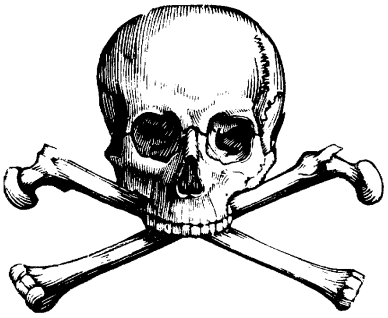
Annual Workplace Safety and Health Conference

HYDROGEN SULFIDE (H_2S) AWARENESS

SCOTT MEASUREMENT SERVICE

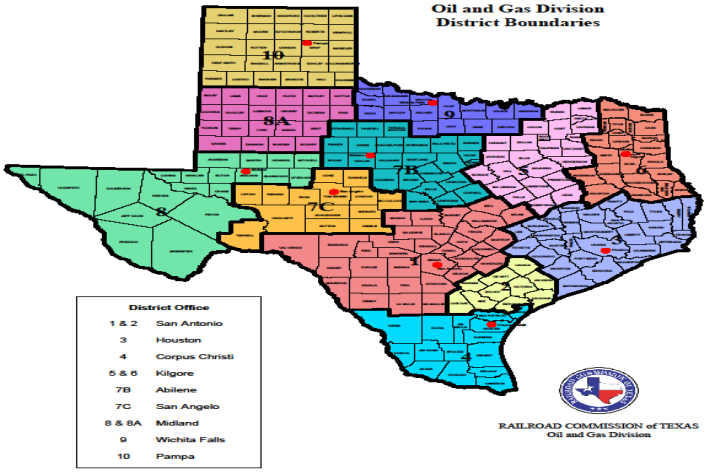
DWC
Division of Workers' Compensation
Texas Department of Insurance

HYDROGEN SULFIDE (H_2S)



SAFETY TRAINING COURSE

Oil and Gas Division District Boundaries

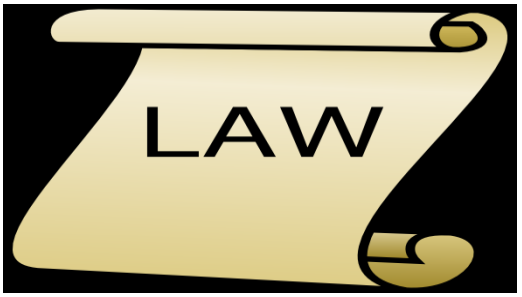


IT'S THE LAW!!

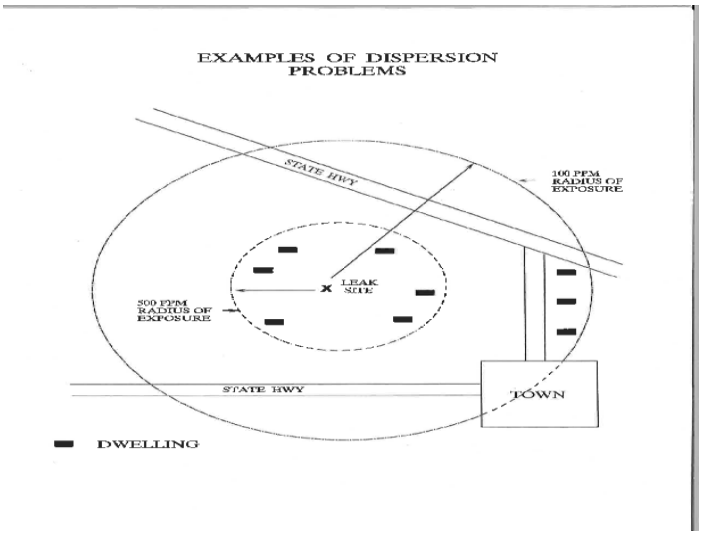
- Statewide Rule 36 is a safety rule designed to protect the general public from the hazards of H_2S resulting from intentional and accidental releases.
- Rule 36 requires immediate notification to the Railroad Commission of any accidental release of H_2S of sufficient volume that presents a hazard and of any H_2S related accident.
- Rule 36 specifies a requirement for a contingency plan. The contingency plan is NOT a game plan but a logical step-by-step approach to an emergency. Whenever the radius of exposure includes a public area or is equal to or exceeds 3000 ft, a contingency plan is required.

