construction as Poly propylene is not a suitable choice • On Spillage of bromine, left a black mark in crate and then can't be reused as low aesthetic value • One can't identify bromine is spilled inside

• Safe Handling as compared with Wooden crate • Crate reuse cycle ratio is not less than 12 • Accident chances are minimum	

Merits and Demerits of Wooden Crates

Merits:	**Demerits:**
• Saw dust filled crates to absorbs Shocks during transit is working better than Plastic crate arrangement. • In Case of Spillage of bromine is not remaining content in crates, no bromine smell can be judged like Plastic crates after opening. • No Extra Care during Transit.	• Natural Resource depletion for manufacturing wooden crate. • In Case Spillage Damage the ground in stationary position and Damage the Truck Chassis in case of Transit. • In case of spillage, Saw Dust heats up and damages other bromine bottles in crates • Weight of one filled bromine crate is almost 10 kg more than Plastic crate, hence Carrying capacity is lower than Plastic. • Dimensionally, Wooden Crates are bigger by 50 mm than Plastic

Mitigation of spillage

Dispatch Quantity is generally varying from minimum 50 Crates to maximum 475 No of Crates either in Wooden or Plastic. Hence, at higher transport quantity, hazard level is accordingly increased. General observation is Max 2-3 Bottles usually break during transit which may be due to bad road condition.

Sodium Thiosulfate solution of 3-5% w/w is used to mitigate such spillages. Providing 5 kg Sodium thiosulfate powder along with truck carrying bromine crates is a good practice.

3.4 Packaging Instructions

This instruction relates to UN No. 1744. - P804 Packaging instructions for Bromine or Bromine Solution

The following packaging are authorized provided the general provisions of 4.1.1 and 4.1.3 are met and the packaging are hermetically sealed:

1. Combination packaging with a maximum gross mass of 25 kg, consisting of one or more glass inner packaging(s) with a maximum capacity of 1.3 litres each and filled to not more than 90% of their capacity; the closure(s) of which shall be physically held in place by any means capable of preventing back-off or loosening by impact or vibration during carriage, individually placed in metal or rigid plastics receptacles together with cushioning and absorbent material sufficient to absorb the entire contents of the glass inner packaging(s), further packed in.

- 1A1, 1A2, 1B1, 1B2, 1N1, 1N2, 1H1, 1H2, 1D, 1G, 4A, 4B, 4N, 4C1, 4C2, 4D, 4F, 4G or 4H2 outer packaging

2. Combination packaging consisting of metal or polyvinylidene fluoride (PVDF) inner packaging, not exceeding 5 litres in capacity individually packed with absorbent material sufficient to absorb the contents and inert cushioning material in 1A1, 1A2, 1B1, 1B2, 1N1, 1N2, 1H1, 1H2, 1D, 1G, 4A, 4B, 4N, 4C1, 4C2, 4D, 4F, 4G or 4H2 outer packaging with a maximum gross mass of 75 kg. Inner

packaging shall not be filled to more than 90% of their capacity. The closure of each inner packaging shall be physically held in place by any means capable of preventing back-off or loosening of the closure by impact or vibration during carriage;

3. Packaging consisting of:

Outer packaging:

Steel or plastics drums (LA1, 1A2, 1H1 or 1H2) tested in accordance with the test requirements in 6.1.5 at a mass corresponding to the mass of the assembled package either as a packaging intended to contain inner packaging, or as a single packaging intended to contain solids or liquids, and marked accordingly;

Inner packaging* :

Drums and composite packaging (1A1, 1B1, 1N1, 1H1 or 6HA1) meeting the requirements of Chapter 6.1 for single packaging, subject to the following conditions.

(a) The hydraulic pressure test shall be conducted at a pressure of at least 300 kPa (3 bar) (gauge pressure);

(b) The design and production leak proofness tests shall be conducted at a test pressure of 30 kPa (0.3 bar);

(c) They shall be isolated from the outer drum by the use of inert shock-mitigating cushioning material which surrounds the inner packaging on all sides,

(d) Their capacity shall not exceed 125 litres;

(e) Closures shall be of a screw type that are:

(1) Physically held in place by any means capable of preventing back-off or loosening of the closure by impact or vibration during carriage;

(2) Provided with a cap seal;

(f) The outer and inner packaging shall be subjected periodically to an internal inspection and leak proofness test according to (b) at intervals of not mote than two and a half years; and

(g) The outer and inner packaging shall bear in clearly legible and durable characters:

(1) the date (month, year) of the initial test and the latest periodic test and inspection of the innet packaging, and

(2) (ii) the name or authorized symbol of the expert who carried out the tests and inspections,

4. Pressure receptacles, provided that the general provisions of 4.1.3 6 are met

(a) They shall be subjected to an initial test and periodic tests every 10 years at a pressure of not less than 1 MPa (10 bar) (gauge pressure);

(b) They shall be subjected periodically to an internal inspection and leak proofness test at intervals of not more than two and a half years;

(c) They may not be equipped with any pressure relief device,

(d) Each pressure receptacle shall be closed with a plug or valve(s) fitted with a secondary closure device; and

(e) The materials of construction for the pressure receptacle, valves, plugs, outlet caps, luting and gaskets shall be compatible with each other and with the contents

3.5 ISO tank containers

The ISO containers and frames are usually of steel construction. The tanks are lined with lead or nickel plating. They are fitted with either two or three valves. Frame sizes for ISO tank containers are the

standard 8' X 8' X 20'. Platform and valve heights vary by ISO capacity and design style.

3.6 Marking, Labeling and Placarding

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.

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.

Indian Standards for Labelling IS: 1260 (Part I)-1973

Every container should carry the illustrations of 'powerful oxidizing agent' and 'corrosive' symbols as depicted in Fig. 9 and Fig. 15 of

IS: 1260 (Part I)-1973

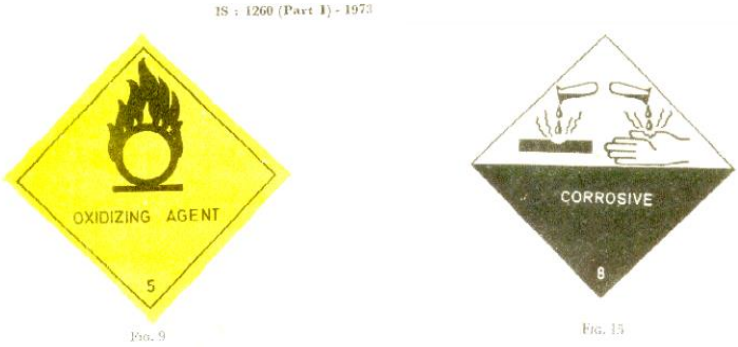


FIG. 9 FIG. 15

The container shall carry the following label:

'May ignite a combustible material upon contact. Causes severe burns to eyes and skin. Vapours are hazardous. Do not inhale them. Use with proper ventilation. In cause of contact flush with water immediately and get first aid. If eyes are involved, consult a medical specialist'.

This label may be used with any other illustration/descriptions.

For transportation in India, Central Motor Vehicles (CMV) Act and Hazardous Transboundary Movement Regulations should be followed. For specific international transportation guidelines, please refer to IMDG

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.

International standards on the transport of dangerous goods are derived from the recommendations of the UN Committee of Experts. These recommendations are contained in the so-called "Orange Book" and form the basis of a series of codes covering the classification, packaging and labelling of dangerous goods for transport by road, rail, sea and air. These codes are abbreviated (and commonly referred to) as follows:

ADR – Carriage of dangerous goods by road

RID – Carriage of dangerous goods by rail

IMDG – Carriage of dangerous goods by sea

ICAO – Carriage of dangerous goods by air

These international codes are then adopted by UN signatory countries into their national legislative systems, with supplementary local provisions as appropriate.

3.7 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 CFR176.84: 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»)

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 packaging (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.

3.8 Testing, Inspection and Maintenance

Before Shipment

After filling has been completed, each packaging unit to be 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.

Periodic test

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

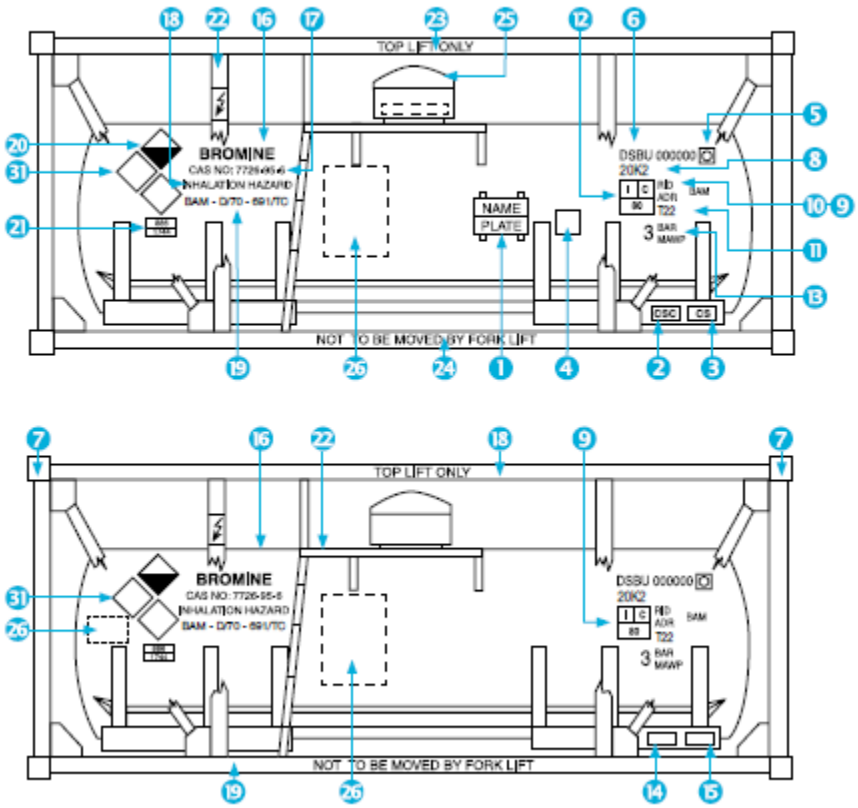
- Checking ancillary equipment including valves, safety valve, platform and ladder.
- Thorough external examination including corrosion, dents or mechanical damage, missing or loose bolts, required markings, and checking that the framework and supports are in satisfactory condition.
- Inspection of the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

Maintenance

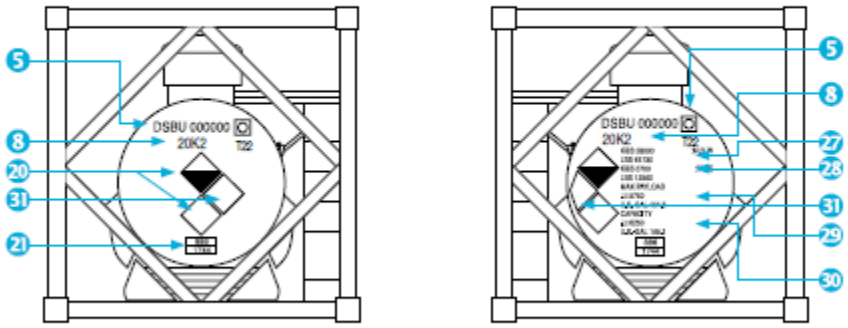
Each Isotank returned by a customer should be checked thoroughly, and any unit failing to meet requirements should be referred to the workshop for maintenance

3.9 Sample Marking of Bromine Isotanks

Side Views



End View



Right *Left*

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 and owner identification number

7 Isotank number on frame

8 International Standards Organization (ISO) Identification

- 2 Letter Country Code
- 2 Digit Container Size Code
- 2 Digit Container Type Code

9 Maximum Allowable Working Pressure 3 BAR

10 Isotank size

11 Date of next test

12 Name of substance, BROMINE

13 Chemical Abstract Service (CAS) Number, 7726-95-6

14 “INHALATION HAZARD”

15 Hazard diamond placard marking:

- Corrosive — (Model 8) with number “8” in bottom corner
- Toxic — (Model 6.1) with number “6” in bottom corner

16 ADR Orange placard:

- United Nations (UN) number — 1744
- Hazard number — 886

17 Ladder location marking

18 “TOP LIFT ONLY”

19 “NOT TO BE MOVED BY FORKLIFT”

20 Valve identification markings

21 Shipper’s emergency response instructions

22 Gross shipping weight

23 Tare weight

24 Maximum net weight

25 Maximum payload volume

26 Marine Pollutant

3.10 Bromine Storage

A) For use in bulk

Store drum, tank truck or ISO quantities of bromine in lead or lead-lined steel tanks, which feed to the process or reaction. For larger storage vessels where bottom outlets cannot be used, pump bromine out of the tank with nickel or plastic pumps. Contact your supplier representative for specific recommendations.

