DANGER!
HYDROGEN SULPHIDE GAS
MAY BE PRESENT

How to deal with hydrogen sulphide gas

in tanneries and effluent treatment plants

UNITED NATIONS
INDUSTRIAL DEVELOPMENT ORGANIZATION

The paper *How to deal with hydrogen sulphide gas* was prepared based on UNIDO safety handbook series prepared by J. Buljan, J. Hannak, G. Jayaraj and technical inputs by I. Kral and M. Straka.

INTRODUCTION

One of the biggest safety risks in tanneries and effluent treatment plants is the evolvement of hydrogen sulphide (H_2S). A colourless gas, heavier than air that is invisible and has a strong unpleasant odour in low concentration.

Strong, pungent and unpleasant odour is generally felt in and around poorly managed/maintained tanneries and *effluent* treatment plants.

The sulphide content in tannery effluent results from the use of sodium sulphide and sodium hydrosulphide and from the breakdown of hair in the unhairing process. When the pH of the effluent drops below 9.5, hydrogen sulphide evolves from the effluent: the lower the pH, the higher the rate of evolution. Characterised by a smell of rotten eggs, a severe odour problem occurs.

Hydrogen sulphide is a flammable gas which burns with a blue flame, giving rise to sulphur dioxide, a highly irritating gas with a characteristic odour. Mixtures of hydrogen sulphide and air in the explosive range may explode violently; since the vapours are heavier than air, they may accumulate in depressions or spread over the ground.

Even a low level of exposure to the gas induces headaches and nausea, as well as possible damage to the eye. At higher levels, death can rapidly set in and countless deaths attributable to the build-up of sulphide in sewage systems have been recorded. This is why strict segregation of beamhouse and tanyard streams is a must as well as early removal of sulphide in effluent, usually by catalytic oxidation.

CHARACTERISTIC OF HYDROGEN SULPHIDE GAS

Hydrogen Sulphide is colourless, flammable, extremely hazardous gas

- **highly corrosive effect**, particularly on concrete and metal structures as well as electrical cabling and installations. Tanners and managers of effluent treatment plants are very familiar with the phenomenon, since substantial maintenance work is required every year to deal with the effects of the gas.
- **heavier than air** and thus can collect in pools of sewage sludge, pits, paddles, man holes of the collection conveyance system in tanneries and effluent treatment plants.
- **flammable** and may form an explosive mixture with air. Open fire or smoking could be a source of ignition.
- **poisonous** when inhaled (see next page)

POISONING EFFECTS OF HYDROGEN SULPHIDE GAS

Extremely toxic and irritating gas
Can cause instant death

WHO IS AT RISK?

Any worker engaged in cleaning of pits or maintenance of collection and conveyance system, receiving sumps, screen chambers etc. falls in the high risk group for exposure to H_2S gas.

Any other person in a tannery or effluent treatment plant in the risk locations may be exposed to a higher concentration of H_2S gas.

Unaware and unprotected rescuers of persons who may have accidentally fallen into a tank or pit in an effluent treatment plant.

The effect on the human beings who absorb the gas through accidental inhalation ranges from drowsiness, nerval problems, loss of consciousness to death in case the concentration exceeds the prescribed threshold exposure limits.

The characteristics of the gas enable one to smell it so long as it is in very low concentration, without having an adverse effect on health of a human being. Poisoning occurs at higher concentrations only. At these levels the person loses the ability to smell it, often leading to the wrong assumption that no H_2S gas is present.

Table 1 show the symptoms and effects at specific concentrations (in part per million) in the air and time of exposure. The symptoms may vary depending on concentration of the gas in atmosphere, duration of exposure, health condition of the person exposed, smoking habits and other factors.

Generally, the symptoms of exposure to gas manifest themselves strongly in newly recruited workers.