Form H-9

- For drilling operations, Form H-9 must be filed 30 days prior to commencement of drilling operations. A form H-9 must be filed for a well in a field classified as an H_2S field even if the well contains no H_2s gas.
- In the state of Texas, all persons working in the oil field where H2S concentrations are known MUST complete a H_2S certification course ANNUALLY.

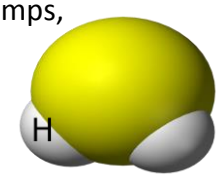


Dispersion Problems

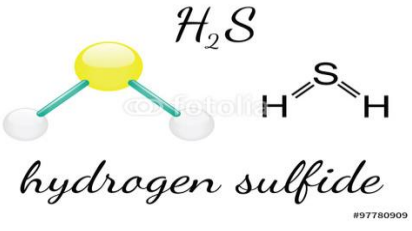


What Is Hydrogen Sulfide?

- H_2S is the chemical symbol for Hydrogen Sulfide
- Two parts hydrogen and one part sulfur
- Other names: Dihydrogen Monosulfide-Sewer Gas-Sulfur Gas
- Highly toxic. **IT CAN KILL YOU!!!**
- Result of decomposition of organic matter, plant or animal: anything carbon based-in the absence of oxygen gas. This process is commonly known as anaerobic digestion. It may develop in low-oxygen environments such as swamps, sewers, and polluted water.



H_2S

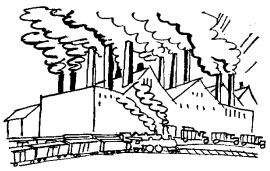


- H_2S also occurs in volcanic gases, natural gas, and in some sources of well water.
- H_2S is a naturally occurring gas mixed with natural gas or dissolved in oil or brine and is released upon exposure to atmospheric conditions.
- The human body produces small amounts of H_2S and uses it as a signaling molecule. H_2S delivers information to proteins in the body. The proteins act on information to perform critical function in the body.

HYDROGEN SULFIDE SOURCES

Naturally Occurring

- **Oilfields - Drilling & Production**
- **Mines**
- **Volcanoes**



Chemical Processes

By-Product of Chemical Process

- **Pulp/Paper Industry**
- **Felt Makers**

Decay or Putrefaction of Organic Material

- **Fishing Industry**
- **Tanneries**
- **Municipal Sewers**
- **Landfills**

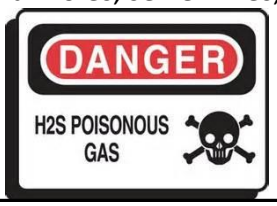
HAZARDOUS CHARACTERISTICS

- H_2S is the second most toxic gas known to man.
- The most toxic is hydrogen cyanide
- PEL of H_2S = 10 ppm
- PEL of HCN = 10 ppm

TOXIC

PROPERTIES and CHARACTERISTICS

- Colorless gas – cannot see it
- Small quantity has an unpleasant odor commonly described as rotten eggs
- Cannot be smelled in large concentration
- Paralyzes olfactory nerve in nose and destroys sense of smell temporarily
- Flammable: LEL of 4.3 percent & UEL of 46 percent
- Heavier than air, with a vapor density of 1.189 @ 32 F and will settle in low-lying areas such as manholes, sewer lines, and manure pits. 19 percent heavier than air.



