AFROX
A Member of The Linde Group

Packaged Chemicals

Sulphur Dioxide

Contents

Specification

Appearance

Sulphur dioxide is a clear colourless liquid, free from visible impurities

Strength	99,9% minimum SO_2 (m/m)
Water content	100 p.p.m. maximum (m/m)
Oil Content	10 p.p.m. maximum (m/m)
Residue on evaporation	10 p.p.m. maximum (m/m)
Sulphuric acid content	Nil

Properties

Physical Properties

Chemical formula	-	SO_2
Boiling point at 101,3 kPA	-	10°C
Density as a gas at 0°C	-	2,92 kg/m^3
Density as a liquid at 0°C	-	1,43 g/cm^3
Latent heat of vaporization at Boiling point	-	397,3 kJ/kg
Freezing point of liquid	-	75,5°C
Molecular weight	-	64,07
Critical temperature	-	157,1°C
Critical pressure	-	7,86 MPa
Specific heat of liquid at 0°C	-	1,331 kJ/kg
Specific heat ration of gas, Cp/Cv At 25°C and 100 kPa	-	1,285
Viscosity of gas at 25°C	-	0,0128 mPa.s
Vapour density (air=1)	-	2.26

Chemical Properties

Sulphur dioxide is a colourless, non-flammable, non-explosive gas at ordinary temperatures and pressures. It is 2,26 times denser than air and although not toxic, it is extremely irritating to the eyes and to the respiratory system. The gas has a characteristic pungent odour which gives ample warning of its presence. Concentrations from 3 to 5 p.p.m. (v/v) in air are easily detected by smell.

Sulphur dioxide gas is readily liquefied under a pressure of approximately 390 kPa (abs) at 25°C. The gas is sparingly soluble in water to form a solution of sulphurous acid which slowly oxidizes to sulphuric acid when exposed to air.

Anhydrous sulphur dioxide is non-corrosive to steel and other commonly used metals. In the presence of moisture, however, sulphur dioxide is extremely corrosive to such materials. For example, the accidental dilution of gas emanating from leaking container, with water, has been known to corrode a 25mm diameter hole through 12mm of steel in less than twenty-four hours.

Uses

In the Wine Industry

Sulphur dioxide is extensively used in the manufacture of wine. It destroys moulds, bacteria and wild yeast prior to the introduction of the pure yeast culture necessary for good fermentation. Techniques of application vary: in some instances either the gas or liquid is passed straight into the wine: in others, the sulphur dioxide is added in the form of a 5% solution in water. Sulphur dioxide is also used as a sterilizing medium for wine bottles.

In the Manufacture of Fruit Juices and Cordials

Sulphur dioxide is one of the few permitted preservatives in food manufacture. Large quantities are used in the fruit juice and cordial industry to improve the flavour and prevent colour deterioration of the products.

In the Preservation of Fruit in Cold Storage

A small stream of sulphur dioxide gas is bled into the atmosphere of cold rooms and this effectively counteracts discolouration of fruit and stems. Alternatively, the fruit may be dipped in a dilute solution of sulphur dioxide in water before being packed into cold storage.

In Sugar Manufacture

Sulphur dioxide is used in large quantities as a refining and bleaching agent for sugar. The raw juices are treated with lime and sulphur dioxide which precipitate suspended and dissolved impurities.

In the Fumigation of Grain

Where stocks of grains and cereals become contaminated with weevils, fumigation with sulphur dioxide proves effective. At the same time that infestation is being eliminated the grain is bleached and its appearance thus improved.

Petroleum Refining

Liquid sulphur dioxide is used as an extractant in the refining of petroleum products by the Edeleaneau process due to its preferential extraction of aromatics, unsaturated and sulphur compounds.

Miscellaneous

Sulphur dioxide has application in the manufacture of sheet glass; as an over-voltage inhibitor in the electrolytic refining of metals; in the preparation of glue and various food proteins such as soya bean protein, casein and gelatine.

Containers

- Cylinders
- Portable Tanks

Handling and Storage

As soon as possible after delivery the customer should check containers of sulphur dioxide for leaks and, if found, take appropriate action as detailed in Detection and Correction of Leaks.