Protect storage tanks from moisture or humid air as bromine will absorb moisture from the air. When exposed to air having a normal summer dew point of 5-10 °C (40 – 50 °F), bromine will equilibrate at about 70 – 80 ppm water. Bromine this wet can cause severe corrosion of many metals. Keep a slight positive pressure (0.1 inch of H_2O) on the storage tanks by purging with dry (-40 °C/ -40 °F dew point) air or nitrogen into the tank.

B) For bulk storage

Store in either a glass-lined steel or lead-lined steel storage tank, properly designed for bromine's weight. Glass-lined steel tanks are not advised in active seismic areas. Stored bromine must be protected from temperatures below -7 °C (20 °F) to prevent freezing. Storage tanks should be located in concrete paved and diked areas so that any leak or spill can be contained

3.11 General Storage Recommendations

- Bromine is usually stored in lead lined containers and nickel drums or in glass bottles. Earthenware, stoneware and Monel metal containers may also be used for storage of bromine.
- For authorized containers, an outage (vacant space over liquid) of not less than 10 percent of the capacity of the container is required.
- Bromine should be stored in a cool well-ventilated area avoiding direct sunlight. The temperature of storage area should not go below — 7°C to prevent freezing.
- Bromine should be stored away from other chemicals and organic chemicals.
- Bromine vapours from reaction vessels or storage tanks should be vented through an alkali absorber preferably kept under constant pressure. The vent line should be purged with dry air.
- Electrical fittings in area where bromine vapours are likely to be present should be able to withstand the corrosive effect and should be of vapour proof construction, wiring being in tight, rigid metal conduits.
- Glass or porcelain piping, free from stresses or strains, is highly satisfactory with polytetrafluoroethylene (PTFE) and asbestos sheathed gaskets on flange joints.

3.12 In the laboratory

Bromine for laboratory or pilot plant use is usually purchased in glass bottles. Pour, siphon, or pump bromine into small glass, ceramic, or lead feed vessels with stopcocks

4.0 TRANSPORTATION AND RELATED SAFE HANDLING PRACTICES

4.1 Driver Safety Measures

Transport Safety

Make sure that the driver familiar with the truck and the iso-container; it's length, width, maximum speed, height, braking, turning circle etc.

As bromine is so heavy, it can only be filled into tanks at 88-92% of the tank volume. This is to prevent the bromine from surging and causing the unit to become unstable.

Bromine transport is only allowed via approved pre-determined routes. These routes should be notified to the emergency services in that area for emergency response/training purposes. Major truck roads

are to be used apart from collection/delivery points and avoid urban or densely populated areas if possible by use of bye- passes or ring roads (beltways).

'Black-spots' should be avoided wherever possible and avoid peak times where volume of traffic causes congestion.

If bad weather or road conditions occur, safe parking areas are to be selected based on the following hierarchy:

- Secure lorry parks.
- Service station lorry parks.
- Off road parking, well-lit and if possible, not accessible to the general public.
- Stopping is forbidden in built up areas, in front of schools or high media profile locations.
- Do not park within 5 metres from any building.

Maintenance of the vehicle should be based on age or mileage .

Daily checks should be performed on the vehicle for:

- Oil leakages or damage to the cooling water system.

- Check level of cooling water, oil, fuel, lubrication, brake fluid, battery and windscreen wash bottle.
- Check tyre pressure. Ensure tyres are within legal requirements.
- Check wheel studs.
- Ensure that lights, brake lights and hazard lights are in good working order. Clean if necessary.
- Fire extinguishers; check the expiry date and replace if necessary.
- Check for the presence of wheel blocks and twist locks and ensure that they are in good condition
- Tools
- Hazard and warning signs
- Check the presence of PPE
- Check of the vehicle for any damage

The iso-container should be checked before embarking on the journey to ensure:

- That there is no sign of any leaks.
- That the iso-container does not have any obvious signs of corrosion.
- That the frame is not damaged.
- That the dome is sealed. Check the platform under the dome on leakages by customer's premises.
- That no items (twist locks, gloves etc.) have been left behind on the isocontainer.
- All twist locks are tightened.
- Should any damage be observed, please notify the respective team

Transport Security

The security advice for drivers is:

BE SECURE

Never give lifts; it is illegal to carry unauthorized persons when transporting dangerous goods. When you leave your vehicle, always lock it and always take your keys with you. Never leave them in the cab. Keep doors and windows closed and locked

PLAN AHEAD

Plan your route beforehand. That way you will not have to stop to ask directions. If you know exactly where you are going, no-one can mislead you with wrong directions.

BE AWARE

Avoid talking about loads or routes with other drivers or customers (including over radios or phones). Be cautious if you are forced to stop, for example, at the scene of an accident or an emergency, or at police stops.

PARK SAFELY

Avoid unnecessary stops.

If you have to stop, stay close to and keep watch on the vehicle and unit at all times. Use security devices if fitted

4.2 Drivers' Loading Checklist

The following is a suggested checklist, based on 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.

Firefighting 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. (as a good practice)

Equipment required for each member of the vehicle crew:

❏ Protective gloves

❏ Eye protection (goggles)

❏ Emergency escape mask

❏ 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. The validity of the license shall expire not later than one year after inspection date.

❑ Driver has valid license to operate hazardous material vehicles.

❑ The vehicle is not carrying any materials incompatible with bromine at the same time (explosives, flammables, radio- active 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.

❑ Containers have been fastened with all the twist lock corner fittings

4.3 Requirements for vehicle crews, equipment, operation and documentation

(1) Transport unit Maximum permissible mass	(2) Minimum number of Fire extinguishers	(3) Minimum total capacity per transport unit	(4) Extinguisher suitable for engine or cab fire. At least one with a minimum capacity of:	(5) Additional extinguisher(s) requirement. At least one extinguisher shall have a minimum capacity of:
≤ 3.5 tonnes	2	4 kg	2 kg	2 kg
> 3.5 tonnes ≤ 7.5 tonnes	2	8 kg	2 kg	6 kg
>7.5 tonnes	2	12 kg	2 kg	6 kg
The capacities are for dry powder devices (or an equivalent capacity for any other suitable extinguishing agent).				
The fire extinguishers shall be subjected to inspections in accordance with authorized national standards in order to guarantee their functional safety. They shall bear a mark of				

compliance with a standard recognized by a competent authority and a mark indicating the date (month, year) of the next inspection or of the maximum permissible period of use, as applicable.

The fire extinguishers shall be installed on the transport units in a way that they are easily accessible to the vehicle crew. The installation shall be carried out in such a way that the fire extinguishers shall be protected against effects of the weather so that their operational safety is not affected. During carriage, the date shall not have expired.

The following equipment shall be carried on board the transport unit:

- For each vehicle, a wheel chock of a size suited to the maximum mass of the vehicle and to the diameter of the wheel;
- Two self-standing warning signs;
- Eye rinsing liquid; and

for each member of the vehicle crew

- A warning vest (e.g. as described in the EN ISO 20471 standard);
- Portable lighting apparatus;
- A pair of protective gloves; and
- Eye protection (e.g. protective goggles).

Additional equipment required for certain classes:

- An emergency escape mask3 for each member of the vehicle crew shall be carried on board the transport unit for danger label numbers 2.3 or 6.1;
- A shovel;
- A drain seal;
- A collecting container.

Requirements Concerning the training of the vehicle crew

Scope and general requirements concerning the training of drivers

Drivers of vehicles carrying dangerous goods shall hold a certificate issued by the competent authority stating that they have participated in a training course and passed an examination on the particular requirements that have to be met during carriage of dangerous goods.

Drivers of vehicles carrying dangerous goods shall attend a basic training course. Training shall be given in the form of a course approved by the competent authority. Its main objectives are to make drivers aware of hazards arising in the carriage of dangerous goods and to give them basic information indispensable for minimizing the likelihood of an incident taking place and, if it does, to enable them to

take measures which may prove necessary for their own safety and that of the public and the environment, for limiting the effects of an incident. This training, which shall include individual practical exercises, shall act as the basis of training for all categories of drivers. The competent authority may approve basic training courses limited to specific dangerous goods or to a specific class or classes. These restricted basic training courses shall not confer the right to attend specialized training courses.

Drivers of vehicles or MEMUs carrying dangerous goods in fixed tanks or demountable tanks with a capacity exceeding 1 m^3, drivers of battery-vehicles with a total capacity exceeding 1 m^3 and drivers of vehicles or MEMUs carrying dangerous goods in tank-containers, portable tanks or MEGCs with an individual capacity exceeding 3 m^3 on a transport unit, shall attend a specialization training course for carriage in tanks. The competent authority may approve tank specialization training courses limited to specific dangerous goods or to a specific class or classes. These restricted tank specialization training courses shall not confer the right to attend the specialized training courses mentioned below.

Drivers of vehicles carrying dangerous goods of Class 1, other than substances and articles of Division 1.4, compatibility group S, or Class 7 shall attend specialization training courses, as applicable.

All training courses, practical exercises, examinations and the role of competent authorities shall comply with the provisions mentioned in requirements concerning training of drivers.

All training certificates conforming to the requirements of this section and issued by the competent authority of a Contracting Party shall be accepted during their period of validity by the competent authorities of other Contracting Parties.

Special requirements concerning the training of drivers

The necessary knowledge and skills shall be imparted by training covering theoretical courses and practical exercises. The knowledge shall be tested in an examination.

The training body shall ensure that the training instructors have a good knowledge of, and take into consideration, recent developments in regulations and training requirements relating to the carriage of dangerous goods. The training shall be practice related. The training shall also include individual practical exercise.

Structure of training

Training shall be given in the form of a basic training course and, when applicable, specialization training courses. Basic training courses and specialization training courses may be given in the form of comprehensive training courses, conducted integrally, on the same occasion and by the same training body.

Subjects to be covered by the basic training course shall be, at least:

1. General requirements governing the carriage of dangerous goods;
2. Main types of hazard;
3. Information on environmental protection in the control of the transfer of wastes;
4. Preventive and safety measures appropriate to the various types of hazard;

5. What to do after an accident (first aid, road safety, basic knowledge about the use of protective equipment, instructions in writing, etc.);
6. Marking, labelling, placarding and orange-coloured plate marking;
7. What a driver should and should not do during the carriage of dangerous goods;
8. Purpose and the method of operation of technical equipment on vehicles;
9. Prohibitions on mixed loading in the same vehicle or container;
10. Precautions to be taken during loading and unloading of dangerous goods;
11. General information concerning civil liability;
12. Information on multimodal transport operations;
13. Handling and stowage of packages;
14. Traffic restrictions in tunnels and instructions on behaviour in tunnels (prevention of incidents, safety, action in the event of fire or other emergencies, etc.);
15. Security awareness.

Subjects to be covered by the specialization training course for carriage in tanks shall be, at least:

(a) Behaviour of vehicles on the road, including movements of the load;

(b) Specific requirements of the vehicles;

(c) General theoretical knowledge of the various and different filling and discharge systems;

(d) Specific additional provisions applicable to the use of those vehicles (certificates of approval, approval marking, placarding and orange-coloured plate marking, etc.).

Subjects to be covered by the specialization training course for the carriage of substances and articles of Class 1 shall be, at least:

(a) Specific hazards related to explosive and pyrotechnical substances and articles;

(b) Specific requirements concerning mixed loading of substances and articles of Class 1.

Subjects to be covered by the specialization training course for the carriage of radioactive material of Class 7 shall be, at least:

(a) Specific hazards related to ionizing radiation;

(b) Specific requirements concerning packing, handling, mixed loading and stowage of radioactive material;

(c) Special measures to be taken in the event of an accident involving radioactive material.

Teaching units are intended to last 45 minutes. Normally, not more than eight teaching units are permitted on each training day.

The individual practical exercises shall take place in connection with the theoretical training, and shall at least cover first aid, firefighting and what to do in case of an incident or accident.

Initial training programme

The minimum duration of the theoretical element of each initial training course or part of the comprehensive training course could be as follows:

Basic training course	18 teaching units
Specialization training course for carriage in tanks	12 teaching units
Specialization training course for carriage of substances and articles of Class 1	8 teaching units
Specialization training course for carriage of radioactive material of Class 7	8 teaching units

For the basic training course and the specialization training course for carriage in tanks, additional teaching units are required for practical exercises which will vary depending on the number of drivers under instruction.