PROPERTIES and CHARACTERISTICS

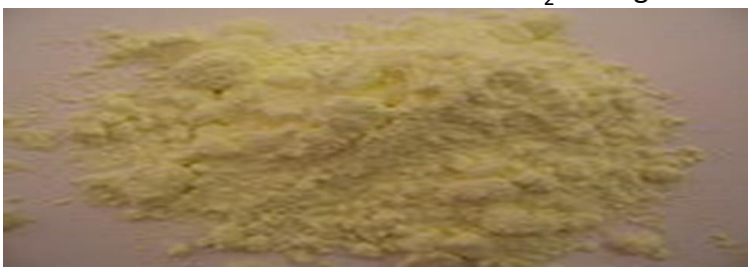
- Auto ignition temperature is 500 F; smoking prohibited
- Will explode when ignited
- Excess H_2S is frequently burned or flared
- Burns with pale blue flame
- H_2S is soluble in both water and liquid hydrocar
- H_2S dissolves in water forming a weak hydro sulfurous acid
- Heat and agitation causes H_2S gas to be released from fluids

PROPERTIES and CHARACTERISTICS

- H_2S is readily dispersed by the wind.
- Always try to stay upwind of the H_2S source.
- If trapped downwind: move crosswind then upwind to rescue yourself.
- Use "buddy system."
- Can create a pyrophoric substance called iron sulfide in pipes and tanks, which will spontaneously ignite upon contact with air.
- Can cause sulfide stress cracking in metal.

Iron Sulfide

- H_2S reacts with iron and steel, which forms iron sulfide that can be ignite spontaneously when in contact with humid air or water!
- Iron sulfide treated with acids results in H_2S being released.



Corrosive

- H_2S dissolves in water to form a weak acid that corrodes and pits metals.

Metallurgy

H_2S may react with iron and steel, causing hydrogen embrittlement or sulfide stress cracking. This lowers safety factors in tubular and pressure vessels.

SO_2 Sulfur Dioxide

- Produces **Sulfur Dioxide (SO_2)** also toxic, colorless, smells like burned match, very offensive to respiratory system and eyes.
- You may feel SO_2 on your skin if your skin is wet.
- Sulfur dioxide-SO_2 is acid gas and can cause chemical pneumonia and scarring of the lungs.
- SO_2 is heavier that air and twice as heavy as H_2S.
- SO_2 is not flammable and will not burn because it is a by-product of the incomplete combustion of H_2S.

Sulfur Dioxide

- Short-term exposures to high levels of sulfur dioxide can be life-threatening.
- Exposure to 100 ppm of sulfur dioxide is considered immediately dangerous to life and health (IDLH).
- PEL for SO_2 is 2 ppm.
- Sulfur dioxide may cause heart problems and respiratory disorders in younger children and elders.

Toxicity

- H_2S is highly toxic. This gas will kill you!!!
- It will suffocate you by attaching itself to the red blood cells in your bloodstream and prevent them from carrying oxygen to the tissues and organs of the body.
- As the toxic gas builds up in your bloodstream, you will find yourself breathing faster and faster. The faster you breathe, the more H_2S enters your lungs. It will paralyze the respiratory control center in your brain.
- You will cease to breathe and cardiac arrest may follow. Depending on the concentration of the gas, this can happen in as fast as 3 minutes or less.
- Alcohol or drugs can enhance or quicken this process.

Measurement of Gas

- PPM = parts of gas per million parts of air by volume (i.e., 1 percent = 10,000 ppm)
- If one inch represents one ppm of gas, this would be like comparing one inch in 15.5 miles in distance.
- If one second represents one ppm of gas, this would be like comparing one second in 11.5 days.

Acceptable Exposure Limits

- What is a part per million? PPM
- One part per million = one part in a million parts
- 1 ounce in 31.25 tons, or 1 minute in 1.9 years
- Permissive exposure limit (PEL) – Maximum 10 ppm during an 8-hour workday. Also known as time-weighted average (TWA).
- Short-term exposure limit – maximum 15 ppm for 15 minutes four times per workday.

H_2S Exposure Levels

- PEL – 10 ppm / 8-hr. TWA
- PEL – 6.6 ppm / 12-hr. TWA
- PEL – 5 ppm / 16-hr. TWA
- STEL – 15 ppm / 15 min
- Ceiling concentration – 50 ppm / once 10 min
- Human lethal concentration 100-800 ppm / 5 min.
- Revised IDLH – 100 ppm

Recommended Exposure Limits

- The American Conference of Governmental Industrial Hygienists (ACGIH) recommended lower thresholds for detection of hazardous gases in 2010.
- ACGIH put into place the following limits for H2S:
- Threshold limit valve (TLV): 1 ppm
- Short-term exposure level (STEL): 5 ppm
- These are just guidelines – **NOT** legal requirements. ACGIH believes that these lower exposure levels will create a safer work environment.

