Workplace Health and Safety

Bulletin

WORK SAFE ALBERTA

Hydrogen Sulphide at the Work Site

Hydrogen sulphide (H_2S) occurs naturally in the earth in crude petroleum, natural gas reservoirs, volcanic gases and hot springs. Hydrogen sulphide is also produced from

- the breakdown of human and animal wastes by bacteria,
- industrial activities such as food processing,
- coke ovens,
- kraft paper mills,
- rayon textile manufacturing,
- wastewater treatment facilities,
- sulphur production,
- tar and asphalt manufacturing plants,
- tanneries, and
- refineries.

In Alberta, workers are exposed to hydrogen sulphide most often during drilling and production of natural gas, crude oil and petroleum products. Hydrogen sulphide can accumulate in sewers, sewage treatment plants or hide storage pits in the tanning industry. Well drillers, tunnel workers and miners may be exposed when underground pockets of hydrogen sulphide are encountered. Hydrogen sulphide is also a raw material used to manufacture inorganic sulphides, sulphuric acid and thiols (also known as mercaptans).

In Alberta, workers are exposed to hydrogen sulphide (H2S) most often during drilling and production of natural gas, crude oil and petroleum products.

Government of Alberta
Employment and Immigration

Hydrogen sulphide is a colourless and poisonous flammable gas with a strong smell of rotten eggs. It is also known as sewer gas and stink damp. It can be detected by smell at concentrations ranging from 0.01-0.3 parts per million (ppm). **However, relying solely on its odour is not a good idea because at concentrations above 100 ppm it deadens a person's sense of smell within a few minutes**. The pure gas is heavier than air and can collect in low areas such as sewers, pits, tunnels and gullies.

However, relying solely on its odour is not a good idea because at concentrations above 100 ppm it deadens a person's sense of smell within a few minutes.

Hydrogen sulphide can react with rust or corrosion deposits on equipment to form iron sulphide. This reaction occurs in an oxygen free atmosphere where hydrogen sulphide gas is present or where the concentration of hydrogen sulphide is greater than that of oxygen. This happens most often in closed vessels, tanks or pipelines. Iron sulphide is a pyrophoric material, which means that it can ignite spontaneously when it is exposed to air. For more information on this hazard and safe work practices, refer to the following Workplace Health and Safety Bulletin:

http://employment.alberta.ca/documents/WHS/WHS-PUB_pi002.pdf
Controlling Explosive Atmospheres in Vessels, Tanks and Piping Systems (PI002)

High concentrations (between 4.3% and 46% of gas by volume in air) can catch fire and explode if there is a source of ignition. When the gas is burned, other toxic gases, such as sulphur dioxide are formed. Hydrogen sulphide is incompatible with strong oxidizers, such as nitric acid or chlorine trifluoride, and may react violently or ignite spontaneously. When hydrogen sulphide is released into the air, it will form sulphur dioxide and sulphuric acid in the atmosphere.

Health effects

Hydrogen sulphide is extremely toxic. Workers are exposed when they inhale hydrogen sulphide in air, and this toxic gas is quickly absorbed by the lungs. It is believed that exposure to hydrogen sulphide prevents the brain from using oxygen by inhibiting the enzyme cytochrome oxidase.

Short-term exposure

Short–term (acute) exposure to hydrogen sulphide can cause irritation to the nose, throat, eyes and lungs. Exposure to higher concentrations can cause very serious health effects, and even death. Table 1 provides a summary of the health effects from short-term exposure.

Table 1: Health effects from short-term exposure to hydrogen sulphide

Concentration (ppm)	Health effect
0.01 - 0.3	Odour threshold
1-20	Offensive odour, possible nausea, tearing of the eyes or headaches with prolonged exposure
20-50	Nose, throat and lung irritation; digestive upset and loss of appetite; sense of smell starts to become fatigued; acute conjunctivitis may occur (pain, tearing and light sensitivity)
100-200	Severe nose, throat and lung irritation; ability to smell odour completely disappears.
250-500	Pulmonary edema (build up of fluid in the lungs)
500	Severe lung irritation, excitement, headache, dizziness, staggering, sudden collapse (knockdown), unconsciousness and death within a few hours, loss of memory for the period of exposure
500-1000	Respiratory paralysis, irregular heart beat, collapse and death without rescue.
>1000	Rapid collapse and death

It is important to note that the symptoms of pulmonary edema (build up of fluid in the lungs), such as chest pain or shortness of breath, can be delayed for up to 72 hours after exposure.