Table 1. **Human health effects of hydrogen sulphide at various concentrations – exposure via inhalation**

Exposure in ppm	Time	Effect on unprotected person
0.03	No limit	No effect
0.03-2		Odour threshold
10	Up to 8 hours	No effect
10-20		Threshold for eye irritation
20-200		Headache, nausea, general weakness, pain in legs
200-500	1 min.	Irritation of nose & throat, vertigo, blurring of vision, loss of consciousness lasting a few minutes
500-900	1 min.	Profound coma, muscular spasm-twitching convulsions, disorientation after recovery
900 and above	1 min.	Instant coma and death

ppm = part per million in air

A concentration of 15 ppm is internationally acknowledged as short term exposure limit (STEL) also indicating the maximum permissible exposure level in the work environment. However recently, the American Conference of Governmental Industrial Hygienists (ACGIH) changed their recommended threshold limit values (TLVs) for airborne hydrogen sulphide (H_2S) exposure. From 1976 thru 2009, the ACGIH 8-hour time weighted average TLV (TLV-TWA) was 10 parts per million (ppm), and the 15-minute short-term exposure limit TLV (TLV-STEL) was 15 ppm. In 2010 the ACGIH adopted a TLV-TWA of 1 ppm, and a TLV-STEL of 5 ppm for H_2S. In the United States the ACGIH TLV is not a regulatory limit, however these guidelines are developed from scientific data gathered by ACGIH over several years on the health effects of H_2S exposure and represent exposures that “all workers may

be repeatedly exposed, day after day, over a working lifetime, without adverse health effects".

HYDROGEN SULPHIDE FORMATION AND RISKS LOCATIONS

The liberation and presence of hydrogen sulphide gas is likely in the following locations in tanneries and effluent treatment plants:

IN TANNERIES

- ⇨ Drainage and sewage pits where effluent from liming, deliming and pickling stage may be mixed (e.g. tannery internal pre-treatment system).
- ⇨ In drums, paddles or pits during pickling, when acid is added to inadequately delimed skins and hides still containing sulphide from the liming stage.
- ⇨ In drums, paddles or pits which are used for liming, deliming as well as pickling.
- ⇨ In chemical stores due to intermixing of incompatible chemicals, mainly acids with sodium sulphide flakes (due to poor handling and storage practices, chemical accident e.g. acid spills, etc.).
- ⇨ Reaction of liming liquors, or other liquors containing sulphide, with acidic liquors (e.g. acids, pickle, tanning) can cause a hazardous release of hydrogen sulphide.

Inadequate process safety management practices are often the cause of such reactive accidents

IN EFFLUENT TREATMENT PLANTS

- ⇨ Any manhole and opening of the collection and conveyance system.
- ⇨ Receiving sumps and screen chambers.
- ⇨ Anaerobic tanks and lagoons.
- ⇨ Valve chambers and any other pit.

⇨ Any tank containing some sludge, even if nearly empty

In the other locations in tanneries or effluent treatment plants, H_2S gas concentration is usually in the non dangerous range.

CONFINED SPACES

A confined space as is a location that is large enough and so configured that an employee can bodily enter and perform assigned work, has limited or restricted means for entry or exit and is not designed for continuous employee occupancy. Confined spaces exist in every tannery and effluent treatment plant and many workers may come into contact with one during the course of their work. Confined spaces include storage bins, sewers, tanks, vaults, pits and many more locations that have cramped spaces and narrow openings.

A permit-required confined space have one or more of the following characteristics:

1. Contains or has a potential to contain a hazardous atmosphere;
2. Contains a material that has the potential for engulfing an entrant;
3. Has an internal configuration such that an entrant could be trapped or asphyxiated by inwardly converging walls or by a floor which slopes downward and tapers to a smaller cross-section; or
4. Contains any other recognized serious safety or health hazard (such as a fall hazard).

In tanneries most of confined spaces are identified as a permit-required confined space and an employee will need access to the space, then the employer must develop a written program that complies with legislation.

Permit-required confined spaces pose serious hazards. Along with difficult access, confined spaces often present problems such as inadequate ventilation or noxious air. Unfortunately, two-thirds of deaths in confined space rescue situations occur to people trying to rescue someone else. The critical nature of these rescues sometimes leads to poorly planned attempts.

Adequate planning, preparation and practice, along with proper equipment, are necessary to keep employees safe while working in and around confined spaces

FALL PROTECTION AND CONFINED SPACES

When entering a confined space, a worker must be attached to an independent lifeline for adequate fall protection and retrieval.

A complete retrieval system should consist of:

1. A man rated winch to be attached to personnel at all times during the descent and work below grade.
2. Tripod
3. Full Body Harness
4. Work Winch to raise and lower materials only.
5. PPE – helmet, working gloves, suit,
6. H_2S detector
7. Self Contained Breathing Apparatus (SCBA)

If the concept of fall protection or the use of this equipment is new to an employee involved in the confined space program, the employee must be trained in inspection and use of fall protection equipment as well as general fall protection issues.