The total duration of the comprehensive training course may be determined by the competent authority, who shall maintain the duration of the basic training course and the specialization training course for tanks but may supplement it with shortened specialization training courses for Classes 1 and 7.

Refresher training programme

Refresher training undertaken at regular intervals serves the purpose of bringing the drivers' knowledge up to date; it shall cover new technical, legal and substance-related developments.

The duration of the refresher training including individual practical exercises shall be of at least two days for comprehensive training courses, or at least one half the duration allocated to the corresponding initial basic or initial specialization training courses as specified for individual training courses.

A driver may replace a refresher training course and examination with the corresponding initial training course and examination.

Approval of training

The training courses shall be subject to approval by the competent authority. Approval shall only be given with regard to applications submitted in writing.

The following documents shall be attached to the application for approval:

(a) A detailed training programme specifying the subjects taught and indicating the time schedule and planned teaching methods;

(b) Qualifications and fields of activities of the teaching personnel;

(c) Information on the premises where the courses take place and on the teaching materials as well as on the facilities for the practical exercises;

(d) Conditions of participation in the courses, such as number of participants.

The competent authority shall organize the supervision of training and examinations.

Approval shall be granted in writing by the competent authority subject to the following conditions:

(a) The training shall be given in conformity with the application documents;

(b) The competent authority shall be granted the right to send authorized persons to be present at the training courses and examinations;

(c) The competent authority shall be advised in time of the dates and the places of the individual training courses;

(d) The approval may be withdrawn if the conditions of approval are not complied with.

The approval document shall indicate whether the courses concerned are basic or specialization training courses, initial or refresher training courses, and whether they are limited to specific dangerous goods or a specific class or classes.

If the training body, after a training course has been given approval, intends to make any alterations with respect to such details as were relevant to the approval, it shall seek permission in advance from the competent authority. This applies particularly to changes concerning the training programme.

Examinations

Examinations for the basic training course.

After completion of the basic training, including the practical exercises, an examination shall be held on the corresponding basic training course.

In the examination, the candidate must prove that he has the knowledge, insight and skill for the practice of professional driver of vehicles carrying dangerous goods as provided in the basic training course.

For this purpose, the competent authority shall prepare a catalogue of questions. Questions in the examination shall be drawn from this catalogue. The candidates shall not have any knowledge of the questions selected from the catalogue prior to the examination.

A single examination for comprehensive training courses may be held.

Each competent authority shall supervise the modalities of the examination; including, if necessary, the infrastructure and organization of electronic examinations, if these are to be carried out.

The examination shall take the form of a written examination or a combination of a written and oral examination. Each candidate shall be asked at least 25 written questions for the basic training course. If the examination follows a refresher training course, at least 15 written questions shall be asked. The duration of these examinations shall be at least 45 and 30 minutes respectively. The questions may be of a varying degree of difficulty and be allocated a different weighting.

Every examination shall be invigilated. Any manipulation and deception shall be ruled out as far as possible. Authentication of the candidate shall be ensured. All examination documents shall be recorded and kept as a print-out or electronically as a file.

Written examinations may be performed, in whole or in part, as electronic examinations, where the answers are recorded and evaluated using electronic data processing (EDP) processes, provided the following conditions are met:

(a) The hardware and software shall be checked and accepted by the competent authority;

(b) Proper technical functioning shall be ensured. Arrangements as to whether and how the examination can be continued shall be made for a failure of the devices and applications. No aids

shall be available on the input devices (e.g. electronic search function), the equipment provided shall not allow the candidates to communicate with any other device during the examination;

(c) Final inputs of each candidate shall be logged. The determination of the results shall be transparent;

(d) Electronic media may be used only if provided by the examining body. There shall be no means of a candidate introducing further data to the electronic media provided; the candidate may only answer the questions posed.

Examinations for specialization training courses for carriage in tanks or carriage of substances and articles of Class 1 or radioactive material of Class 7

After having sat the examination on the basic training course and after having attended the specialization training course for carriage in tanks or carriage of substances and articles of Class 1 or radioactive material of Class 7, the candidate shall be allowed to take part in the examination corresponding to the training.

This examination shall be held and supervised on the same basis as for basic training course.

With respect to each specialization training examination, at least 15 written questions shall be asked. If the examination follows a refresher training course, at least 10 written questions shall be asked. The duration of these examinations shall be at least 30 and 20 minutes respectively.

If an examination is based on a restricted basic training course, this limits the examination of the specialization training course to the same scope.

Certificate of driver's training

The certificate shall be issued:

(a) After completion of a basic training course, provided the candidate has successfully passed the examination;

(b) If applicable, after completion of a specialization training course for carriage in tanks or carriage of substances and articles of Class 1 or radioactive material of Class 7, or after having acquired the knowledge, provided the candidate has successfully passed an examination;

(c) If applicable, after completion of a restricted basic or restricted tank specialization training course, provided the candidate has successfully passed the examination in accordance with

The certificate issued shall clearly indicate its limited scope of validity to the relevant dangerous goods or class(es).

The date of validity of a driver training certificate shall be five years from the date the driver passes an initial basic or initial comprehensive training examination.

The certificate shall be renewed if the driver furnishes proof of participation in refresher training and has passed an examination in the following cases:

(a) In the twelve months before the date of expiry of the certificate. The competent authority shall issue a new certificate, valid for five years, the period of validity of which shall begin with the date of expiry of the previous certificate;

(b) Prior to the twelve months before the date of expiry of the certificate. The competent authority shall issue a new certificate, valid for five years, the period of validity of which shall begin from the date on which the refresher examination was passed.

Where a driver extends the scope of his certificate during its period of validity, by meeting the above requirements, the period of validity of a new certificate shall remain that of the previous certificate. When a driver has passed a specialization training examination, the specialization shall be valid until the date of expiry of the certificate.

The certificate shall have the layout of the model shown below. Its dimensions shall be in accordance with ISO 7810:2003 ID-1 and it shall be made of plastic. The colour shall be white with black lettering. It shall include an additional security feature such as a hologram, UV printing or guilloche patterns.

The certificate shall be prepared in the language(s) or one of the languages of the country of the competent authority which issued the certificate. If none of these languages is English, French or German, the title of the certificate, the title of item 8 and the titles on the back shall also be drawn up in English, French or German.

Training of persons other than the drivers holding a certificate, involved in the carriage of dangerous goods by road

Persons whose duties concern the carriage of dangerous goods by road shall have received training in the requirements governing the carriage of such goods appropriate to their responsibilities and duties. This requirement shall apply to individuals such as personnel who are employed by the road vehicle operator or the consignor, personnel who load or unload dangerous goods, personnel in freight forwarding or shipping agencies and drivers of vehicles other than drivers holding a certificate, involved in the carriage of dangerous goods by road.

MISCELLANEOUS REQUIREMENTS TO BE COMPLIED WITH BY THE VEHICLE CREW

Passengers	Apart from members of the vehicle crew, no passengers may be carried in transport units carrying dangerous goods.
Use of fire-fighting applications	Members of the vehicle crew shall know how to use the fire-fighting appliances.
Prohibition on opening packages	A driver or a driver's assistant may not open a package containing dangerous goods.
Portable lighting applications	The portable lighting apparatus used shall not exhibit any metal surface liable to produce sparks.
Prohibition on smoking	Smoking shall be prohibited during handling operations in the vicinity of vehicles and inside the vehicles. This prohibition of smoking is also applicable to the use of electronic cigarettes and similar devices.
Running the engine during loading or unloading	Except where the engine has to be used to drive the pumps or other appliances for loading or unloading the vehicle and the laws of the country in which the vehicle is operating permit such use, the engine shall be shut off during loading and unloading operations.

Use of the parking brakes and wheel chocks	No vehicles carrying dangerous goods may be parked without the parking brakes being applied. Trailers without braking devices shall be restrained from moving by applying at least one wheel-chock.
Use of cables	In the case of a transport unit equipped with an anti-lock braking system, consisting of a motor vehicle and a trailer with a maximum mass exceeding 3.5 tonnes, the connections shall be connecting the towing vehicle and the trailer at all times during carriage.

REQUIREMENTS CONCERNING THE SUPERVISION OF VEHICLES

Vehicles carrying dangerous goods in the quantities shown in special provisions for a given substance shall be supervised or alternatively may be parked, unsupervised, in a secure depot or secure factory premises. If such facilities are not available, the vehicle, after having been properly secured, may be parked in an isolated position meeting the requirements of (a), (b) or (c) below:

(a) A vehicle park supervised by an attendant who has been notified of the nature of the load and the whereabouts of the driver;

(b) A public or private vehicle park where the vehicle is not likely to suffer damage from other vehicles; or

(c) A suitable open space separated from the public highway and from dwellings, where the public does not normally pass or assemble.

The parking facilities permitted in (b) shall be used only if those described in (a) are not available, and those described in (c) may be used only if facilities described in (a) and (b) are not available.

Loaded MEMUs shall be supervised or alternatively may be parked, unsupervised, in a secure depot or secure factory premises. Empty uncleaned MEMUs are exempted from this requirement.

4.4 Nicer Globe Initiative

Nicer Globe®, is a Responsible Care® initiative for transportation safety of chemicals in India, under the aegis of Indian Chemical Council (ICC). Nicer Globe enables chemical industry with globally acclaimed Standards, Infrastructure & Services for safe, secure & efficient transportation through collaborative industry efforts. Nicer Globe initiative aims to improve

- Transport & Distribution Safety
- Chemical Emergency Response
- Transport Security

For more details, please visit: http://nicerglobe.in

5.0 SAFE HANDLING PRACTICES ON PREMISES

5.1 General Site Recommendations

Since bromine is a regulated hazardous material, storage and operating areas should be carefully supervised. 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.

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. 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.
- 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. Firefighting 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 ISO tanks 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 ISO tanks may be stacked 2 high in such a manner that each receptacle can be inspected without having to move other receptacles. Empty ISO tanks may be stacked 3 high.
- The concrete surface under the ISO tank storage positions should have a slope 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 local regulations if applicable.

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

5.2 Materials of Construction - Recommendations

The following materials can be used for handling bromine in liquid form at

temperatures up to 58 ^{o}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 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 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.

5.3 Engineering Materials

Bromine is shipped with a very low water content (typically less than 30 ppm). However, bromine is hygroscopic and if improperly handled, water content can quickly increase to 300 ppm. As the water content in- creases so does the corrosive potential of bromine, making the storage of bromine under dry nitrogen or dry air necessary (dewpoint should be less than -40 °C/ -40 °F). Bromine with water content of less than 30 ppm is non- corrosive to many non-ferrous metals including lead, nickel, tantalum. Bromine is extremely reactive with titanium and aluminum and contact with these metals must

be avoided. Glass lined steel and ceramic materials (excluding carbon and graphite) are resistant to bromine. Do not use ordinary polymeric resins with bromine.

Lead

Lead and lead-lined steel are commonly used, versatile materials for in-process equipment and storage containers for dry bromine. A protective layer of lead bromide (which can be washed away by inorganic acids) forms on the interior of the vessel, making it suitable for use with bromine of up to 75 ppm water, at room temperature. If bromine contains less than 30 ppm water, it may be handled in lead equipment to

58.8 °C (137.8 °F). Lead-lined steel vessels used for bromine storage must be constructed and/or modified by certified personnel in accordance with ASTM standards.

Nickel and nickel alloys

Nickel, Monel®, Hastelloy® B, and Hastelloy® C containers are appropriate only for storage and handling of bromine with less than 30 ppm water at room temperature. Nickel may be used with dry (less than 30 ppm water) bromine up to 400 °C (752 °F).

Tantalum

Tantalum equipment can be used for wet or dry bromine, in temperatures of up to 149 °C (300 °F). However, in the presence of some organic materials, bromine will corrode tantalum.

Steel and stainless steel

Bromine and its vapors are severely corrosive to steel and stainless steel making them unacceptable for use in bromine process systems.

Glass and ceramics

Although inherently fragile, tempered glass, porcelain, fused silica, chemical stoneware and acid brick are acceptable materials for use with both wet and dry bromine at various temperatures.

Glass-lined steel

Due to its excellent chemical resistance and physical strength, glass-lined steel makes a versatile construction material for use with bromine. Glass-lined steel equipment must withstand a 20,000-volt spark test and can be used at temperatures up to 138 °C (280 °F).