Workers who survive a serious hydrogen sulphide exposure (concentrations above 500 ppm) may recover completely or suffer long-term health effects. In some cases, there can be permanent nervous system effects, such as fatigue, anxiety, irritability, as well as impaired learning and memory. Some of these effects may be the result of less oxygen reaching the brain during a severe hydrogen sulphide exposure. Workers who experience knockdown (unconsciousness) tend to have a greater chance of having permanent effects to the respiratory system, with symptoms such as shortness of breath on exertion, wheezing, chest tightness, hypersensitive airways and permanent lung damage.

Some research indicates that short-term exposure to lower concentrations of hydrogen sulphide (1-10 ppm) may cause health effects. However, significantly more research is needed before such effects can be confirmed.

Long-term exposure

Hydrogen sulphide does not accumulate in the body. Repeated or prolonged exposure has been reported to cause low blood pressure, headache, nausea, loss of appetite, eye inflammation and chronic cough.

The following health effects due to long-term (chronic) exposure to hydrogen sulphide have also been reported in the scientific literature:

- reduced lung function (smoking together with hydrogen sulphide exposure may worsen this effect),
- neurological effects such as headaches, nausea, depression, weakness, personality changes. Exposure to other reduced sulphur gases such as dimethyl sulphide and thiols (mercaptans) at the same time may contribute to this effect,
- eye irritation,
- irritation to the mucous membranes, and
- damage to the cardiovascular system.

More research is needed to confirm the human health effects from chronic exposure.

More research is needed to confirm the human health effects from chronic exposure.

Hydrogen sulphide has not been classified as a carcinogen by the International Agency for Research on Cancer (IARC).

Treatment of hydrogen sulphide exposure

Workers who are overcome by hydrogen sulphide must be quickly and carefully rescued to ensure that additional victims are not created in the process. Workers who do not have the necessary protective equipment must not attempt to rescue others. Rescue workers must be provided with, and wear, a positive pressure supplied air respirator and other personal protective equipment appropriate to the hazards that are present. Resuscitation must be prompt and close medical supervision of the individual is required for at least 48 hours following exposure.

Workers who are overcome by hydrogen sulphide must be quickly and carefully rescued to ensure that additional victims are not created in the process.

First aid measures

- Immediately remove the victim from further exposure. Designated rescuers must wear properly fitting, positive pressure self-contained breathing apparatus (SCBA) and other required safety equipment appropriate to the work site.
- If the worker is not breathing, apply cardio-pulmonary resuscitation in the nearest safe area.
- Remove contaminated clothing, but keep the individual warm.
- Keep conscious individuals at rest.
- Be aware of possible accompanying injuries (e.g. the victim may have fallen when they were overcome) and treat them accordingly.
- If the victim's eyes are red and painful, flush with large amounts of clean water for at least 15 minutes.
- Ensure the worker receives medical care as soon as possible. The worker must not be allowed to return to work or other activities.

Preventive measures

Avoiding exposure to hydrogen sulphide is the best way to protect health. Options that should be considered include the use of the following (in order of preference):

- engineering controls
- administrative controls
- personal protective equipment.

Avoiding exposure to hydrogen sulphide is the best way to protect health.

Engineering controls

Engineering controls are used to eliminate exposure to a substance. Engineering controls remove the substance from the air or provide a barrier between the worker and the substance. Examples of engineering controls that can be used to prevent exposure to hydrogen sulphide include the use of:

- ventilation to control hydrogen sulphide concentrations in the air
- closed systems that vent to a flare, and
- treatment methods to remove hydrogen sulphide from liquid and gas streams.