Toxicity Table

- **0.01-1.5 ppm** – Odor Threshold – when rotten egg smell is noticeable to approximately 50 percent of a human panel that can detect the presence of an odor without being able to identify it.
- **2-5 ppm** – Moderate rotten egg odor – prolonged exposure may cause nausea, tearing of eyes, headaches, or loss of sleep.
- **10 ppm** – OSHA-permissible exposure limit (PEL). Beginning of eye irritation.
- **20 ppm** – Acceptable ceiling concentration established by OSHA. Develop possible fatigue, loss of appetite, headache, irritability, poor memory, and dizziness.
- **50-100 ppm** – Eye irritation leading up to eye damage – “gas eye.” Loss of smell after 2-15 minutes (olfactory fatigue). Altered breathing, drowsiness after 15-30 minutes. Death may occur after 48 hours.

Toxicity Table

- **100-150 ppm** – Olfactory nerve is paralyzed after a few inhalations, and sense of smell disappears.
- **200-300 ppm** – Pulmonary edema with the possibility of death.
- **500-700 ppm** – Staggering, collapse in 5 minutes. Strong stimulation of the central nervous system leading to loss of breathing.
- **800 ppm** – Lethal concentration for 50 percent of humans for 5 minutes of exposure.
- **1000 ppm** – Immediate collapse with loss of breathing, even after inhalation of a single breath.

Engineering Controls

Effective in certain situations. Three primary engineering controls used with H_2S:

- Containment
- Ventilation – natural or manufactured
- Flaring – flare stack

Ventilation

- An exhaust ventilation and enclosure to control the amount of H_2S in the air may be used.
- Stringent control measures, such as process enclosure to prevent product release into the workplace, should be used.
- Use non-sparking ventilation systems; approved, explosion-proof equipment; and intrinsically safe electrical systems in areas where H_2S is used or stored. Filter the contaminated air before it is directly exhausted to the environment.

Flare Stack

- If the flare stack is burning away 100,000ppm H_2S and is burning at 80 percent efficiency, what is the ppm of H_2S in the exhaust plume?

100,000ppm.
The flare stack is burning 80% of the volume ***not*** the concentration.

Factors Affecting Dispersion of Gas

- Wind
- Topographic condition and vegetation
- Temperature of gas vs. ambient temperature
- Humidity - moisture content of gas
- Composition of gas - buoyancy of gas
- Leak mechanics and escape rate
- Plume rise

Safety Controls

- Tailgate meetings
- Education
- Buddy system
- Be wind-aware
- Eliminate ignition sources
- Keep non-essential personnel out of area
- Checking safety equipment

H_2S Detection Equipment

- Four ways to detect H_2S
  - Lead acetate strips
  - Colorimetric tubes
  - Hand-help portable electronic detectors
  - Fixed electronic detection systems
  - **YOU CANNOT RELY ON YOUR NOSE TO TELL HOW MUCH POISON GAS (H_2S) IS PRESENT!!!!**
  - **Olfactory accommodation/Paralysis Occurs about 50-100 PPM**

H_2S Protection

- Before entering areas where hydrogen sulfide may be present, air must be tested for the presence and concentration by a qualified person using air monitoring equipment, such as H_2S detector tubes or a multi-gas meter that detects the gas.
- If the gas is present, the space/area must be ventilated continually to remove the gas.
- If the gas cannot be removed, the person entering the area must use appropriate respiratory protection and any other necessary personal protective, rescue, and communication equipment.
- Entering a dangerous IDLH area(at or above 100 ppm) can only be made using a full face piece pressure demand self-contained breathing apparatus (SCBA) with a minimum service life of 30 minutes, or a combination full face piece pressure demand supplied air respirator with an auxiliary self-contained air supply.