As a general safety precaution cylinders and portable tanks should be handled with care and, to avoid damage to the valves, the protection covers should not be removed until the containers are in the required position for discharge. By the same token the covers should be replaced immediately after the containers have been emptied.

Containers should be used in order of receipt and returned as soon as they are empty. Any sign of corrosion in the vicinity of the valves usually indicates a leak. In the presence of moisture, such containers must be emptied promptly and returned. An accompanying indication of the defect will facilitate an assessment as to their suitability for further use.

Cylinders and Portable Tanks

Cylinders and portable tanks of sulphur dioxide must be stored in a cool, dry place, out of direct sunlight and protected from corrosive agents. Containers must never be stored in an area where they may be exposed to fire as they could explode due to the expansion of the liquid sulphur dioxide.

The pressure in the containers, provided some liquid is present, is the vapour pressure of sulphur dioxide at the temperature of storage (see Table 2, page 11). It is most important to realise that this pressure is dependant only on the temperature and not on the quantity of sulphur dioxide in the container. The only accurate method of determining the actual sulphur dioxide content of a container is by weighing the container and subtracting its tare. Weighing operations are always carried out with the valve protection covers removed.

The valves on all containers are inspected prior to each filling and are known to be in working order when they leave the factory. Usually the valves open without difficulty but if not used over a long period the valve spindles occasionally become tight and will not turn easily. Neither excessive force on the key nor lubricants or penetrating oil should be used. The correct procedure for easing a tight spindle is as follows. Take the container out-of-doors to an area where the discharge of small quantities of sulphur dioxide will be innocuous. Stand the container upright and hold a black-hot soldering iron in contact with the valve body for about two minutes; then try opening the valve with the key. This treatment will usually be successful in freeing the spindle. If it remains tight, the assistance of an Afrox technical representative must be sought. The use of a naked flame for heating is extremely dangerous and must never be permitted.

Leaks of gas may occasionally occur at the valve gland; these can be stopped by turning down the gland nut very gently. On cylinders and on portable tanks the gland nut has a right-hand thread.

Hoists for handling the portable tanks should be certified for a lifting load of at least three tons. The use of a lifting bar is recommended; Afrox will supply drawings to assist customers who wish to have such bars made.

Materials of Construction

Almost all common materials of construction are resistant to anhydrous liquid sulphur dioxide and the dry gas; these include cast iron, mild steel, copper, brass and aluminium. Sulphur dioxide in the presence of water forms sulphurous acid which is highly corrosive, therefore the wet gas or solutions of the material should be stored and handled in ceramics, glass, stone and certain stainless steels such as Worthite and Durimet 20. Carbon, graphite, hard rubber, butyl rubber, chemical lead, rigid PVC and polyethylene are appropriate for use in certain applications but Afrox should be consulted if any doubt exists as to their suitability. For very hot, dry gas, Inconel is recommended.

Gaskets for use with the anhydrous liquid and the dry gas can be made from any of the common materials of construction. Where wet sulphur dioxide is involved, PTFE is a good gasket material.

A discharge facility for sulphur dioxide containers should preferably incorporate metal tubing with welded or brazed couplings. Should it prove impractical, as with container tanks, to use metal tubing, flexible connections should be made using suitable high-pressure hose. One recommended type is "Afriflex No 6072"; this is a neoprene wire-braided hose available from the manufacturers, Flexible Tubing Africa Ltd, and is normally supplied complete with appropriate end fittings.

Withdrawal of Sulphur Dioxide from Containers

When gas is withdrawn from a container the temperature, and thus the vapour pressure, of the sulphur dioxide will drop. The lower the pressure the slower will be the discharge of gas. When liquid is withdrawn there is no cooling effect and hence no drop in either pressure or liquid discharge rate.

When large volumes of gas are to be withdrawn, water at room temperature can be sprayed onto the external surface of the container to obviate undue cooling or icing-up. Alternatively, the container can be stood vertically in a tank of water to a level about half that of the container height. The application of hot water or direct heat to a container must never be permitted because the resultant increase in internal pressure can cause explosive rupturing of the container. Neither must water be permitted to come into contact with a leaking container.