Flaring

Flaring is the controlled burning of gas. It is a technique that is used by the petroleum industry to remove waste gases from crude oil. However, when hydrogen sulphide is burned, another toxic gas, sulphur dioxide, is produced. Flaring can also contribute to emissions of greenhouse gases. For these reasons, flaring is becoming a less popular way of dealing with waste gases in petroleum products.

For more information:

The Alberta Energy and Utilities Board has published a document "Guide 60: Upstream Petroleum Industry Flaring, Incinerating and Venting", which is available on line at:

www.ercb.ca/docs/documents/directives/Directive060.pdf

The Canadian Association of Petroleum Producers (CAPP) also has a number of publications on sour gas flaring and venting available on their web site:

www.capp.ca/library/publications/SourGasFlaringVenting/Pages/default.aspx#h8aS7Pttbzbg

Chemical treatment

Chemical treatment can be used to remove hydrogen sulphide from crude oil, gas and water streams. Hydrogen sulphide treatment for crude oil is used to reduce overall sulphur levels in the product. The most common method is called the Claus Process (hydrogen sulphide is separated from the gas stream by extraction and then converted to less toxic substances using combustion and chemical reaction). Where hydrogen sulphide is present in off-gases from wastewater treatment or other industrial processes, there are a variety of scrubbers and filters that can be used. In water, hydrogen sulphide can be treated by chlorination, manganese greensand filters, aeration, ozonation, activated carbon and biofilters.

Hydrogen sulphide treatment of drilling fluids, along with proper pH control, should be used to reduce the amount of hydrogen sulphide that is recirculated. Caution is needed when handling drilling fluid that has been exposed to hydrogen sulphide. This is because hydrogen sulphide can move from the liquid into the vapour space of the storage tank and will be released when the tank is opened.

Caution is needed when handling drilling fluid that has been exposed to hydrogen sulphide.

Sulphide stress cracking

Hydrogen sulphide gas is corrosive to metals and can cause metal fatigue, leading to sulphide stress cracking. Metals that are satisfactory for equipment used in hydrogen sulphide environments are described in the National Association of Corrosion Engineers (NACE) Standards:

Hydrogen sulphide gas is corrosive to metals and can cause metal fatigue leading to sulphide stress cracking.

- MR0175/ISO15156, *Petroleum and Natural Gas Industries – Materials for use in H_2S-Containing Environments in Oil and Gas Production*, and
- MR0103-2003, *Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments.*

The Canadian Petroleum Safety Council (Enform), Alberta Recommended Practice (ARP) 2 *"Completing and Servicing Critical Sour Gas Wells"* provides a summary of industry recommended practices for sour gas wells, including details on equipment to be used in sour gas environments. It also includes information from the NACE standards. It is available at:

http://www2.enform.ca/862

The NACE standards are available for purchase at:

www.nace.org

Administrative controls

Work practices that can be implemented to reduce potential exposure to hydrogen sulphide include:

- educating workers about the hazards associated with hydrogen sulphide and symptoms of overexposure. Workers must participate in training and monitoring programs in the workplace. Courses such as "H_2S Alive" and First Aid are recommended when workers may be exposed to hydrogen sulphide at the work site.
- developing safe work procedures for environments that may contain hydrogen sulphide, and training workers in these procedures.
- proper maintenance and training for engineering controls and other equipment used to control exposure.
- using personal or area monitoring equipment where there are potential sources of hydrogen sulphide. This equipment should have audible alarms that will warn workers when concentrations are too high. These instruments should be set to alarm at a level no higher than the Occupational Exposure Limit (OEL) for hydrogen sulphide.

Courses such as "H2S Alive" and First Aid are recommended when workers may be exposed to hydrogen sulphide at the work site.

Safe work practices

Evaluating the hazard from hydrogen sulphide must be included in the hazard assessment for the work site. Table 2 provides some sample questions that should be asked when assessing safety procedures for hydrogen sulphide.