Colorimetric Tubes

- Colorimetric tubes contain a chemical reagent which is sealed in a glass tube. The tube is graduated to read in parts per million (PPM) or percentage. To use the tube, break both ends and insert the end pointing toward the arrow into the pump. When the pump is activated, it will draw or pump a measured amount of air into and through the tube.
- If there is any H_2S in the sample of air, the chemical reagent will stain. The stain will travel a portion of the length of the tube depending on how strong the concentration of gas was.
- NEVER USE ONE NAME-BRAND TUBE IN A DIFFERENT NAME-BRAND PUMP!!
- Tubes have a limited shelf life of approximately 2 years.
- Colorimetric tubes are site-specific. You must check each area separately.

Portable Electronic Monitors

- Battery operated with sensors cells with an audible alarm and sometimes a flashing light.
- Some monitors have multi-gas detection capabilities.
- All monitors should be bump-tested daily.

Personal Monitor Limitations

- The battery and sensor are sensitive.
- They work from a chemical reaction.
- The reaction uses the chemical up.
- When the chemical is used up, the battery or sensor dies.

Fixed H_2S Monitor

- Fixed H_2S monitors are usually found on driling rigs or in gas plants.
- Monitor is set up in a centralized location.
- Sensors are remotely located at various locations around the hazard site and then wired back into a central monitoring station and alarms.

H_2S Location Sign In/Out Box

- Typical sign-in box containing a sign-in sheet.
- Everyone must sign in and out when entering or leaving the location.

H_2S Location Entry Warning Sign

- Typical entry warning sign used on H_2S locations.
- A colored flag will be placed in the corner of the sign to indicate current danger status.
- When an alarm sounds, leave the area for a safe zone and do not return until the area is **SAFE**.

H2s Condition Level

CONDITION GREEN

CONDITION YELLOW

CONDITION RED

Condition Green

- **Possible Danger – No Alarms**
- All personnel on location must have a current one-year H_2S certificate from a formal H_2S course.
- Beards and sideburns must be trimmed as necessary to ensure that the seal on the SCBA face piece will be free of hair.
- Upon arrival at well site, report to supervisor to receive H_2S briefing.
- **NO SMOKING** except in specifically designated areas.
- Inspect and practice putting on your specific breathing apparatus.
- Know the location of the **Safe Briefing and Assembly Areas**.
- Remain **Wind Conscious** at all times. Be prepared to move across and **Upwind** in the event of an emergency involving an H_2S release.

Condition Yellow

- **Moderate Danger – Intermittent Audible Alarm and Yellow Flashing Light – 10 - 50 ppm H_2S**
- Go to **UPWIND** safe briefing area if you are not specifically designated to control the well.
- Be alert for change in weather conditions.
- Check your safety equipment for readiness.
- During an emergency, use the **BUDDY SYSTEM** to prevent anyone from entering or being left alone in a contaminated area.
- Report any indications of H_2S to a supervisor.
- Extinguish **ALL SOURCES OF IGNITION** after an alarm has been activated.

Condition Red

- **Extreme Danger - Continuous Audible Alarm and Red Flashing Light. > 50 ppm H_2S**
- **Same precautions as in Condition "Yellow."**
- **Don your SCBA.**
- **Remain in safe briefing area or assembly area and await instructions for evacuation.**
- **Provide assistance to anyone who may be injured by toxic gases.**
- **Personnel must ensure that their breathing apparatus is properly fitted and operational before entering an H_2S-contaminated area.**

Personal Protective Equipment

- Supplied air respirator
- SCBA
- Work line
- Escape pack

H_2S Protective Equipment

- When hydrogen sulfide cannot be removed from the air, the only way to protect yourself from H_2S gas effects is to remove yourself from gas by:
- physically removing yourself from area, or
- putting on a self-contained breathing apparatus (SCBA) or work-line device.

Supplied Air Respirators

- Self-contained breathing apparatus
- Airline respirator
- Escape pack

Air-Purifying Respirators

No !
Not !!
Never !!!