The first fall protection consideration when working near or preparing to enter a confined space relates to the access area itself. When a hatch or cover is removed to provide access to a confined space, as is

the case with manhole covers, the opening immediately must be guarded with a railing, temporary cover or some sort of barrier to prevent an accidental fall into the space. All workers, not just those entering the confined space, need to be outfitted with fall protection. An employee inadvertently may become overwhelmed by fumes when the cover is removed, which could result in loss of consciousness. Therefore, it is important for those working near the opening to wear either a restraint lanyard, preventing them from reaching the edge of the opening, or an arrest lanyard or lifeline, to stop a fall in progress, before the cover is even removed.

PREVENTIVE MEASURES

Measures aiming at reducing the risk of liberation and harmful effects of hydrogen sulphide gas:

- ✓ Detect and monitor the level of hydrogen sulphide in risk areas
- ✓ Check storage practices of chemicals and store sulphide containing materials away from acidic materials (thus, even avoiding accidental mixing).
- ✓ Keep floats from liming and deliming separated from those from pickling and tanning.
- ✓ Have risk areas well ventilated all the time to dilute concentration of H_2S gas.
- ✓ Reduce discharge of sulphate containing streams such as from pickling and chrome tanning.
- ✓ Prohibit smoking in all risk areas.

FLOATS SEGREGATION

Hydrogen sulphide gas is very often evolved by the mixing of sulphide containing liming liquors/waste water (alkaline) and tanyard effluents (acidic), especially in deep channels and pits and at higher concentrations when the typical (warning!) smell is not pronounced. Strict segregation of alkaline and acidic streams to ensure that the pH will not fall below 9.5 is essential.

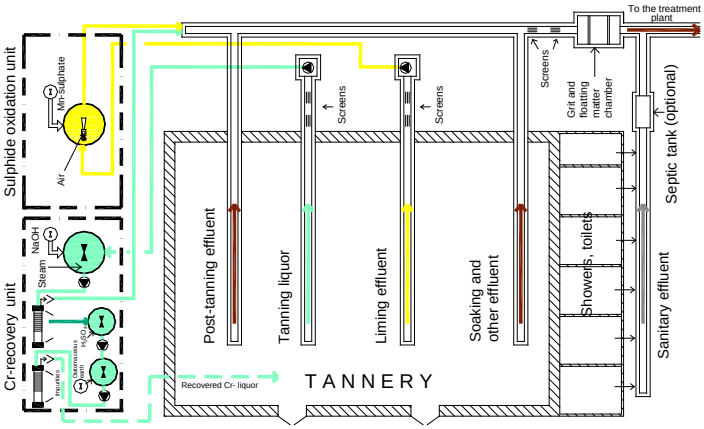

Figure 1: The main tannery streams, segregation

Hydrogen sulphide gas is quite easily eliminated by catalytic oxidation using manganese sulphate as a catalyst before being mixed with acid effluent or being discharged to the general mixing tank which generally has a pH of 8.5– 9.

It is useful to recall once again the properties of hydrogen sulphide gas, H_2S, still by far the most frequent killer in tannery accidents, mainly in inadequately ventilated spaces and especially in pits and channels.

SAFE WORK PRACTICES

DETECT AND MONITOR

If, appropriate install automatic monitoring equipment or provide personal detectors to detect the level of hydrogen sulphide.

Before letting any worker (in a tannery or effluent treatment) descend into any tank, pit or such depressed areas, **always** first test for presence of hydrogen sulphide gas.

Three primary types of instruments are used to detect and monitor H_2S exposures:

i. fixed area detectors
ii. portable area detectors, and personal detectors
iii. indicative lead acetate paper.

❖ Fixed-Area Detection stations

Fixed area detectors alert operators to leaks and releases in the workplace and have typically been set to alarm at concentrations of 10 to 15 ppm. Fixed-area detection stations may be mounted in areas where a risk of H_2S formation is present (effluent treatment plant, beamhouse department). One or two sensors can be attached to each detection station. The stations are mounted in open areas and continuously monitor for H_2S in the work area atmosphere.