In situations where the application of water to containers is impractical, consideration should be given to the installation of a system in which two, or more, containers can be connected in parallel to discharge gas simultaneously, each at a reduced rate. When still higher gas discharge rates are required, a stream or electrically-heated vaporizer can be used, fed with liquid sulphur dioxide from one or more containers. The pipe work and non-return valves of any installation incorporating containers connected in parallel must be properly engineered to ensure that there is no possibility of liquid flow from one container to another. This condition can arise due to any variation in temperature, and hence pressure differential, between containers. Such a condition could cause a container to become overfilled and, if closed off by a valve, constitute an explosion hazard in the event of any slight increase in temperature. Where liquid sulphur dioxide could become trapped between two closed valves a drain facility should be provided.

Cylinders

The dip pipe is so positioned that an upright cylinder will always discharge gas. If the cylinder is positioned horizontally with the valve outlet facing upwards, liquid will be withdrawn; if the cylinder is rolled through 180º so that the valve outlet faced the ground, gas will be withdrawn.

Afrox has introduced new duo valve full length dip tube cylinders into the South African market. The customer can now withdraw both gas and liquid while the cylinder is in the normal upright position. This is a much safer operation as the cylinder no longer has to be inversed or laid down in order to withdraw liquid.

Portable Tanks

When discharging a portable tank it must be positioned horizontally with the two outlet valves in the vertical plane i.e. the outlet on one valve should face upwards and that of the other should face down. The upper valve will then deliver gas and the lower one liquid.

Prevention of Contamination by Moisture

After discharging any cylinder or portable tank of sulphur dioxide, care must be taken to close all valves tightly to prevent atmospheric moisture, which could cause corrosion, from being drawn into the containers. In addition, precautions must be taken to prevent moisture from being sucked into a container during discharge. This applies particularly when containers are connected to absorption type plants which do no incorporate devices for preventing the suck-back of sulphited liquid. If an empty container is allowed to remain coupled to an ordinary absorption plant, the residual sulphur dioxide in the pipeline will slowly dissolve in the liquid, causing the sulphited solution to be drawn back through the pipe into the container. This will result in serious corrosion of the container and its valve.

When gas is withdrawn from a sulphur dioxide container, suck-back can be prevented by means of either a barometric leg or a Woulfe-bottle trap. A barometric leg is made by interposing a vertical loop of piping, at least 10m high, between the gas container and the absorption vessel. This ensures that while a vacuum may be created, the water or sulphited liquid cannot rise above the bend of the leg and the container is thereby safeguarded.

If the installation of a 10m high leg is inconvenient or impractical, the Woulfe-bottle trap can be used. The three-necked Woulfe-bottle, termed the lute vessel, should be of at least one litre capacity. One neck is connected to the outlet of the sulphur dioxide container, the pipe just entering the bottle. The central neck is fitted with a dip pipe reaching almost to the bottom of the bottle. The third neck carries a pipe to an empty two-necked Woulfe-bottle which, in turn, feeds the sulphur dioxide to the absorption system. The second Woulfe-bottle is to ensure that no fluid passes back into the lute vessel.

The height of the dip pipe connected to an upper (empty) aspirator is such that the pressure which is exerted by the column of luting liquid is greater that the pressure due to the head of water or other liquid against which the gas is discharged. If this liquid head were less, the gas would escape through the vertical tube instead of bubbling into the absorber liquid. The luting fluid is frequently sulphuric acid but there is no reason why another fluid should not be used, even water can be employed. When a vacuum starts developing, air is pulled in through the aspirator and dip pipe, thus preventing the development of sufficient suction to cause suck-back.

Bulk Storage Installations

The bulk storage of sulphur dioxide as a liquefied gas presents certain difficulties mainly due to the high coefficient of thermal expansion of the liquid. In the design of suitable storage pressure vessels the requirements of certain Government Acts must be complied with. The principal features of such a storage installation are that the tanks must be of ample proportions to cater for fluctuations in demand and delivery and allow sufficient latitude to ensure that they can never be completely filled due to expansion of the liquid.

Bulk storage requires expert planning; consequently prospective customers should consult Afrox prior to the design of any bulk storage installation. It must be stressed that Afrox will only supply sulphur dioxide to those customers whose storage installations are of approved design and which have passed an inspection prior to the first delivery.