Breathing Apparatus

- All breathing apparatus contain **Class D breathing air – not oxygen!**
- ELSA Escape Air Pack – usually 5 minutes air for **escape only**.
- Supplied Air Apparatus – attached to large bottles of breathing air or a compressor with hoses. Also contains a 5-minute bottle of air worn by worker to be used for moving to another work-line or escape from contaminated area. The hose restricts the user to return by the same route taken when entering the area.

Breathing Apparatus

- Self Contained Breathing Apparatus (SCBA) – used to work in contaminated area, rescue of downed worker, or escape from contaminated area.
- Only positive pressure regulators are allowed in H_2S environments. This means the air flows constantly from the regulator to the face piece, keeping a constant pressure inside the face piece.

How Much Air??

- One 30-minute cylinder contains 45 ft^3
- At maximum work: 4.6 ft^3 minute
- 30-minute pack lasts less than 10 minutes!!!
- All workers using a breathing apparatus should have an attendant or helper ready and available. Workers in H_2S areas must know how to perform artificial respiratior

H_2S Air Cascade Trailer

Special Problems in Respirator Use

- Facial hair – facial hair between the sealing surface of the respirator face piece and the wearer's skin may prevent an effective seal.
- Contact lenses – may be worn with full face respirator.
- Corrective spectacles – should not be worn if equipped with temple bars or straps that interfere with the respirator face seal.
- Psychological disturbances – claustrophobia is a definite hazard to the wearer of a respirator.
- Facial disfigurements – scars, false teeth, bad acne, and broken jaws all effect the integrity of the seal.

Signs of H_2S Exposure

- Eye irritation
- Confusion
- Respiratory irritation
- Pulmonary edema
- Excitement
- Headaches
- Dizziness
- Disorientation
- Nausea

Target Organs

- The primary route of exposure is inhalation, and the gas is rapidly absorbed by the lungs.
- When a person breathes H_2S gas, it goes directly through the lungs and into the bloodstream.
- To protect itself, the body oxidizes the H_2S as rapidly as possible into a harmless compound.

Nose

Lungs

Target Organs

- If so much gas is inhaled that the body cannot oxidize all of it, the H_2S builds up in the blood and poisons the individual.
- The nerve center in the brain that controls breathing is paralyzed, the lungs stop working, and the person is asphyxiated.

Liver

Respiratory control center

Individual Variables

Smoker/Non-Smoker

Physical Condition

Drug/Alcohol Compatibility

Age

Body mass

Four Factors in How H_2S Affects an Individual

- Duration – length of time a person is exposed.
- Frequency – how often a person has been exposed.
- Intensity – what concentration a person was exposed to.
- Variables associated with the individual
  - Individual susceptibility
  - Person's physiological makeup:
    - Body mass
    - Overall physical condition
    - Age
    - Smoker/nonsmoker
    - Personal biochemistry

H_2S Incidents

- Accidents associated with H_2S continue to occur. People tend to disregard the danger, and down they go. Many times, they die.
- Hydrogen sulfide was used by the British Army as a chemical weapon during World War I. It was not considered to be an ideal war gas, but, while other gases were in short supply, it was used on two occasions in 1916.

H_2S Incidents

- **Incident #1** – On February 2, 1975, an experimental gas injection well pipe connection ruptured in Denver City, Texas and killed nine people. H_2S leaked from a gas injection well 150 yards from the home of a resident.
- It was a damp, foggy morning with barely a breeze — conditions that proved to be deadly. Found were the bodies of seven people in two running vehicles. The eighth family member was found next to one of the cars. The ninth victim was an Atlantic Richfield Company pumper who had gone to check on the oil well upon hearing a gas leak alarm. Authorities later found him in his pickup in a ditch on the side of the road.
- The Denver City tragedy spurred a state resolution calling for the Texas Railroad Commission to investigate recent hydrogen sulfide deaths and warn residents living near gas injection wells.