❖ Portable and personal detectors

Portable gas detection instruments allow instantaneous and accurate reading of gas concentration. Portable area detectors are used to test confined spaces and general work areas to confirm elevated levels of H_2S are not present. Personal detectors are worn by employees and will sound an audible alarm at levels of 10 to 15 ppm. A wide variety of reliable and well regarded H_2S detectors which measure and alarm in the 10 ppm range are available to industry.

- ⇨ Portable instrument for immediate reading of hydrogen sulphide gas concentration (optional with TWA. STEL. peak and average readings), using electro-chemical sensor
- ⇨ Range: 0-500 or 1000 ppm, in 1 ppm increments
- ⇨ Operating temperature: at least 0- 50 degrees Celsius
- ⇨ Operating humidity (non-condensing): <95%;
- ⇨ Pre-setting TWA and STEL (as per OSHA)
- ⇨ Audible alarm
- ⇨ Battery operated
- ⇨ Accessories: Hand aspirator for measurement of gas in pits, tanks, manholes and confined space, carrying case.

Figure 2: Personal hydrogen sulphide detector
Source: Crowcon

For personal protection personal single gas detector is compact and lightweight yet is fully ruggedized for the toughest of industrial environments. Featuring simple operation, it has a large easy to read display of gas concentration, and audible, visual and vibrating alarms in case of achieving limited concentration of hydrogen sulphide.

ACCIDENTAL RELEASE MEASURES

Uncontrolled releases should be responded to by trained personnel using pre-planned procedures. Proper protective equipment should be used. In case of a release, clear the affected area, protect people, and respond with trained personnel. Adequate fire protection must be provided.

In case H_2S gas has been detected, take measures to neutralise the gas present:

- ⇨ Sprinkle hydrogen peroxide or mix with iron sulphate.
- ⇨ Properly ventilate low areas. *Never use pure oxygen, which can react strongly with hydrogen sulphide gas.*

Remember
Hydrogen sulphide is heavier than air

Even, if no gas has been detected, make sure of the following:

1. The worker, when entering the risk areas, is wearing
   - ⇨ a safety harness with an attached life line.
   - ⇨ gloves, boots, goggles
   - ⇨ respiratory apparatus all the time.

2. Another worker outside the risk area is holding the loose end of the life line.

3. Both workers have a clear way of communicating with each other in case of an emergency.

INFORM AND TRAIN

- ⇨ Inform and train all workers, especially casual labourers, about precautionary measures and safe practices.
- ⇨ Train all workers about emergency procedures in case hydrogen sulphide is detected.
- ⇨ Affix warning signs on gas poisoning in the risk locations.

SUPERVISE AND INSTRUCT

- ✓ During maintenance work of the conveyance and collection system, have the workers supervised by an experienced person all the time.
- ✓ Make sure workers use protective equipment provided to them.

Remember!

Display of poor work practices are a result of poor managerial and supervisory practices.

EMERGENCY AND FIRST AID MEASURES

Time is the most crucial factor in rescuing victims of poisoning by hydrogen sulphide gas. Hydrogen sulphide gas, entering the human body through respiratory system and producing tissue toxicity, impairs functioning of brain due to failure of respiratory system.

MAKE HASTE SLOWLY!

In case of hydrogen sulphide gas release, be calm, methodical and quick.

1. **Protect yourself** – do not forget to use appropriate safety equipment (safety harness with life line, respiratory apparatus, gloves, boots)
2. Immediately remove victim from accident area.
3. Look for the following
   - ⇨ Is there failure of breathing and pulse?
   - ⇨ Is the poisoning light or severe?
   - ⇨ Is there severe bleeding?
   - ⇨ Is the shock light or severe?
4. Start artificial respiration, if victim is not breathing, it must begin at once as every second gained is helpful.
5. Place victim on side, face down, if unconscious.
6. Stop bleeding by pressing on the pressure point and press firmly on bleeding area with a pad.
7. Treat for shock. Place victim on the side and cover with blanket to keep warm.
8. Arrange for transport to nearest doctor or hospital and inform relatives.
9. At doctor's or hospital give attending doctor full details about accident conditions and first medical aid measures provided.

DO NOT!

- ⇨ Do not administer any drinks or food, If victim is unconscious!
- ⇨ Never induce vomiting, if victim is unconscious!

BE PREPARED!