Table 2: Sample Questions to Ask About Hydrogen Sulphide at the Work Site

Question
1. Has the potential for a release of H_2S into the atmosphere at levels of 10 ppm or greater been evaluated?
2. Does every worker on the work site know where and how an uncontrolled release of H_2S could occur?
3. Does every worker know what precautions to take when there is a potential for an H_2S release?
4. Do workers know what to do in case of an emergency?
5. Have the areas which require the mandatory use of breathing apparatus been identified?
6. Does every worker who could be exposed to H_2S have appropriate training?
7. Is there a procedure to test the atmosphere for H_2S concentrations and are workers trained in this procedure?
8. Is all the necessary equipment readily available to workers who require it?
9. Are you certain that your workers follow safe work practices developed by your organization?
10. Have you determined if you need a code of practice for operations involving H_2S?

If the answer to any of the questions in Table 2 is "no", workers may be in danger from exposure to hydrogen sulphide.

For more information:

Recommended safe work practices for the petroleum industry can be found in the American Petroleum Institute publications:

- *Recommended Practice for Safe Drilling of Wells Containing Hydrogen Sulfide*, API Recommended Practice 49
- *Conducting Oil and Gas Processing and Gas Processing Plant Operations Involving Hydrogen Sulfide*, API Recommended Practice 55

These publications are available online at:

http://www.api.org/Standards/epstandards

Enform has additional documents on work practices for sour gas. These documents can be found online at:

http://www.enform.ca/publications/irps/criticalsourdrilling.aspx
Critical Sour Drilling, IRP1

http://www.enform.ca/media/3583/irp2_final_2007.pdf
Completing and Servicing Critical Sour Wells, ARP2

Monitoring for hydrogen sulphide

There is a variety of monitoring equipment available, depending on the purpose of the monitoring. It is important to select monitoring equipment that fits the needs of the work environment. When selecting monitoring equipment, the user should also check for substances that could interfere with the equipment. For example, some gases such as hydrogen can interfere with the instrument sensor and mask the presence of hydrogen sulphide. Hydrogen sulphide monitors may also detect other reduced sulphur compounds such as thiols (mercaptans).

Monitoring equipment for hydrogen sulphide should be set to alarm at no higher than the OEL for hydrogen sulphide. It is also very important that the instrument be calibrated and operated properly. More information on the proper operation of monitoring equipment for hydrogen sulphide is provided in the section of this document on regulatory requirements.

Hydrogen sulphide is frequently encountered in work environments (e.g. oil and gas industry, sewage treatment plants) where other flammable or combustible gases are present. In these work environments, it is recommended that monitoring be done for both hydrogen sulphide and other flammable/combustible vapours so the hazards can be properly assessed.

Hydrogen sulphide is frequently encountered in work environments (e.g. oil and gas industry, sewage treatment plants) where other flammable or combustible gases are present.

Personal Protective Equipment

If it is not practicable or feasible to use engineering or administrative controls to reduce the potential for exposure to hydrogen sulphide, or if these measures are not sufficient, the employer must provide workers with appropriate personal protective equipment. Respiratory protective equipment is used to protect workers from inhaling airborne contaminants. There are many types of respirators available and it is important to select the correct level of respiratory protection depending on the type of work being done and the airborne concentrations that may be encountered.

Since hydrogen sulphide is irritating to the eyes, air-tight goggles or full-face respirator masks should be worn.

A full-facepiece positive pressure supplied air respirator is needed for work areas where hydrogen sulphide concentrations exceed the OEL. The National Institute for Occupational Safety and Health (NIOSH) specifies an IDLH (immediately dangerous to life or health) concentration for hydrogen sulphide of 100 ppm. NIOSH allows the use of air purifying respirators for hydrogen sulphide only for escape purposes at concentrations below the IDLH concentration. Above the IDLH concentrations, or for emergency or planned entry into unknown concentrations, a full-facepiece positive pressure supplied air respirator must be used. Whatever the type of respirator used, the worker must be clean-shaven where it seals to the skin of the face and must be fit-tested for the type of equipment being used.