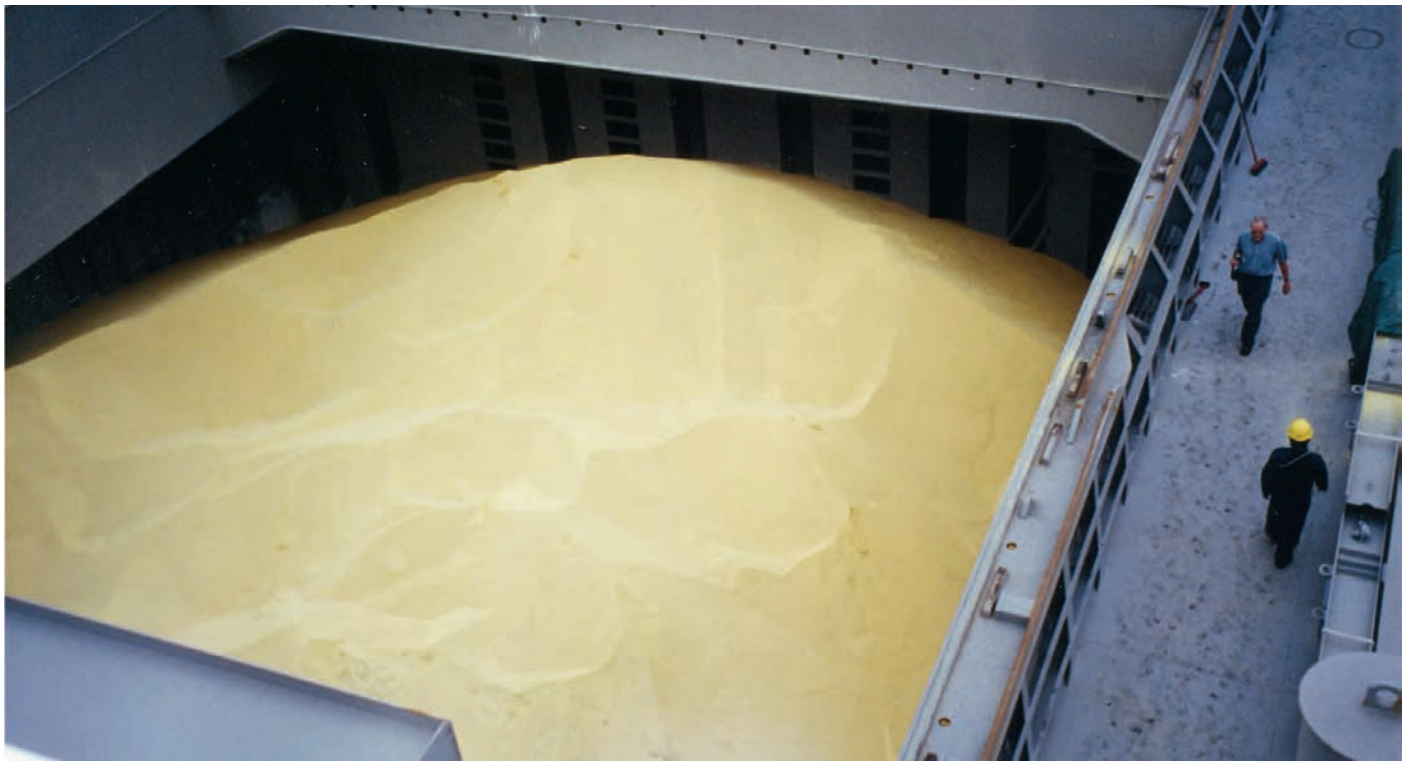
Detection and Correction of Leaks

Possible hazards in the handling of sulphur dioxide are ruptured supply lines, broken gauge glasses and leaking joints. When a leak occurs, only an authorised person should attempt to rectify it. If the leak is serious, a suitable BA set must be worn.

Leaks of sulphur dioxide in lines or equipment are readily detectable using an ammonia solution which can be introduced to the suspect area either on a swab or by suing a squeeze bottle; dense white fumes will be formed near the source of the leak. The exact location can be pin-pointed using a pipe cleaner soaked with ammonia solution.