- Review and up-date emergency plans regularly
- Train all staff in rescue operations and emergency procedures and first medical aid
- Keep leak proof breathing apparatus, safety harness with life line and first medical aid kit ready

HOW TO FIND OUT THAT IT IS HYDROGEN SULPHIDE POISONING?

⇨ There is smell of rotten egg at the accident site.

⇨ Dark discolouration of coins in the pocket of the victim may confirm presence of hydrogen sulphide gas.

TIP

To quickly diagnose degree of poisoning check for the following:

Light poisoning

- ⇨ Acute eye problems
- ⇨ Redness in the conjunctiva. blurring of vision
- ⇨ Swelling of eye lids
- ⇨ Vesicle formation on corneal surface
- ⇨ Convulsions

Severe poisoning

- ⇨ black discolouration of skin
- ⇨ slate blue cyanosis

Poisoning symptoms from exposure to hydrogen sulphide gas over a longer period are:

- ⇨ headache
- ⇨ vertigo
- ⇨ dry mouth
- ⇨ stomach distress
- ⇨ general weakness
- ⇨ disorientation
- ⇨ high blood pressures

HOW TO BE PREPARED?

Proper training and equipment to perform quick, safe rescue is essential in any operation where risk locations or confined spaces must be entered.

- ⇨ Keep the emergency equipment exclusively ready for emergency purposes in properly marked locations *(see annex for list of equipment and specifications).*
- ⇨ Keep all safety equipment clean and in good order.
- ⇨ Inform first aiders and yourself on required measures to be taken in case of hydrogen sulphide gas poisoning.
- ⇨ Practice rescue of accident victims from all risk locations in your tannery or effluent treatment plant, in particular from tanks, pits, manholes.
- ⇨ Prominently display contact numbers of fire brigade and hospital.
- ⇨ Liaise with next fire brigade to assure their immediate assistance in case of emergency.
- ⇨ Liaise with your company doctor and the next hospital to assure their preparedness in case of an emergency.

RESPIRATORY PROTECTION

SELF CONTAINING BREATHING APPARATUS (SCBA)

SCBA stands for Self Contained Breathing Apparatus. The term "self-contained" indicates that the breathing apparatus does not require a remote air supply. SCBA means that the equipment provides a micro environment disconnected from any external pollutants or chemicals. SCBA is suitable for entry and rescue work in Immediate Danger to Life and Health (IDLH) areas

Any SCBA consists of three main components:

- ⇨ A high pressure cylinder
- ⇨ Regulator to control the pressure
- ⇨ Inhalation unit (mouthpiece and mouth mask) are linked together and attached to a carrying frame.

Figure 3: SCBA

SCBA mask provides the wearer a well-equipped environment with fresh air delivered to the mask breathing air from a tank. The air tank, which is under high pressure, usually will provide enough air up to an hour, but a larger version available last longer. This is required under circumstances where there is no safe air supply available, and where the operator must be provided with a safe supply of air to enable them to survive.

Check whether there is a filling station nearby your place!

AIR LINE SUPPLY SYSTEM

The airline trolley and supply system use airline breathing apparatus, providing safe and proven solutions for virtually any breathable airline situation.

The airline trolley can provide a compressed air cylinder supply for one or two wearers for one and a half hours or for one person for three hours respectively.

- ⇨ Manually or electric motor operated centrifugal blower
- ⇨ Wire embedded rubber air hose (length at least 15 meters per face mask) with adjustable couplings
- ⇨ One or two fill vision face masks with inhalation and exhalation valves, double sealing frame, speech diaphragm, self demisting inner mask with corrugated tube
- ⇨ Safety belt with manifold harness belt.

Figure 4: Airline supply system

Personal protective equipment

- Elbow length gloves. PVC
- Full body suit made of PVC or similar material suit for maintenance work in manholes, pits and tanks
- Full body type harness, light weight, made of washable canvas, straps for shoulder, waist and legs

FALL PROTECTION EQUIPMENT

When selecting fall protection equipment for confined space entry, exit and rescue, there are three main components:

- ⇨ an anchorage,
- ⇨ body support
- ⇨ connector.

If the confined space requires vertical entry, and there is not a fixed ladder, a davit arm or a tripod is necessary. A tripod is a recommended for task-specific work such as manhole entry. Tripods easily are set-up by one worker and can be transported from one location to another. One limitation of the tripod is the size of the opening it can accommodate.