A full-facepiece positive pressure supplied air respirator is needed for work areas where hydrogen sulphide concentrations exceed the OEL.

For more information:

http://employment.alberta.ca/documents/WHS/WHS-PUB_ppe004.pdf
Guideline for the Development of a Code of Practice for Respiratory Protective Equipment – PPE004

http://employment.alberta.ca/documents/WHS/WHS-PUB_ppe001.pdf
Respiratory Protective Equipment: An Employers' Guide – PPE001

www.cdc.gov/niosh/npg/npg.html
NIOSH Pocket Guide to Chemical Hazards

www.cdc/gov/niosh/idlh/idlh-1.html
Documentation for Immediately Dangerous to Life or Health Concentrations (IDLH)

CSA Standard, Z94.4-02, *Selection, Use and Care of Respirators*

Although the use of personal protective equipment may initially seem to be less costly, there will be ongoing maintenance and training costs. Workers must be trained on the protective equipment they are using. Employers must monitor use and ensure the protective equipment is properly maintained. In some cases, personal protective equipment can create a hazard to workers, e.g. heat stress, limited vision, allergic reactions to the equipment material. These issues must be evaluated when personal protective equipment is selected.

Regulatory requirements

Exposure limits

The Alberta occupational health and safety (OHS) legislation has specific requirements related to hydrogen sulphide. The 8-hour OEL is 10 ppm, and the ceiling OEL is 15 ppm. If work shifts are longer than 8 hours, the exposure limit must be reduced.

For more information:

http://employment.alberta.ca/documents/WHS/WHS-PUB_ch055.pdf
The Effects of Unusual Work Schedules and Concurrent Exposures on Occupational Exposure Limits – CH055

OELs apply to all workers who may be directly or indirectly exposed to hydrogen sulphide in the workplace. It is important to note that OELs represent standards for the protection of most healthy workers.

Code of practice

A code of practice is required for work sites where there may be more than 10 kg of hydrogen sulphide present as a pure substance, or in a mixture in a concentration over 0.1% by weight and at least 10 kg of hydrogen sulphide in aggregate. The code of practice should include:

- company policy and persons responsible for the code of practice
- safe work procedures
- required personal protective equipment
- worker training requirements
- emergency procedures and designated emergency personnel.

A code of practice is required for work sites where there may be more than 10 kg of hydrogen sulphide present as a pure substance, or in a mixture ion a concentration over 0.1% by weight and at least 10 kg of hydrogen sulphide in aggregate.

CAPP has produced the document "Occupational Health and Safety of Hydrogen Sulphide (H_2S)" to assist in the development of a code of practice for hydrogen sulphide. It is available online at:

http://www.capp.ca/library/publications/healthSafety/pages/pubInfo.aspx?DocId=61443#Ju1xKdcgKETf

Exposure monitoring

When conducting monitoring for hydrogen sulphide to comply with the OEL, a method specified in Section 20 of the OHS Code must be used.

When a direct-reading instrument is used to measure hydrogen sulphide exposure, it must be used, calibrated and maintained according to the manufacturer's instructions. In addition, the employer is responsible to ensure that the instrument is operating properly when it is used at the work site. More details on calibration of direct-reading instruments is included in Appendix A of this document.

When a direct-reading instrument is used to measure hydrogen sulphide exposure, it must be used, calibrated and maintained according to the manufacturer's instructions.

Additional requirements

Additional work site requirements include:

- Development of safe work procedures.
- Ensuring that an emergency response plan is developed for the work site and that personnel are designated for emergency response activities. These workers must be provided with required training, personal protective equipment and other equipment needed.
- Training of workers on health hazards associated with exposure to hydrogen sulphide and the safe work procedures developed by the employer.
- Ensuring that the need for ventilation is properly assessed and systems that are installed are properly designed and maintained. Workers also need to be trained on the proper operation of these systems.
- Provision of appropriate protective equipment, including respirators, where concentrations of hydrogen sulphide cannot be controlled below safe limits and determined during the hazard assessment.