Leaks are usually not serious and in most cases can be readily controlled. When they occur, the supply of sulphur dioxide must be shut-off immediately by closing the appropriate valve. Leaks at unions or fittings can often be eliminated by tightening the connection. If a leak in a supply line is caused by corrosion, the line must be emptied of sulphur dioxide before any repair work is done.

A leaking container should be moved to an open area, if possible, to minimize the hazard from the sulphur dioxide gas. Sometimes a leak can be diminished by placing the container so that the leak is at the top. This ensures that gaseous sulphur dioxide is discharged and not liquid. Never spray a leaking container with water otherwise the formation of corrosive sulphurous acid could aggravate the leak. If the gas can be vented rapidly into process equipment of a stock tank, the cooling effect due to evaporation will often lower the pressure in the container to a point where it can be moved or the leak repaired. As a last resort, the sulphur dioxide can be vented into an alkaline solution such as lime, caustic soda or soda ash, care must be taken to avoid any suck-back of solution into the sulphur dioxide container.



Safety

Full safety precautions are given on a wall poster, available from Afrox, which should be displayed where sulphur dioxide is used.

Health Hazard

Sulphur dioxide gas is non-poisonous but it is intensely irritating to the eyes, throat and upper respiratory system. Inhalation of the gas at concentrations from 8 to 12 p.p.m. (v/v) in air causes throat irritation, coughing, constriction of the chest and smarting of the eyes. A concentration of 500 p.p.m. causes irritation to the upper respiratory tract that it results in a feeling of suffocation at the first breath.

Sulphur dioxide liquid in contact with the skin or eyes produces a powerful freezing effect that can cause severe frostbite. There are no known systemic effects of acute exposure to sulphur dioxide liquid.

First Aid

- First aid should be started at once in the event of contact with liquid sulphur dioxide to high concentrations of the gas. A doctor must be notified immediately.
- Move the patient into fresh air or out-of-doors.
- Make the patient sit down with head, neck and back supported.
- Do not permit him/her to walk.
- Remove sulphur dioxide-soaked clothing and loosen any tight clothing. Keep the patient comfortably warm but not hot.
- The patient must try to suppress any desire to cough and must take short, shallow breaths whenever this is possible as the coughing spasms are often involuntary and not capable of being controlled. To obtain relief, the patient should inhale the steamy atmosphere from 10 millilitres of Friars Balsam in one litre of boiling water.
- If the patient breathes with difficulty or his skin starts turning blue, administer oxygen. Should breathing stop, apply artificial respiration.
- If liquid sulphur dioxide enters the eyes or comes into contact with the skin, irrigate the affected areas with water for at least 20 minutes.

Hints for Doctors

Oxygen administration is most effective if expiration is made against four to six millilitres of water. Pulmonary distress may be aided by parenteral administration of Aminophylline. If incipient pulmonary oedema develops, large doses of cortisone should be administered intravenously.

Tables

Table 1 gives the solubility of sulphur dioxide in water at a pressure of one atmosphere and various temperatures. Table 2 gives the vapour pressure of anhydrous sulphur dioxide at various temperatures. Table 3 gives the density of aqueous sulphur dioxide solutions of various concentrations at 15,5ºC.

TABLE 1	
Temperature	% SO_2 by mass
0	18,0
5	15,6
10	13,2
15	11,2
20	9,5
25	7,9
30	6,6
35	5,7
40	4,8
45	4,2
50	3,6
55	3,1
60	2,6

Table 1: Solubility of sulphur dioxide in water at 100 kPa abs (one atmosphere) at various temperatures

TABLE 2	
Temperature	Pressure (guage) kPa
0	18,0
5	15,6
10	13,2
15	11,2
20	9,5
25	7,9
30	6,6
35	5,7
40	4,8

Table 2: Vapour pressure of sulphur dioxide at various temperatures.

TABLE 3	
Temperature	% SO_2 by mass
0,5	1,002
1,0	1,004
1,5	1,006
2,0	1,009
2,5	1,011
3,0	1,014
3,5	1,016
4,0	1,019
4,5	1,021
5,0	1,024
5,5	1,026
6,0	1,029
6,5	1,031
7,0	1,034
7,5	1,036
8,0	1,039
8,5	1,041
9,0	1,044
9,5	1,046
10,0	1,049

Table 3: Density at 15,5 ºC of sulphur dioxide solutions of various concentrations.

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