Figure 5: Tripod; winch; full body harness

Proper equipment to perform quick, safe rescue is essential in any operation where confined spaces must be entered. Typically, the safest and most effective fall protection systems include self-retracting lifelines. These lifelines should be integrated with a retrieval system in all confined space entry situations; this allows the entry attendant to perform a non-entry rescue, should it become necessary.

FIRST MEDICAL AID KIT

with minimum content:

- ⇨ Antiseptic lotion, powder or cream
- ⇨ Sterile dressing in dust proof packets
- ⇨ Adhesive plaster
- ⇨ Triangular bandage
- ⇨ Scissors
- ⇨ Bum cream
- ⇨ Resuscitation pump or Amyl nitrate capsules (for use in case of gas poisoning)

PREVENTING TRAGEDY

There may be no better indication of the need for confined space safety training and equipment than an example. Workers at a tannery effluent treatment plant, were trying to fix a faulty pump at the bottom of a manhole. One worker was at the bottom of the hole when he was overcome by hydrogen sulphide fumes. Another worker went down the hole to attempt to rescue him, but he was overcome as well. Another worker followed, then a fourth. All four men tragically died trying to rescue one another.

These types of deaths are preventable. Had the workers been using gas detection devices and wearing harnesses connected to a winch or self retracting lifeline with rescue capabilities, the early warning could have given the entry attendant and other workers enough time to engage the winch and perform a non-entry rescue.

Identifying potentially hazardous spaces and putting together a written program is minimum requirement to prevent accidents and tragedy. Furthermore, proper equipment selection and training along with practice entering, exiting and performing rescues is necessary to keep employees safe while working in and around confined spaces.

NEVER attempt a rescue in an area that may contain hydrogen sulphide without using appropriate respiratory protection and without being trained to perform such

HYDROGEN SULPHIDE GAS AT ONE LOOK

IMPORTANT DATA	
Chemical name **Formula**	Hydrogen sulphide H_2S
Physical state	Colourless gas, with characteristic odour of rotten eggs in low concentrations
Physical danger	The gas is heavier than air and may travel along the ground; distant ignition possible.
Chemical danger	Heating may cause violent combustion or explosions. The gas decomposes on burning producing toxic gas including sulphur dioxide. Reacts violently with strong oxidants, causing fire and explosion hazard. Attacks many metals and some plastics.
Routes of exposure	The substance can be absorbed into the body by inhalation
Inhalation risk	A harmful concentration of this gas in the air will be reached very quickly on loss of containment
Occupational exposure limits	10 ppm over eight hours (as TWA) 15 ppm over 15 min (as STEL)
Effects of short term exposure	The gas irritates the eyes and the respiratory tract. Inhalation of the gas may cause lung oedema and affect the central nervous system. Exposure may result in coma and death. Some effects may be delayed (see note)
Physical properties	Boiling point:-60°C Melting point: -85°C Relative vapour density (air=1): 1.19 Flash point: Flammable gas Auto-ignition temp.: 260°C Explosive limits (vol% in air): 4.3-46%
Environmental data	The substance is very toxic to aquatic organisms

HAZARD	SYMPTONS	PREVENTION/ FIRST AID
Fire	Highly flammable	Avoid open fire flame
Explosion	Gas/air mixture are explosive	Use explosion proof electrical equipment and lighting

EXPOSURE	SYMPTONS	PREVENTION/ FIRST AID
Inhalation	Cough, dizziness, headache, sore throat, lung oedema unconsciousness	Ventilation, local exhaust or breathing protection; fresh air; rest; artificial respiration; medical attention
Eyes	Redness. Pain.	Safety goggles, or eye protection in combination with breathing protection
Ingestion		Do not eat, drink or smoke during work

Note:

- ⇨ Use of alcoholic beverages enhances the harmful effect.
- ⇨ The symptoms of lung oedema often do not manifest until a few hours have passed and they are aggravated by physical effort. Rest and medical observation are therefore essential.
- ⇨ Specific treatment is necessary in case of poisoning with this substance: the appropriate means with instructions must be available.
- ⇨ The substance blocks the sense of smell.
- ⇨ The odour warning when the exposure limit is exceeded is insufficient.