H_2S Incidents

- **Incident # 2** – January 11, 2010, Garden City, TX – one worker was killed and three others were injured in a Texas gas processing plant due to a leakage of H_2S gas. The accident occurred at an oilfield site in Glasscock County.
- They were working atop a tank battery when apparently one of the workers fell down as a result of "knockout effect." In higher concentrations, it desensitizes the human nose taking away sense of smell, and hence the "knockout effect".
- What is surprising in this case is that all workers were reportedly wearing hydrogen sulfide gas monitors, which are supposed to measure H_2S concentration in the ambient air and sound an alarm if dangerous levels are detected.

H_2S Incidents

- It is not clear whether the instruments did not work, or whether the workers simply ignored them. The workers were rushed via an air ambulance to a hospital, but it was too late for one of them.
- **Incident #3**, 2005 – a vacuum truck driver in Pearsall went to gauge a tank that he was told had 25ppm H_2S produced fluid in it prior to taking a load. When he opened the tank hatch, he got hit in the face with a large concentration of H_2S and died before he could do much more than turn around.
- All of these incidents once again highlight the safety precautions that must be taken when dealing with hydrogen sulfide gas.

Contingency Plan

When approaching the jobsite, take precautions to ensure a safe entry.

- Observe condition signs and audiovisual alarms.
- Check for wind direction.
- Look for personnel and their activity.
- Enter the jobsite slowly.
- Have a minimum of two defined alternate escape routes, preferably roads.
- Require continuous monitoring or detections equipment, along with an adequate audiovisual system. Portable detectors provide additional safety.

Contingency Plan

- Gas ignition hazards must be eliminated. “No smoking” enforced.
- Minimum of two defined alternate escape routes, preferably roads.
- Continuous monitoring or detections equipment is required, along with an adequate audiovisual system. Portable detectors provide additional safety.
- Strategically placed explosion proof mechanical ventilators can reduce exposure.

Contingency Plan

- H_2S awareness training and regular drills are a must. Practice makes proficient.
- Observe wind direction indicators, i.e., windsocks and streamers.
- Avoid low-lying areas since H_2S is heavier than air.
- Use "buddy" system for mutual safety.
- Maintain and observe warning signs.
- Post emergency numbers.
- Locate emergency safe briefing areas at least 250 feet from source of gas.

Contingency Plan

- Evacuate in an upwind/uphill direction. Report to briefing area immediately.
- If trapped downwind, do not turn upwind and try to escape. Try to quarter the wind to get to the less concentrated areas of the gas. Then turn upwind and rescue yourself.
- Do not return to the area until someone using proper detection equipment has re-evaluated the area and approved it safe to re-enter.

KEEP CALM!!!!!

- Main point: **DO NOT PANIC**
- Don your breathing apparatus. Do not attempt a rescue until you have donned your breathing apparatus.
- Remove the victim from the hazardous area.
- Provide first aid in a safe area.

Rescue Procedures

- Do not panic.
- Report to the emergency briefing area.
- Put on full rescue unit (30-minute SCBA) before attempting a rescue, or you, too, will become a victim.
- Help anyone in distress.
- Remove the victim to fresh air immediately.

Rescue Procedures

- Remove any wet clothing from victim.
- Assure an open airway and check breathing. If breathing, maintain victim at rest and administer oxygen if available.
- If not breathing, start artificial respiration immediately. Start CPR.
- Call an ambulance and get victim medical treatment.
- Keep victim lying down, keeping the airway passage open.

Rescue Procedures

- Conserve body heat and do not leave unattended.
- If eyes are affected, wash thoroughly with clean water. Cold compresses may be helpful.
- People exposed to high concentrations of H_2S often vomit. They may need assistance in keeping their airway open once they regain consciousness.
- Victims with minor exposure and not unconscious – send to doctor to be checked and do not allow return to work until next day.
- NEVER attempt a rescue in an area that may contain H_2S without using appropriate respiratory protection and without being trained to perform such a rescue.

Conclusion

- To work in or around H_2S requires that you obtain additional specialized training to meet OSHA requirements.
- H_2S gas is dangerous to the uninformed and complacent person.

Be alert, be knowledgeable, stay alive!!