5.4 Safety Practices in The Work Area

General instructions

- Read and follow all directions and warning labels carefully.
- Inform all personnel of the potential hazards of contact with bromine and train them in appropriate first-aid procedures.
- Store and handle bromine over drip pans drained by a sump that is vented to a scrubber system.
- Bromine handling areas should be clearly marked and restricted to qualified and trained personnel only.

- Maintain and clean uncontaminated equipment, floors, and work areas.
- Immediately contain and clean up all bromine spills.
- Wear approved respiratory equipment and protective clothing.
- Carefully release anhydrous ammonia vapor to neutralize bromine vapors in the air. Be careful not to over apply anhydrous ammonia.
- Pour soda ash solution or hypo solution[1] on the liquid bromine to neutralize.
- Using cold water, wash neutralized bromine to a sump for disposal.
- Open doors and windows to ventilate.
- Avoid contact of bromine with strong reducing agents, strong alkalis, metals, wood, paper products, fabric, grease, and oil or other combustible materials.

Ventilation

- Restrict bromine vapor concentration in the work area to less than 0.1 ppm with adequate exhaust hoods, ventilation systems, and scrubbers. Analyze the air for bromine concentrations to ensure proper control.
- Transfer or repackage bromine only in a controlled, closed environment.
- Positive exhaust ventilating systems must be used in enclosed areas where bromine is handled.

Containers and storage

- Empty shipping containers completely.
- Do not return used or recycled bromine or other bromine containing liquids in containers as this could lead to catastrophic container failure.
- Store bromine containers in dry, well-ventilated areas, protected from moisture and excessive heat or cold.
- Store only in approved bromine containers. Never store in containers that resemble food or beverage packaging.
- Check all equipment used for bromine handling or processing for deterioration, as well as leaky valves and couplings. Proper maintenance requires periodic cleaning and drying with nitrogen.
- Protect bromine-handling equipment from strong alkalis, reducing agents, other metals, wood, fabric, paper, grease, and oils.

5.5 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.

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.

[1] Hypo solution: dissolve 57 kgs of sodium thiosulfate and 1 kgs of soda ash in 709 liters of water.

A sample medical record is provided on the following page.

5.6 Medical Record for Employee Exposed

Periodic health checks have to be done on employees, aligned to Indian legal requirements

5.7 Operator/Driver Safety Training

The 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.

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
- Firefighting
- Selection and use of personal protection equipment
- Respiratory protection
- Emergency procedures

5.8 Exposure Limits

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

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 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, 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) Short Term Exposure Limit (STEL)	0.1 ppm 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 OES/STEL	 0.1 ppm (0.7 mg/m^3) 0.2 ppm (1.3 mg/m^3)

5.9 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.

Detector Tubes

- 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.

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.

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.

5.10 Hazards Associated with Bromine

Health Hazards

Either as a liquid or as a vapour, bromine acts as a local irritant and corrosive on contact with body tissues. Vapours are irritating to eyes, skin and respiratory tract. The threshold limit value (TLV) for bromine in air is 0.1 ppm (0.7 mg/m3) for 7 to 8 hours workday and 40 hours work week.

Acute Toxicity

Local effects — Liquid bromine produces a mild cooling sensation on first contact with the skin. This is followed by sensation of heat.

If bromine is not removed immediately the skin becomes red and finally brown. Such a contact will result in destruction of the skin are

involved and development of an indolent, slow healing ulcer. Bromine is especially hazardous to the tissues of the eyes; severely painful and destructive burns may result from contact with either liquid or concentrated vapour.

Systemic effects — Bromine has excellent warning properties and systemic intoxication is unlikely. Lachrymation is caused by concentrations less than 1 ppm, while 10 ppm concentration would cause extreme upper respiratory irritation which will not be voluntarily borne. Concentrations of 40-60 ppm are dangerous to life on exposure for 0.5 to 1 hour, those of 500-1 000 ppm are rapidly fatal to short exposure. If bromine vapours are present in a confined space, severe respiratory tract injury may result followed by pulmonary edema, pneumonia and respiratory failure.

Chronic Toxicity

Because of the extremely irritating nature and intolerability to body tissues, chronic systemic poisoning or local effects are unlikely.

Fire Hazards

Bromine itself will not burn but it is a strong oxidizer. Dry bromine will react violently with the metals — Aluminum, titanium, mercury and potassium. Due to its high reactivity with many other substances, the heat of reaction may raise the temperatures to the ignition points of combustible materials. Neutralization of bromine with an alkali will produce bromates which when dry may be hazardous from a fire and explosion standpoint.

5.11 Procedures for The Safe Handling of Bromine

Extreme care must be exercised in the storage, handling, shipping and use of bromine. Bromine vapors can irritate skin, eyes, and mucous membranes. Contact with liquid bromine can cause severe burns. The readily identifiable color and pungent odor gives immediate warning of bromine's presence.

At a concentration of only one part per million (ppm), bromine is easily detectable and even lesser amounts can cause eye irritation. Verify exposure limits in each region or country. Safety is the personal responsibility of everyone working with or around bromine. Supervisory personnel must know and enforce the recommended safe handling practices outlined in this guide.

General

The general handling practices given below should be followed:

- All handlers should be aware of the potential hazards of bromine and of appropriate first-aid measures.
- Exhaust hoods and ventilation should be adequate to maintain the concentration of bromine vapour in the work area below 0.1 ppm. Air analyses will be necessary for proper control.
- Safety showers and eye-wash fountains should be immediately at hand where contact is at all likely.
- If there is significant risk of exposure an operator should not handle bromine without available assistance in the area.
- Bromine, in any breakable package or line, should be kept at as low a level as possible above protection pans.
- Storage and operations should be over drip pans draining to a sump.
- Sumps shall be ventilated to prevent general escape of vapours into inhabited areas.

Glass Bottles

Hermetically sealed glass containers should be first cooled and then opened with extreme caution.

- The lead cap should be loosened cautiously and taken off the bottle.
- Mechanical means of siphoning instead of mouth suction should be used to siphon bromine from the bottle.

5.12 Recommended Checklist for a Bromine Handling Facility

#	Parameter	Yes/No/NA	Comments
A	**Basic information about the site**		
A.1	Away from populated areas		
A.2	At least 25 meters from public road or railway		
A.3	Corrosive and toxic hazard signs displayed		

A.4	Area surrounded by curb or dike with no sewer connection		
A.5	Sump for collecting spills available		
A.6	Fire resistant building construction		
A.7	Impervious floor		
A.8	Operational area cordoned from flammables and consumables		
A.9	Reinforced road for emergency vehicles		
A.10	Minimal pits and confined spaces		
A.11	No aluminum-based electrical fittings		
A.12	Dust and vapor-tight electrical fittings		
A.13	Area enclosed and secure		
A.14	Remote eating, changing and smoking areas		
A.15	Safety training is given on a regular basis		
A.16	Emergency plan is well documented		
A.17	Good housekeeping and personal hygiene practiced		
A.18	Personal protection equipment used when unloading or handling		
B	**Consents & NOCs**		
B.1	Consent under the Air / Water / Hazardous waste from the Pollution Control Board		
B.2	Fire NOC of the premises		
B.3	Licensed / Consented storage capacity		
C	**Receipt of Bromine and related safety checks**		
C.1	Certified / trained drivers (in transporting hazardous chemicals)		
C.2	The engine is shut off and keys are put in appropriate place		
C.3	The crew knows how to use fire-fighting appliances		
C.4	No smoking signage around the transport unit or in the vicinity of the vehicle during handling operations		
C.5	TREM CARD		
C.6	Appropriate quantity of Sodium Thiosulphate (bags)		
C.7	Containers / trucks equipped with Global Positioning System (GPS) and route predefined		
C.8	Hazard Identification symbol and emergency telephone number displayed as per HAZCHEM CODE		
C.9	Appropriate PPEs in Truck (refer to PPE section)		
C.10	MSDS		
D	**Storage and Handling - General**		

D.1	Sufficient bromine storage tank capacity or an empty ISO tank to accommodate the transfer of bromine from a leaking container		
D.2	Area where bromine is used or stored is enclosed to avoid entry of unauthorized persons and animals		
D.3	Adequate lighting is available to allow surveillance at night		
D.4	Personnel escape routes clearly marked and maintained without any obstructions including adequately sized doors and windows		
D.5	Adequate water is available for washing and showers		
E	**Storage and Handling - Bromine Tanks**		
E.1	Insulation		
E.2	Sprinkler		
E.3	Area surrounded by curb or dyke		
E.4	Halogen sensors		
E.5	Display of date of inspection of tank and due date of next inspection		
E.6	Good condition of hose used for unloading (ISO certified)		
E.7	Flange Guards		
E.8	NRV at nitrogen padding line		
E.9	Sodium thiosulfate tanks		
E.10	Bromine Spillage handling		
F	**Personal Protective Equipment (PPE)**		
F.1	SCBA		
F.2	Canister / Cartridge type Mask		
F.3	Full-body suit		
F.4	Helmets		
F.5	Gum Boots		
F.6	Hand Gloves		
F.7	Goggles		
F.8	Aprons		
F.9	Online Respirators		
G	**Emergency Preparedness**		
G.1	First Aid room is available		
G.2	Fire-fighting hydrants and extinguishers are available and easily accessible		
G.3	The emergency telephone numbers are displayed at prominent locations and include the fire department, ambulance service, emergency response team, hospital and police		

G.4	A wind sock is provided which is clearly visible from all points on the site and replaced as required (This is required for indicating wind strength and direction)		
G.5	Emergency respirator equipment cabinets are installed not more than 30 meters or ten seconds walking distance from any location in the storage area		
G.6	Showers and eyewash fountains are present at appropriate place, clearly marked, well lit and with unobstructed access		
G.7	Signs are posted prominently at the site entrance and throughout the installation with area maps showing access ways, hydrant locations, emergency showers, location of emergency equipment and emergency telephone numbers		
G.8	Provisions are available for raising a general site alarm in each warehouse or building		
G.9	Adequate provisions exist for the containment of contaminated fire fighting water in the event of a major fire		
G.10	Adequate fire water supply available in case of a major fire		
G.11	Are copies of the MSDS available to storage operation staff?		
G.12	Are the following materials available for containing, neutralizing, and absorbing spills: - Sand bags - Dry slaked lime - Cylinder of anhydrous Ammonia mounted in cylinder trolley and fitted with suitable needle valve and hose on outlet - Sealable "overpacks" Are the above mentioned materials: - Clearly labeled? - Kept in an accessible position?		
G.13	Are the following available for cordoning off any area where a spill has occurred or where a leak has been discovered: - Stanchions? - Reflective tape? - Safety signs?		

5.13 Handling Bromine in The Laboratory

General instructions

All personnel using bromine in a laboratory should be properly trained regarding its characteristics, PPE and equipment requirements, and first aid procedures.

Equipment

1. Air purifying cartridge respirator with proper acid gas or organic vapor/acid gas cartridge(s)
2. Operational safety shower and eyewash.

3. 10-25% aqueous NaOH or hypo solution for spills.

4. Aqueous ammonium hydroxide for bromine vapor neutralization, placed in large surface area dishes to liberate NH3 vapors (do not add directly to liquid bromine).

5. Safety glasses with side shields/chemical safety goggles.

6. Face shield (if required)

7. Neoprene or nitrile gloves and apron, boots, and sleeve protectors (chemical resistant suits are optional for maximum protection).

Storage and transport

1. Bromine should be stored in a properly operating fume hood or well-ventilated cabinet in glass bottles. Store in a cool, dry place where freezing, heat and humidity, and moisture exposure possibilities are minimal.

2. Secondary containment pans with high sides or rubber bottle carriers should be used as a precautionary measure. Second skin plastic coated bottles are also recommended as a safeguard.

3. Bromine bottles should be transported in rubber bottle carriers or a closed container that is sufficiently padded to avoid bottle breakage.

Handling precautions

1. Bromine should be handled by trained individuals. Proper PPE should be worn at all times when handling bromine. Bromine transfer and handling should be done in a fume hood.

2. Proper fume hood operation should be checked prior to use. Sufficient bromine vapor scrubbing measures should be taken (i.e., caustic scrubber or other suitable material). Do not vent bromine vapors directly to the atmosphere.

3. Small quantities of bromine can be transferred by pouring, but larger volumes should be transferred using a lab- oratory scale pump of proper materials of construction.