Calibration of Direct Reading Instruments

"Calibration" refers to an instrument's measuring accuracy relative to a known concentration of a gas. Gas detectors measure the concentration of a gas in an air sample by comparing the sensor's response to its response to a calibration gas. The response of the instrument to the calibration gas serves as a reference point for the instrument. If an instrument's reference point shifts, the reading will shift accordingly and will be unreliable. This is called "calibration drift" and it happens to all detectors over time.

Common causes of calibration drift include:
- gradual degradation of the sensors and drift in electronic components over time
- constant exposure to and use in extreme environment conditions (for example where there are large shifts in ambient temperature or humidity, or high levels of airborne particulates)
- exposure to high (over-range) concentrations of the target gases or vapours
- chronic or acute exposure of the sensors to agents which will poison or inhibit the sensors
- harsh storage and operating conditions (for example dropping the instrument or submerging it in water)
- normal handling of the equipment over time

There are two methods used to verify the accuracy of an instrument, a "bump" test or a full calibration. A bump test is a field calibration of the instrument where it is exposed to a gas containing a known concentration of the substance of interest. The reading on the instrument is compared to the gas concentration, and if it responds within an acceptable tolerance range of the actual concentration, then calibration is verified. The acceptable tolerance will generally be within 10-20% of the concentration used (the user should check with the manufacturer of the instrument to confirm the acceptable tolerance range). A full calibration is much more rigorous, and is usually done when the instrument is serviced at the factory.

Direct-reading instruments used for measuring exposure to hydrogen sulphide must be bump tested each day they are used at the work site to ensure that they are working properly, unless the employer can demonstrate by other means that the instrument readings are accurate. The International Safety Equipment Association (ISEA) has issued a position statement about verification of calibration for direct-reading instruments. They state that the instrument should be bump tested or fully calibrated using the appropriate test gas in accordance with the manufacturer's instructions each day that it is used. If the instrument fails a bump test, it must then be adjusted by a full calibration. More frequent bump tests may be needed if there are environmental conditions that could affect the performance of the sensor (such as sensor poisons). Bump tests may be done less frequently under some conditions, but the interval between testing should never exceed 30 days. Less frequent verification may be appropriate if tests demonstrate that daily adjustments are not needed. This is done during a period of initial use of at least 10 days in the intended atmosphere. During this time, calibration is verified daily to ensure that there is nothing in the environment that may poison the sensors. This period of initial use must be long enough to ensure that the sensors are exposed to all conditions that may adversely affect them. (Note that conditions will be different at each work site; an instrument checked at one work site will need to be re-checked if it is used at another work site.)

For more information:

The policy statement from ISEA can be obtained from their website at:

- www.safetyequipment.org

The US Occupational Safety and Health Administration (OSHA) has a bulletin available online called "Verification of Calibration for Direct-Reading Portable Gas Monitors" at

- www.osha.gov/dts/shib/shib050404.html

The Instrumentation, Systems and Automation Society (ISA) has issued a standard relating to the use of direct-reading instruments for hydrogen sulphide;

- ISA-92.0.01, Part 1-1998 *Performance Requirements for Toxic Gas Detection Instruments: Hydrogen Sulfide*

- ISA-RP92.0.02, Part II-1998 *Installation, Operation and Maintenance of Toxic Gas Detection Instruments: Hydrogen Sulfide*

These documents can be purchased from ISA online at www.isa.org.

Contact us:

Province-Wide Contact Centre

☎ Edmonton & surrounding area:
780-415-8690

☎ Throughout Alberta:
1-866-415-8690

Deaf or hearing impaired
- In Edmonton: **780-427-9999**

or
- **1-800-232-7215** throughout Alberta

Web Site

www.worksafely.org

Getting copies of OHS Act, Regulation & Code:

Queen's Printer

www.qp.gov.ab.ca

☎ Edmonton 780-427-4952

Workplace Health and Safety

http://employment.alberta.ca/whs-ohs

Call any Government of Alberta office toll-free
Dial 310-0000, then the area code and telephone number you want to reach