4. Due to the dense nature of liquid bromine, lab glassware such as receivers (graduated cylinders or flasks) or addition funnels for reactors should be clamped and stabilized to avoid breakage and spills.

5.14 Preventive Measures - Personal Safety Precaution

Personal Hygiene

Workers should be thoroughly instructed and supervised in proper operating procedures to avoid exposure to bromine liquid or vapours. Where exposure is possible, personal protective equipment should be used.

- All contaminated clothing, including gloves, shoes, overalls, etc., should be removed immediately to avoid prolonged contact with bromine and should be thoroughly decontaminated and cleaned before re-use.
- Working areas, storage rooms and unloading areas should be well equipped with safety showers, readily accessible and plainly marked.

- Eye washing fountains or running tap water, such as a bubbler drinking fountain, or a hose should be available for eye irrigation. The location of such equipment should be inspected and tested at fixed intervals to make sure that it is in good working condition at all times.
- Wear chemical safety goggles at all times. When handling Bromine use an approved chemical resistant full-face shield over eyewear. Always carry a full- face respirator with you when handling Bromine in case of emergency. If bromine liquid or vapor contacts the eyes, irrigate immediately with large amounts of running water. Eye fountains are preferable for irrigation. If one is not available, a bubbler drinking fountain or a hose with a liberal, gentle flow may be utilized. The eyelids should be held apart during irrigation to ensure contact of water with all accessible tissues of the eyes and lids. Eyes should be washed continuously for a minimum of 15 minutes. After irrigation, the employee should seek medical attention immediately.
- When in danger of contact with liquid bromine, wear an approved chemical resistant suit or smock that covers the whole body and has sealed cuffs at the hands and feet. In an enclosed area wear clean clothing, protective gloves, and eye and face protection. Never wear clothes that smell of bromine. Wash contaminated clothing and equipment before reuse.
- Wear approved chemical Nitrile or Neoprene gloves. Discard gloves that have been in contact with liquid bromine.
- Wear leather or other equivalent steel-toed shoes. Protective chemical resistant rubber boots should be worn over shoes for extra protection. Discard shoes that have been in contact with liquid bromine.
- For skin contact, the affected area should be flooded immediately with large amounts of water from a safety shower or other source of flowing water. All contaminated clothing, including shoes, should be removed as quickly as possible while the victim is under the shower. Washing should be continued for a minimum of 15 minutes. The victim should receive medical attention immediately.
- To ensure adequate personal protection, protective clothing and equipment should be inspected before each use. Faulty protective clothing and equipment should not be repaired and discarded immediately.

To avoid bromine ingestion:

- Always wash face, hands, and arms before eating.
- Never place bromine contaminated articles in the mouth.
- Don’t siphon or blow out clogged lines or nozzles by mouth.

To avoid inhalation of bromine:

- Stay upwind when loading, unloading, and transporting bromine.
- Have the respirators and self-contained breathing apparatus available. When handling bromine in an enclosed area wear protective clothing and respiratory equipment.
- Adhere to your plant regulations regarding respiratory equipment for bromine handling.

Bromine vapors are so irritating to the eyes, nose and throat that they provide ample warning of the presence of bromine in acutely hazardous concentrations. If overexposure does occur, the exposed individual should be immediately removed from the contaminated area to fresh air. They should be placed in an upright position. They should avoid exertion. If vomiting occurs, turn the exposed individual on their side to avoid choking. Keep them warm. If they do not recover quickly or is coughing and showing signs of respiratory stress, properly trained personnel should administer oxygen. If respiration has ceased, artificial respiration should be administered. The exposed individual should be immediately

removed from the contaminated area to fresh air. They should be placed in an upright position. They should avoid exertion. If vomiting occurs, turn the exposed individual on their side to avoid choking. Keep them warm. If they do not recover quickly or is coughing and showing signs of respiratory stress, properly trained personnel should administer oxygen. If respiration has ceased, artificial respiration should be administered. The exposed individual should receive medical attention immediately.

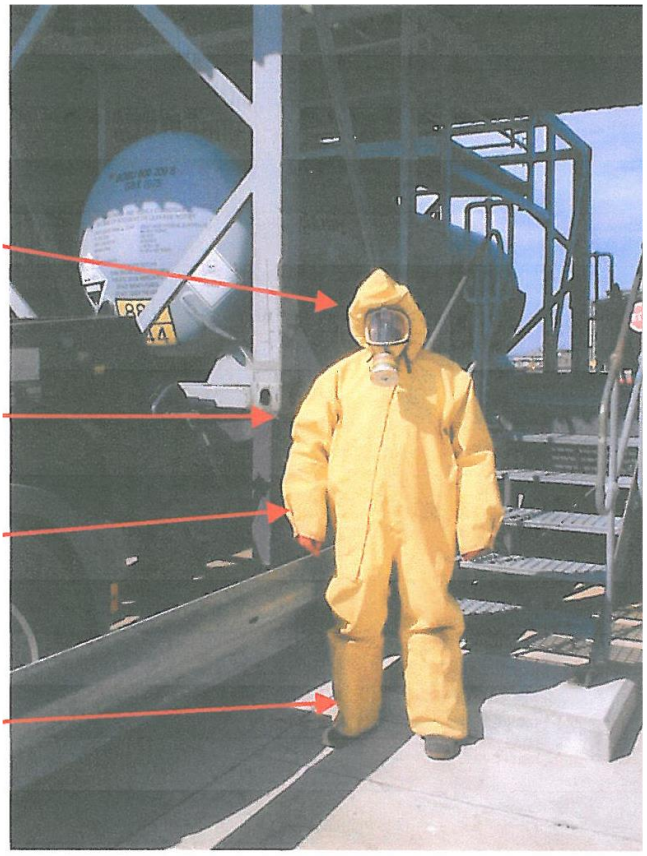
Physical Examinations

Diseases of the heart or lungs should exclude an employee from working with bromine.

5.15 Personal Protective Clothing and Equipment

Personal Protective Equipment

The protective clothing shown **below** is the recommended **minimum** protection that should be worn during emergencies involving bromine.



For escape only, a full-face respirator with acid gas or organic vapour/ acid gas chemical cartridges. Refer to manufacturer recommendations for proper EN/ISO approved cartridge.

PVC/neoprene chemical resistant suit

100% Nitrile rubber or neoprene gloves

PVC Blend Boots or protective shoes

Availability and Use

While personal protective equipment is not an adequate substitute for safe working conditions, adequate ventilation and intelligent conduct on the part of employees working with bromine,

it is in many instances, the only practical means of protecting the worker, particularly in emergency situations. One should keep firmly in mind that personal protective equipment protects only the worker wearing it, and other unprotected workers in the area may be exposed to danger.

Eye Protection

The following personal protective equipment should be used when indicated:

a) Chemical safety goggles — Cup type or rubber framed goggles equipped with approved impact glass or plastic lenses should be worn, whenever there is danger of bromine coming in contact with the eyes. Goggles should be carefully fitted.

b) Face shields — Plastic shields (full length, 20 cm minimum) with forehead protection may be worn in addition to chemical safety goggles where complete face protection is desirable. Chemical safety goggles should always be worn as added protection where there is danger of bromine striking the eyes from underneath or around the sides of the face shield.

c) Spectacle-type safety goggles — Metal or plastic rim safety spectacles with side shields which can be obtained with prescription safety lenses or suitable all-plastic safety goggles may be used where continuous eye protection is desirable, These types, however, should not be used where complete eye protection against bromine is needed.

Respiratory Protection

Severe exposure to bromine may occur in tanks during equipment cleaning and repairs, when decontaminating areas following spills, or in case of failure of piping or equipment. Employees who may be subject to such exposure should be provided with proper respiratory protection and trained in its use and care. Available types are described below

NOTE *— Respiratory protective equipment shall be carefully maintained, inspected, cleaned and sterilized at regular intervals, and always before and after use by another person*.

Self-contained breathing apparatus — Permitting the wearer to carry a supply of oxygen or air compressed in the cylinder and the self-generating type which produces oxygen chemically. These allow considerable mobility. The length of time a self-contained breathing apparatus provided protection varies according to the amount of air, oxygen or regenerating material carried. Compressed oxygen should not be used where there is danger of contact with flammable liquids, vapours, or sources of ignition, especially in confined spaces, such as tanks or pits.

Positive pressure hose masks — The air shall be supplied by blowers requiring no internal lubrication. The wearer shall be able to use the same route for exit as for entrance and shall take precautions to keep the hose line free of entanglement. The air blower shall be placed in an area free of contaminants.

Air-line masks — Supplied with clean breathing air. These are suitable for use only where conditions will permit safe escape in case of failure of the compressed air supply. These masks are usually supplied with air piped to the area from a compressor. It is extremely important that the air supply is taken from a safe source and that it is not contaminated by oil decomposition from inadequate cooling at the compressor. The safer method is to use a separate compressor of the type not requiring internal lubrication. Pressure reducing and relief valves as well as suitable traps and filters must be installed at all mask stations. An alternative arrangement frequently used is high pressure breathing air from cylinders, with demand-type valve and face piece.

Industrial canister type gas masks — Equipped with full face pieces fitted with the proper canister for absorbing bromine vapour. These will afford protection against concentrations not exceeding 1 percent by volume when used in accordance with manufacturer's instructions. The oxygen content of the air must not be less than 16 percent by volume. The masks should be used for relatively short periods only. They may not be suitable for use in an emergency since, at that time, the actual vapour concentration is unknown and also an oxygen deficiency may exit. The wearer must be warned to leave the contaminated area immediately on detecting the odour of a harmful vapour. This may indicate that the

mask is not functioning properly, that the vapour concentration is too high, that the canister is exhausted or that the mask is not properly fitted.

Chemical cartridge respirators — May be used to avoid inhaling disagreeable concentrations of bromine vapour. These respirators, however, are not recommended for protection where toxic quantities may be encountered. (ABEK Type)

Head Protection

Safety helmets should be worn where there is danger from falling objects.

Foot Protection

Leather or rubber safety shoes with built-in steel toe caps are recommended. Rubbers may be worn over leather safety shoes. Leather shoes should be discarded after any contact with bromine.

Body, Skin and Hand Protection

a) Suits made of PVC/ neoprene and properly designed, should be used wherever complete body protection is necessary.

b) Neoprene/ nitrile gloves should be worn to protect the hands from bromine.

c) Sleeves made of suitable protective materials should be worn when the need for complete arm protection is indicated.

When cleaning, inspecting, or repairing tanks, safety equipment, such as safety belts, rescue harness, lifeline, protective clothing and gas masks should be worn as required by the specific nature of the work and the hazards involved. Frequent inspections and necessary repairs should be made of all personal protective equipment so that the wearer will be adequately protected. Rubber and other impervious apparel must be checked frequently for signs of deterioration due to exposure to bromine.

All contaminated clothing, including gloves, shoes, coveralls, etc., should be removed as soon as possible after exposure to avoid prolonged contact with bromine. It should be thoroughly decontaminated and cleaned before re-use.

5.16 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.
- 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.

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

FIGURE 1 - SIDE VIEW OF RECOMMENDED UNLOADING HOOK-UP

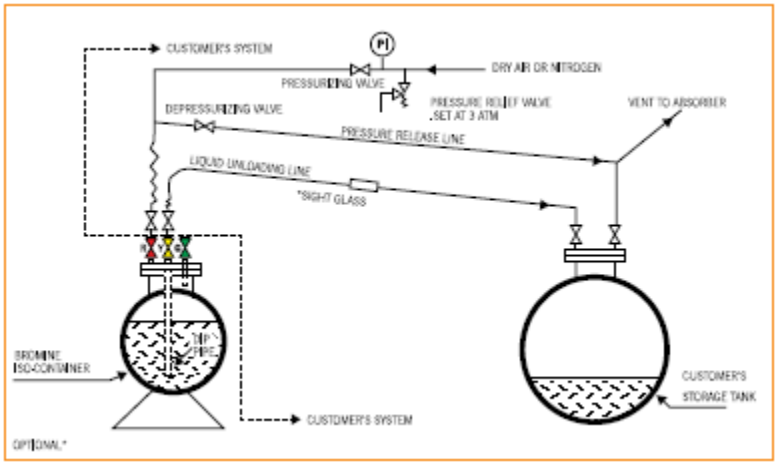
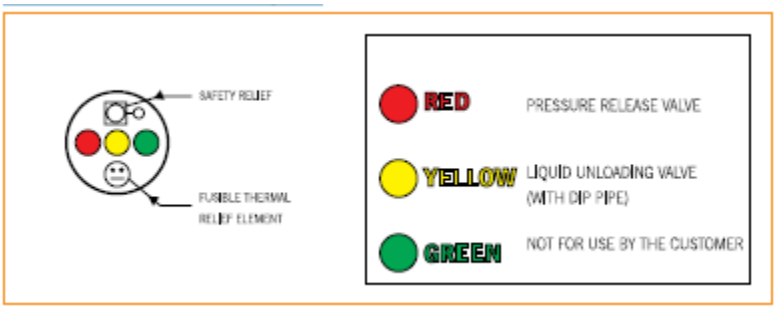


FIGURE 2 - PLAN VIEW OF VALVES ON THE ISO-CONTAINER

(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.
3. Check that all the Iso-container valves are closed, and blind flanges are in place
4. Remove the blind flange above the red valve.
5. Connect your pressure release line to the red valve outlet. Use a new Teflon or Viton gasket fitted for bromine use only.
6. Open the red valve slowly and then the depressurizing valve, to release any pressure which might have developed in the Iso-container.
7. Remove the blind flange above the yellow valve.
8. Connect your unloading line to the yellow valve outlet. Use a new Teflon or Viton gasket fitted for bromine use only.
9. Open the yellow valve and all the valves in your liquid unloading line.
10. Close the depressurizing valve.
11. 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
12. 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. Use a new Teflon or Viton gasket fitted for bromine use only.
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.
17. Leave the red and the yellow valve of the tank and the depressurizing valve open for about 5 minutes to decant bromine residues by gravitation back into the iso-tank and the storage tank.
18. After 5 minutes close all the valves.
19. 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.
20. 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.
21. 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.
22. Close the cover dome and pin it securely.

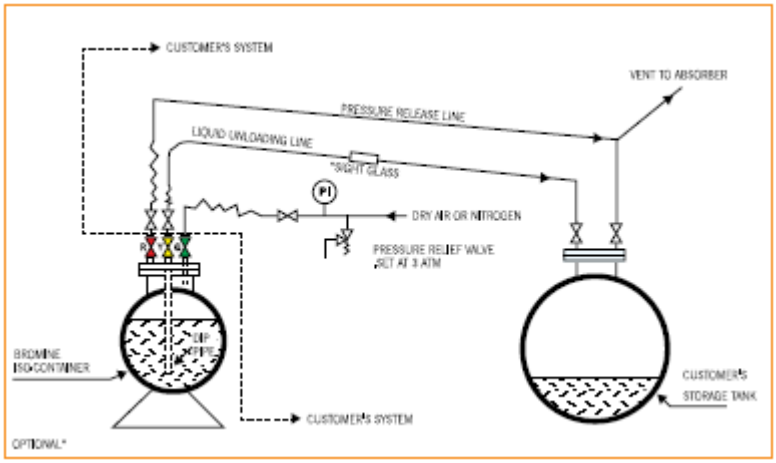
Recommended Procedure for Bromine Unloading (Three Valve System)

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 the supplier.

FIGURE 1 - SIDE VIEW OF RECOMMENDED UNLOADING HOOK-UP



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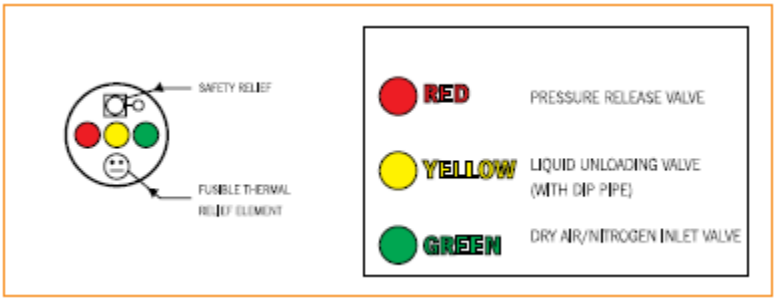
(with the dome cover open)



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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.

3. Check that all the Iso-container valves are closed, and blind flanges are in place.
4. Remove the blind flange above the red valve.
5. Connect your pressure release line to the red valve outlet. Use a new Teflon or Viton gasket fitted for bromine use only.
6. Open the red valve slowly, to release any pressure which might have developed in the Iso-container.
7. Remove the blind flange above the yellow valve.
8. Connect your unloading line to the yellow valve outlet. Use a new Teflon or Viton gasket fitted for bromine use only.
9. Open the yellow valve and all the valves in your liquid unloading line.
10. Close the red valve.
11. Remove the blind flange above the green valve.
12. Connect your pressurizing line to the green valve outlet. Use a new Teflon or Viton gasket fitted for bromine use only.
13. Open the green valve, at first slowly (to check for bromine leaks), then fully, to
14. 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.

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.

5.17 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 counterclockwise, 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.
e) Ensure tight connection.
f) 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.
g) Ensure tight connection.
h) 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.
g) 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.

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).
c) Relieve any pressure in the vessel by opening the red vent valve, slowly and cautiously.
d) Remove the valve and check the flanges. They should be smooth and without deep scratches. If necessary, carefully smooth out any scratches.
e) Check the Teflon envelope gaskets and replace if torn or damaged.
f) 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.
g) 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

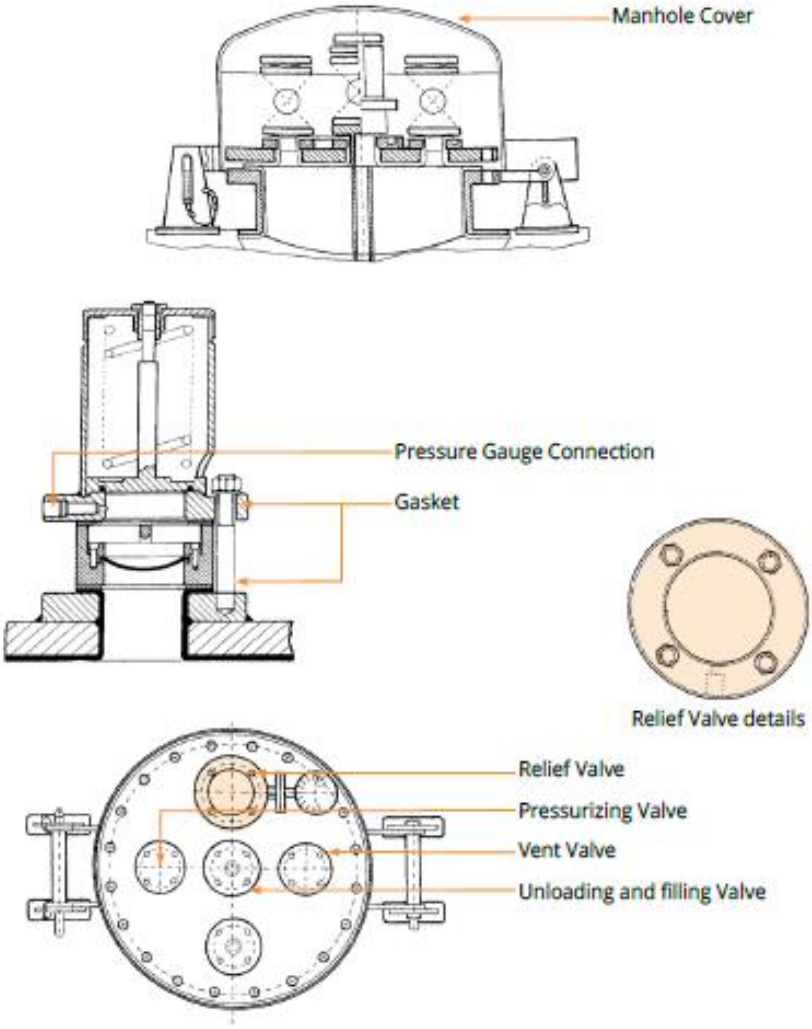
a) Tighten the nuts of the studs on the vessel flange under the valve.
b) If the leak continues, dismantle the blind flange from the red vent valve (for pressure relief). Relieve any pressure in the vessel by opening the red vent valve, slowly and cautiously.
c) Remove the valve and check the flanges. 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.

Isotank Manhole details



5.18 Tank Cleaning and Repairs

- The hazardous nature of tank inspection, cleaning or repairs requires that the foreman and crew be selected and trained carefully. They should be thoroughly familiar with the hazards and safeguards necessary for the safe performance of the work. Written approval should be secured from the plant supervisor before the work is started. All tank work should be done under direct supervision.

- Pipelines into or out of the tank or other equipment should be shut off, disconnected, and a blank flange should be installed for protection against leaks and errors. Valves and cocks in the pipeline should not be relied upon.

- Lock electrical switches in the off position, remove drive belts, and otherwise completely safeguard against accidentally starting the agitating equipment or other moving parts located inside the tank or adjacent to the entrance.

- Before entering a tank and during the work, tests should be made by a qualified person to determine that no further washing is necessary, that no oxygen deficiency exists, and that no harmful gas or vapour is present. Th e tank should be purged continuously with an air stream during all work within the tank.

- Proper personal protective equipment should be worn by anyone entering a tank for inspection, cleaning, or repairs.

- One man on the outside of the tank should keep the men in the tank under constant observation and at least two other men should be available to aid in the rescue, if any, of those in the tank are overcome.

- A hose mask, an airline mask or self-contained breathing apparatus together with rescue harness and lifeline should be located outside the tank entrance.

- The portable electric lights and power tools should be of the three wire, grounded type.

Additional precautions are recommended as follows:

- Drain tank as completely as possible,
- Wash thoroughly with large quantities of water, and
- Dry completely tank by blowing with warm dry air

5.19 Waste Disposal

Waste has to be disposed as per Central Pollution Control Board (CPCB) and the respective State Pollution Control Board (SPCB) guidelines

Source of Waste

The spent alkaline Bromine (KBr, NaBr and NH4Br) and spent Acidic Bromide (Hydro bromic acid) are generated during the manufacturing of Bromine and its derivatives.

Some of Bromine waste generated during bromine glass bottle recycling and bromine ISO tank empty out for inspection or refilling process.

Bromine waste of ISO tankers should be recycled by scrubbing bromine into 10 % Sodium Hydroxide solutions.

The spent alkaline bromide and spent acidic bromide is categorized as hazardous waste at S.No.C2,C4 of schedule 2 and 29.1 & 28.1 of schedule 1 HOWM rules 2016 which are required to be disposed in authorized disposal facility in accordance with authorization condition, when not utilize as resource recovery.

Utilization Process

Spent Alkaline bromide is mixed with water to reduce specific gravity of the solution; the diluted spent alkaline bromide is transferred to reactor, where it is acidify with HCL (30%) to de-emulsify the organic impurities present in the waste. The organic bromide impurities/residues from the bottom is collected in to the drums and sent to ET plant for the disposal purpose, in ETP impurities/residue drum is neutralize with 8 to 9 % lime slurry.

Acidified alkaline bromide solution is fed to stripping column (Packed column) over the top of the column, where chlorine gas and steam passed from the bottom of the tower .During the process chlorine reacts with the alkali and liberates the bromine vapors, Vaporized bromine is passing through condensers to get crude liquid bromine. The acidic effluent generated from the reaction column is transferred to ETP for the neutralization process with lime slurry of 8 to 9 %.

Crude bromine is further subjected to distillation to remove out the traces of impurities.

The flow diagram of the utilization process and neutralization or disposal process is as below

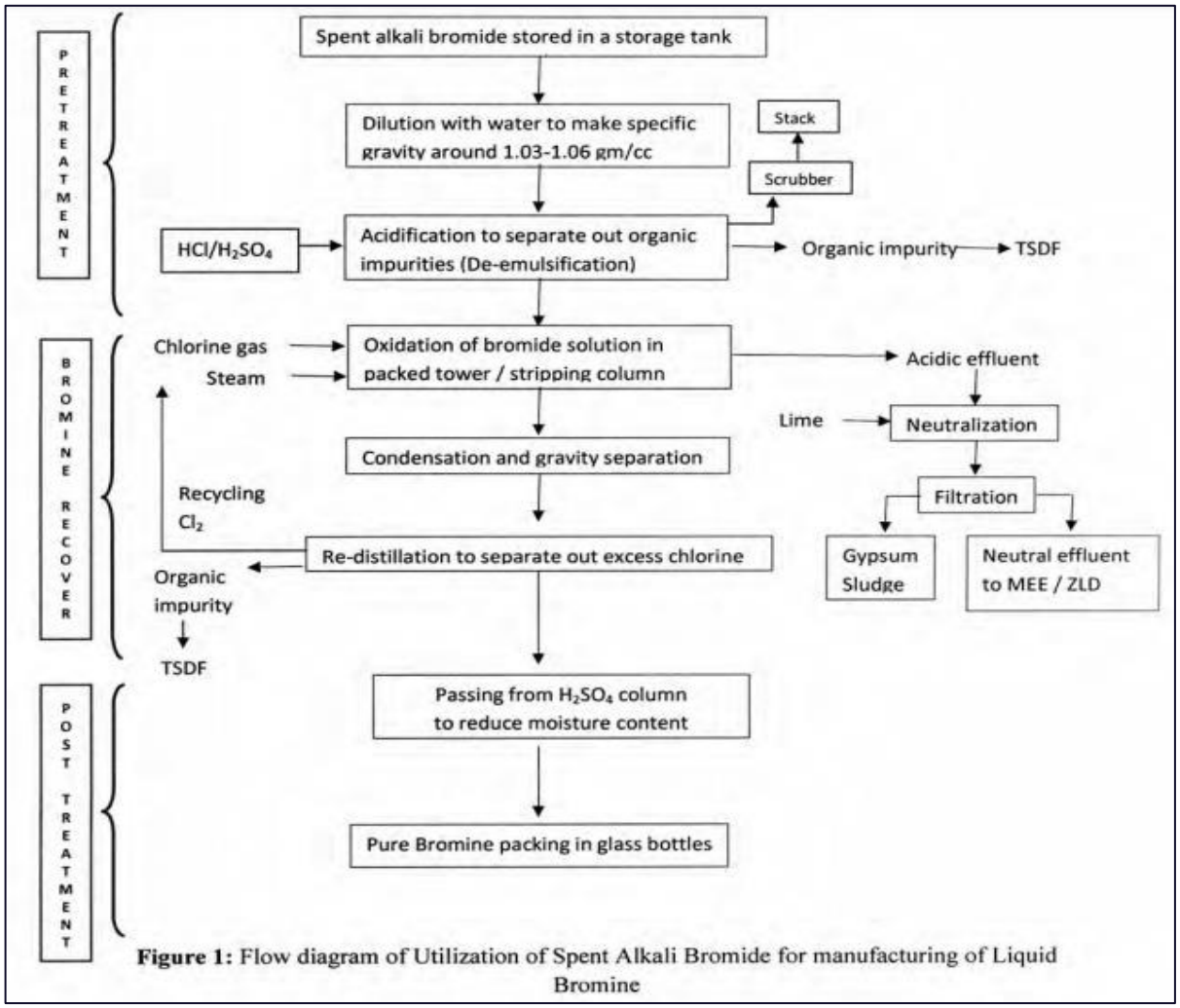


Figure 1: Flow diagram of Utilization of Spent Alkali Bromide for manufacturing of Liquid Bromine

Treatment and disposal of waste brominated water

Waste water generated from striping column, floor washing, spillages, reactor washing, scrubber bleed etc. shall be treated Physico-chemically in an ETP followed by forced evaporation such as Multi effect evaporator (MEE). The condensate from MEE may be sent to CETP for the final disposal. In case CETP is not available condition of zero liquid discharge be enforced by the SPCB/PCC.

Brominated hazardous waste shall be collected and temporarily stored in non-reactive drums/bags under the dedicated hazardous waste storage area and be sent to authorize common TSDF or other authorize facility within 90 days from generation of the waste in accordance with the authorization issued by the concerned SPCB/PCC, Such storage area shall be covered with the proper ventilation facility.

During the process of utilization and handling of hazardous waste, the unit shall comply with the requirements in accordance with the Public Liability Insurance Act, 1991 as amended, wherever applicable.

Records and Return filing:

The unit shall maintain the passbook issued by concern SPCB wherein the following details of each procurement of brominated waste shall be entered:

Address of the sender

Date of dispatch

Quantity procured

Seal and signature of the sender

Date of receipt in the premises

The unit shall maintain the records of hazardous waste utilization, hazardous waste generation, and disposal as per form no.03 & shall file annual return in form no.04 as per rule 20(I) and (2) of hazardous and other waste to concerned CPCB and PCC.

5.20 Neutralization of Laboratory Bromine Waste Streams

Physical hazards/properties

Neutralization of bromine is extremely exothermic. It should be done slowly with sufficient external cooling capacities. Proper materials of construction of all equipment should be observed. Bromine is a strong oxidizer that reacts with some metals and is incompatible with many elastomers and plastics.

All considerations regarding the safety and handling of bromine should be observed when neutralizing bromine waste. Equipment guidelines and first aid procedures for the handling of bromine should be followed.

Apparatus

Assemble, in a fume hood, a 5 liter 3-neck round bottom flask supported at the base and the neck. Equip the flask with a sufficient cooling bath, mechanical stirrer, and a water-cooled or air-cooled condenser vented to a sodium hydroxide scrubber system. Neutralization of bromine waste on a scale larger than that described here is not recommended.

Stoichiometry

Neutralization with sodium bisulfite requires 3 moles of sodium hydroxide, 1 mole sodium bisulfite, and 1 mole bromine. Neutralization with sodium sulfite requires 2 moles sodium hydroxide, 1 mole sodium sulfate, and 1 mole bromine.

The weights and volumes specified include a 10% excess of sodium hydroxide and sodium bisulfite or sodium sulfite. This excess should be observed.

Chemistry

$Br2 + Na2S03 + 2NaOH \rightarrow 2NaBr + Na2SO4 + H20$

$Br2 + NaHSO3 + 3NaOH \rightarrow 2NaBr + Na2SO4 + 2H20$

This neutralization procedure is designed to assure that the final waste stream has been completely neutralized with respect to acidity and oxidation potential. It is also designed for safety and operational handling concerns in a laboratory setting.

Neutralization with bisulfite (based on 100 ml bromine

1. Add 2500 ml of tap water to the flask.

2. Slowly add, with cooling and agitation, 345 ml of 50% sodium hydroxide (NaOH). Note: adjust water charge to achieve target concentration of 2.3 M NaOH if less concentrated sodium hydroxide solution is used.

3. Add 224g sodium bisulfite while stirring.

4. Continue stirring until most of the solids dissolve.

Neutralization with sulfite (based on 100 ml bromine)

1. Add 2500 ml of tap water to the flask.

2. Slowly add with cooling and agitation, 230 ml of 50% sodium hydroxide (NaOH). Note: adjust water charge to achieve target concentration of 1.6 M NaOH if less concentrated sodium hydroxide solution is used.

3. Add 271g sodium sulfite while stirring.

4. Continue stirring until most of the solids dissolve

Procedure

Be aware that organic or metal impurities may change normal characteristics of neutralization (i.e., color changes, foaming, etc.)

1. Slowly, with cooling, add 100 ml of bromine using a clamped addition funnel or pump and graduated cylinder. The addition rate should be slow enough to allow for color dissipation and temperature control below 50°C (122°F).

2. When addition is complete, allow the flask to cool to room temperature.

3. Check the contents with starch KI paper and pH paper to make sure no oxidizer is present, and that pH is > 7. Solution should be colorless. If color persists, slowly add more sodium hydroxide/sodium bisulfite (sulfite) solution.

4. When neutralization is complete, filter off any insoluble material and separate any organic phases. Sodium bromide precipitate can be dissolved in water. The resulting solution should be 11 to 12% sodium bromide. This solution should be disposed of properly as a waste stream.

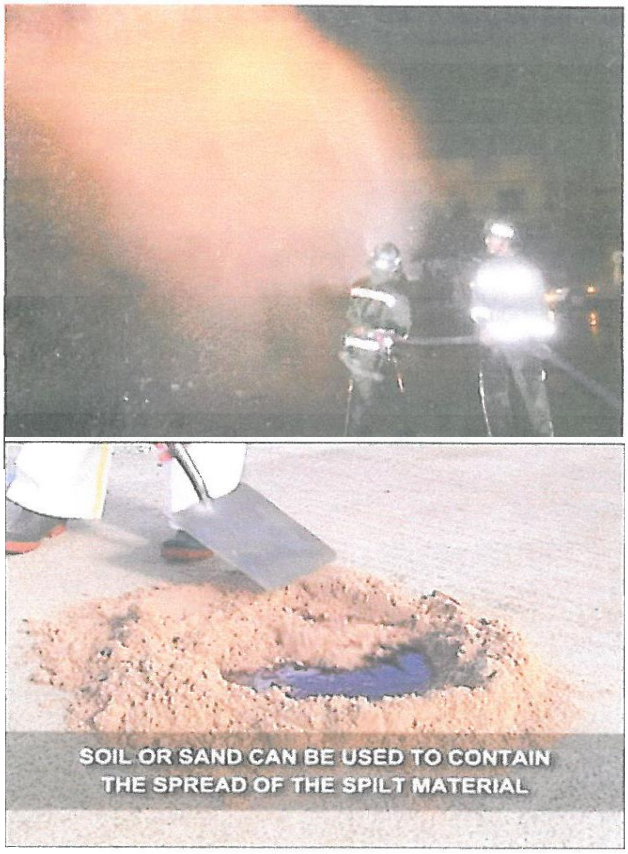
6.0 EMERGENCY PROCEDURES

6.1 Emergency Reporting

All accidents, incidents and near misses must be reported immediately, using your company's emergency contact number. If people are injured in a traffic accident always notify the police and an ambulance.

6.2 Emergency Action

In emergency situations during transport:



1. Depending on the type of the emergency, notify the respective emergency contact number

2. Notify your depot and follow their advice.

3. Make the vehicle safe — switch off the engine etc. and make yourself safe e.g. put on PPE, go upwind.

4. Isolate the area and keep people at a safe distance. Any person not dressed in proper protective clothing and not using an approved self-contained breathing apparatus should be kept a safe distance away.

5. Ensure any casualties are not in danger and get medical assistance if required.

6. Check container for damage but DO NOT attempt to stop leaks.

7. Remember, bromine is not flammable, but fire/heat can cause toxic fumes to be given off.

8. Small spillages can be contained with sand/earth if practicable.

9. Ensure run-off water does not enter watercourses such as rivers/ sewers etc.

NOTE: This list is not exhaustive

Toxicology

Bromine is a very strong oxidant. It is extremely toxic and may prove fatal if inhaled or swallowed. Severe burns may result from skin contact and contact with the eyes may cause blindness. Bromine is extremely destructive to tissue of the mucous membranes and upper respiratory tract. Bromine exposure may result in spasm, inflammation and edema of the larynx and bronchi, chemical pneumonitis and pulmonary edema. Low concentrations of bromine vapor cause irritation, tearing, and inflammation of the eyes. At higher concentrations blepharospasm and photophobia develop and a splash in the eyes causes severe burns and/or blindness. Soft tissue burns may be deep and very slow to heal.

6.3 Recognizing bromine overexposure

Symptoms

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 symptoms of tachycardia, fever, chemical pneumonitis, pharyngeal edema, bronchospasm, pulmonary edema and 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(including lips, tongue and oropharyngeal burns).

Systemic futures: hypochromic shock, laryngeal edema, respiratory complications, systemic toxicity likely after single acute of exposure of bromine

6.4 First aid for bromine exposure

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. Avoid reusing contaminated clothing.

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. Only specific symptomatic treatment is required, monitoring of ECG and vitals should be continued.

No neutralizing compound recommended. Investigations such as endoscopy, chest x-ray, abdominal barium x-rays are recommended.

A medical specialist should be summoned at once in all cases. After initial first aid measures are completed, keep the person quiet, warm, and upright. Provide emergency personnel with information about all materials used by the person, appropriate information about bromine and first aid procedures.

6.5 Spills and Leakage

In the case of bromine spillage, ammonia gas vapors should be released to the area from a safe distance.

1. When handling a leaking bottle, drum, or cylinder of bromine, personal protective clothing, goggles, and NIOSH or equivalent approved self-contained breathing equipment must be worn.
2. Clear contaminated area of non-essential personnel.
3. Maintain a slight ammonia atmosphere throughout the cleanup. Carefully release anhydrous ammonia gas to neutralize bromine vapor, but do not over apply anhydrous ammonia. The ammonia gas will convert bromine to white ammonium bromide “smoke.” Do not allow liquid bromine and liquid ammonia to combine; a violent reaction will occur. Ammonia (16 to 25% by volume) can form an explosive mixture with air.
4. Pour hypo solution, lime and water slurry, or soda ash solution over the spill. Hypo-bromine reactions produce hydrobromic acid. Dry sodium thiosulfate and liquid bromine produce a violent reaction; do not mix them. Hypo solution is prepared by dissolving 220 grams of technical sodium thiosulphate in a litre of water and a 100gm of soda ash. The solution will remain stable for four to six weeks.
5. Using cold water, wash neutralized bromine into a sump for transfer to an approved waste disposal facility where the waste can be processed.

6. Ventilate the area to remove the ammonium bromide and any bromine fumes. Clean the floors and equipment with soap and water.

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 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 Ca(OH)2 water slurry.

6.6 Transportation emergencies

General Recommendations

In emergency situations resulting from vehicle accidents:

- Notify emergency authorities.
- Dress in proper protective clothing, self-contained breathing apparatus.
- Isolate the area and remove any persons affected by the spill.
- Administer immediate first aid and seek medical assistance for those injured.
- Cautiously contain the bromine.
- If the bromine discharge is contained within the transport vessel, with advice from the supplier/manufacturer, transfer the bromine into another container.
- When bromine is escaping from the container, the leak must be stopped. Specialized training or advice may be required to stop leaks. Tightening loose fittings, plugging holes, or reorienting the container are all techniques used to stop or reduce leaks.
- Use materials like clay, sand, or soil to confine bromine to the already contaminated area. Do not use spill pillows or other fibrous materials for containment as they may in- crease the potential for fire.
- Gently cover any pooled bromine with a thin layer of water to minimize bromine vapor emission. While adding water, try not to agitate the bromine pool as this will cause excessive vapor. Placing a thick covering of hydrated limewater slurry over the bromine will slowly neutralize the bromine and stop vapor emissions.
- If the soil has already absorbed the bromine, work lime deep into the ground with water. For large spills, earth moving equipment may be required.

Instructions for Drivers

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)
- Trem (Transport Emergency) Card
- Quantity of hazardous material involved.
- Emergency contact phone number

What to do if you are the first on the scene at a chemical spill.

Though focused on bromine, the following advice applies to situations involving any chemical, as accidents involving bromine might also include other chemicals of a hazardous nature.

General Safety Precautions

Approach Cautiously from Upwind. If wind direction allows, consider approaching the incident from uphill. Resist the urge to rush in; others cannot be helped until the situation has been fully assessed.

Secure the Scene. Without entering the immediate hazard area, isolate the area and assure the safety of people and the environment, keep people away from the scene and outside the safety perimeter. Allow enough room to move and remove your own equipment.

Identify the Hazards. Placards, container labels, shipping documents, material safety data sheets and/or knowledgeable persons on the scene are valuable information sources. Evaluate all available information to reduce immediate risks. As more information becomes available, the response should be further tailored to the situation.

Assess the Situation. Consider the following:

- Is there a fire, a spill or a leak?
- What are the weather conditions?
- What is the terrain like?
- Who/what is at risk: people, property or the environment?
- What actions should be taken: Is an evacuation necessary?
- Is diking necessary? What resources (human and equipment) are required and are readily available?
- What can be done immediately?

Obtain Help. Advise your headquarters to notify responsible agencies and call for assistance from qualified personnel.

Decide on Site Entry. Any efforts made to rescue persons, protect property or the environment must be weighed against the possibility that you could become part of the problem. Enter the area only when wearing appropriate protective gear.

Respond. Respond in an appropriate manner. Establish a command post and lines of communication. Rescue casualties where possible and evacuate if necessary. Maintain control of the site. Continually reassess the situation and modify the response accordingly. The first duty is to consider the safety of people in the immediate area, including your own.

Above All. Do not walk into or touch spilled material. Avoid inhalation of fumes, smoke and vapours, even if no dangerous goods are known to be involved. Do not assume that gases or vapours are harmless because of lack of a smell— odourless gases or vapours may be harmful. Use CAUTION when handling empty containers because they may still present hazards until they are cleaned and purged of all residues.

Who To Call For Assistance

Upon arrival at the scene, a first responder is expected to recognize the presence of dangerous goods, protect oneself and the public, secure the area, and call for the assistance of trained personnel as soon as conditions permit. Follow the steps outlined in your organization's standard operating procedures and/or local emergency response plan for obtaining qualified assistance. Generally, the notification sequence and requests for technical information beyond what is available in this guidebook should occur in the following order:

1. ORGANIZATION/AGENCY

Notify your organization/agency. This will set in motion a series of events based upon the information provided. Actions may range from dispatching additional trained personnel to the scene to activating the local emergency response plan. Ensure that local fire and police departments have been notified.

2. EMERGENCY RESPONSE TELEPHONE NUMBER

Locate and call the telephone number listed on the shipping document. The person answering the phone at the listed emergency response number should be knowledgeable of the materials and mitigation actions to be taken or should have immediate access to a person who has the required knowledge.

Collect and provide as much of the following information as can safely be obtained to your chain of command and specialists contacted for technical guidance:

- Your name, call back telephone number
- Location and nature of problem (spill, fire, etc.)
- Name and identification number of material(s) involved
- Shipper/consignee/point of origin
- Carrier name, rail car or truck number
- Container type and size
- Quantity of material transported/released
- Local conditions (weather, terrain, proximity to schools, hospitals, waterways, etc.)
- Injuries and exposures
- Local emergency services that have been notified

6.7 Leaking containers

- When handling a leaking bottle, drum, or cylinder of bromine, personal protective clothing, goggles, and self-contained breathing equipment must be worn.
- Clear contaminated area of non-essential personnel.
- Maintain a slight ammonia atmosphere throughout the cleanup. Carefully release anhydrous ammonia gas to neutralize bromine vapor, but do not over apply anhydrous ammonia. The ammonia gas will convert bromine to white ammonium bromide “smoke.” Do not allow liquid bromine and liquid ammonia to combine; a violent reaction will occur. Ammonia (16 to 25% by volume) can form an explosive mixture with air.
- Pour hypo solution, lime and water slurry, or soda ash solution over the spill. Hypo-bromine reactions produce hydrobromic acid. Dry sodium thiosulfate and liquid bromine produce a violent reaction; do not mix them.
- Using cold water, wash neutralized bromine into a sump for transfer to an approved waste disposal facility where the waste can be processed.
- Ventilate the area to remove the ammonium bromide and any bromine fumes. Clean the floors and equipment with soap and water.

6.8 Recovery and salvage

- Remove undamaged containers and store for later inspection.
- Under the advice and/or supervision of supplier/manufacturer or their partners, transfer the remaining bromine into other containers.

6.9 Cleaning up the contaminated area

- Spread hypo solution, soda ash solution or lime slurry over the affected area.
- Scrub the area well. Using cold water, wash the neutralizing solution to a sump for transfer to an approved waste facility for processing.
- Use hot soapy wash water and large quantities of rinse water to clean equipment. Dispose of this waste as hazardous waste.
- Replace any porous materials, fabric, leather, wood, and paper products, which have been in contact with bromine.

6.10 Cleaning undamaged containers

- If the container is tightly sealed and there appears to be no danger of contaminating the liquid inside, pour hypo solution over the affected areas.
- Wash with water and dry completely. Should markings and labels be illegible, remark and relabel. If needed, contact the supplier for new Labels

6.11 Fire

- In case of fire, notify the fire department and emergency responders immediately and evacuate the area.
- Everyone should move a safe distance from the fire, upwind of the smoke.
- Wearing self-contained breathing equipment, fire fighters should cool bromine containers with water, fog, or foam.

6.12 Firefighting

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. 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.

7.0 REFERENCES

1. Bromine Safety Handbook, ICL
2. Bromine Safety Handbook, LANXESS
3. Indian Standard IS: 6953 – 1973: Code of Safety for Bromine
4. Indian Standard IS 1260 – 1973: Pictorial marking for handling and labelling of goods, Part 1
5. UN (Orange Book) Recommendations on the Transport of Dangerous Goods
6. European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR)
7. International Maritime Dangerous Goods Code Dangerous Goods List (IMDGC)

8.0 APPENDIX A

8.1 Physical and Chemical Properties of Bromine

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:

$3Na_2CO_3 + 3Br_2 = NaBrO_3 + 5NaBr + 3CO_2$

Slaked Lime:

$6Ca(OH)_2 + 6Br_2 = Ca(BrO_3)_2 + 5CaBr_2 + 6H_2O$

Caustic Soda:

$6NaOH + 3Br_2 = NaBrO_3 + 5NaBr + 3H_2O$

Sodium sulphite:

$Br_2 + Na_2SO_3 + 2NaOH = 2NaBr + Na_2SO_4 + H_2O$

Sodium bisulphite:

$Br_2 + NaHSO_3 + 3NaOH = 2NaBr + Na_2SO_4 + 2H_2O$

Neutralization of gaseous Bromine

Anhydrous Ammonia:

$8NH_3 + 3Br_2 = 6NH_4Br + N_2$

Chemical reactions

Bromine is a very reactive element characterized by a strong oxidizing capability. It forms a wide range of bromine containing compounds on reaction with numerous inorganic and organic substrates. A limited, but typical, illustration of such reactions follows.

Inorganic bromine compound

Bromine readily oxidizes metallic and nonmetallic elements as indicated by the following equations

$3Br_2 + 2Fe_o \xrightarrow{\Delta} 2FeBr_3$

$6Br_2 + P_4 = 4PBr_3$

$3Br_2 + S0 + 4H_2O = 6HBr + H_2SO_4$

$Br_2 + H_2 \xrightarrow{\Delta} 2HBr$

Reaction of bromine with water results in the formation of an aqueous solution of hydrobromic and hypobromous acids. The latter is relatively stable only in solution, decomposing un- der the influence of heat, light, or copper catalysis to produce hydrobromic acid and oxygen.

$Br_2 + H_2O = HBr + HOBr$

Reactions of bromine and ammonia occur readily, and de- pending upon conditions, produce nitrogen and hydrogen bromide, bromamines, or ammonium bromide. The ammonium bromide results in the reaction between hydrogen bromide and excess ammonia. In the vapor and liquid states, bromine and ammonia form ammonium bromide (NH_4Br) at normal temperature and atmospheric pressure.

With strong alkalis at low temperatures in aqueous solutions, bromine reacts to produce bromide and hypobromite salts.

$Br_2 + 2NaOH = NaBr + NaOBr + H_2O$

At elevated temperatures, the hypobromite undergoes an oxidation-reduction reaction to produce bromate and bromide salts.

$3NaOBr = NaBrO_3 + 2NaBr$

The balanced summation of these two reaction equations yields:

$3Br_2 + 6NaOH = 5NaBr + NaBrO_3 + 3H_2O$

Some typical oxidation-reduction reactions of bromine with inorganic compounds under alkaline or acidic conditions are illustrated in the following reactions:

$Br_2 + 2KI = 2KBr + I_2$

$Br_2 + NaNO_2 + H_2O = NaNO_3 + 2HBr$

$2Br_2 + FeSO_4 + 8NaOH = Na_2FeO_4 + Na_2SO_4 + 4NaBr + 4H_2O$

$Br_2 + 2FeSO_4 + H_2SO_4 = Fe_2(SO_4)_3 + 2HBr$

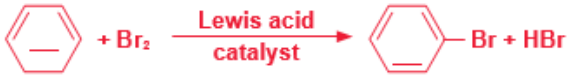
Organic bromine compounds

The reactions of bromine with organic compounds may occur in a variety of ways. Typically, they involve:

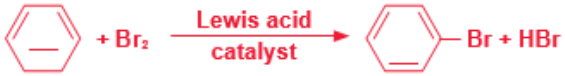
1. The addition of bromine to unsaturated hydrocarbons such as

$H_2C=CH_2 + Br_2 = BrCH_2CH_2Br$

2. The substitution of hydrogen on the organic substrate such as



Reactions can be achieved under a variety of conditions, in liquid or vapor phase, and in the presence or absence of sol- vents or catalysts. Carbon tetrachloride, chloroform, and other halogenated solvents, acetic acid and other lower aliphatic acids, and hydrobromic acid are typically used as solvents. Lewis acid catalysts frequently are employed in the substitution bromination of aromatics and light or peroxide catalysts in the bromination of aliphatics. The choice of catalyst often dictates the course of a reaction.



Some organic bromine compounds are best prepared indirectly by the reaction of other functional groups with bromine derivatives. For example, alkyl bromides, such as methyl bromide, are best prepared by reaction of the corresponding alcohol with hydrogen bromide. Alkyl bromides can also be prepared by the reaction of HBr with olefins.