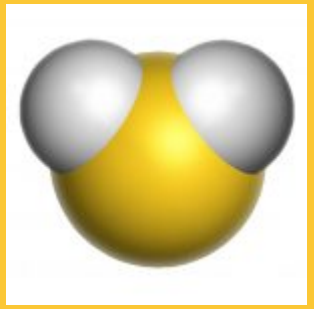
WEST EARTH SCIENCES



H_2S

May 2020

West Geomatics and Environmental Services: helping clients address water, wastewater, reclamation, remediation, closure and abandonment challenges by applying leading-edge tools, innovation and expertise combined with an uncompromising commitment to safety and sustainability.

H_2S Occurs Commonly

- *Within hydrocarbon reservoirs through microbial and thermochemical sulfate reduction*
- *By-product of microbial digestion within anaerobic (oxygen-depleted <0.1 mg/L) environments by sulfate-reducing bacteria:*

$$Sulfate\ (SO_4^{2-}) + organic\ carbon \rightarrow CO_2 + H_2S$$

- *In sewers and wastewater piping, sulfuric acid is generated when H_2S is absorbed into a film (slime) on the crown of the pipe and sulfur-oxidizing bacteria react:*

$$H_2S + O_2 \rightarrow H_2SO_4$$

- *H_2S can be found in sewers, silos, sumps, pits, ponds, mine adits, landfills, wastewater treatment plants, manure piles, hot asphalt paving, food processing, pulp and paper processing, tanning and textile manufacturing*

H2S Fatalities Occur Over Wide Spectrum of Industries

- *Agricultural operation pump house alarm investigation*
- *Grease trap vault cleaning*
- *Bulk milk tank cleaning*
- *Poultry blood wastewater tank cleaning*
- *Waste heat boiler valve replacement in sulfur plant*
- *Water well confined space*
- *Paper mill sulfuric acid spill reaction with wastewater with gas escaping through manhole cover*
- *Utility construction trench*
- *Sewer trench installation*
- *Sewer plug removal*
- *Gas plant*
- *Pump replacement machine shop*
- *Removal of old sewer pipes*
- *Sump pump replacement in wet well*
- *Asphalt mix tank chemical addition*
- *Oil battery tank gauging*
- *Heater Treater Repair*
- *Wastewater Treatment Plant leak repair*
- *Fish factory wastewater slurry pipe installation*
- *Sewer pipe cleaning*
- *Restaurant sewer pump repair*
- *Hog farm utility corridor*
- *Gas well abandonment*
- *Dry well repair*
- *Sewer lift station inspection*
- *Shipyard tank cleaning*
- *Sewer lift station repair*
- *Sewer pipe replacement*
- *Cement truck cleaning*
- *Tannery tank filling*

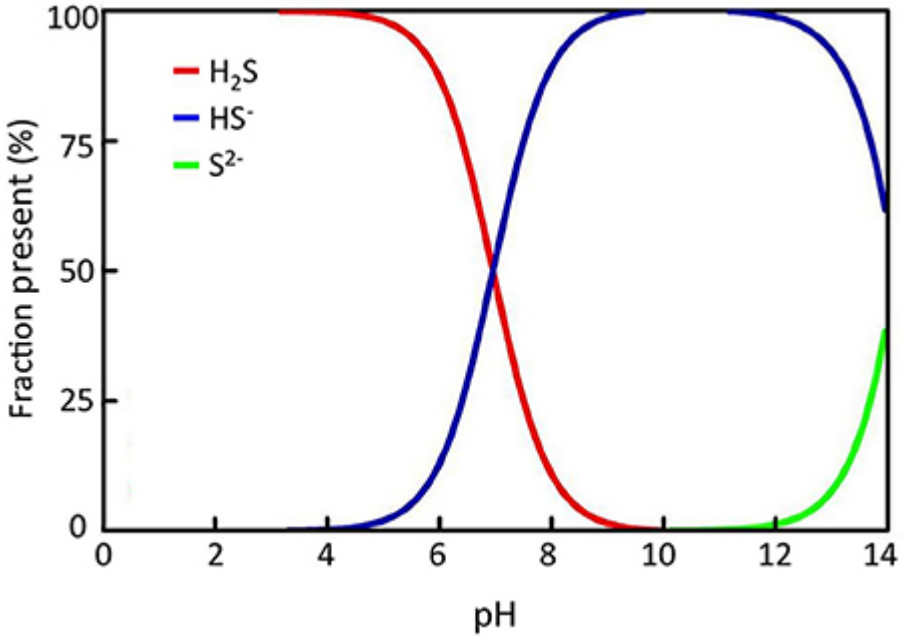
Higher risk industries

- *Hendrickson et al (2004) published analysis of 7 years of data from the 90's with important findings*
- *50% of fatalities occur within 1st year of employment*
- *Fatalities were most common in waste management (24%) and petroleum/natural gas processing (18%)*
- *Poisonings were most common in sewerage (33%) and petroleum manufacturing (23%)*
- *35% of fatalities were in companies with greater than 100 employees with 24% in companies less than 10 workers*

Physical and Chemical Properties

- *Colourless, flammable and highly toxic gas*
- *Denser than air = 1.2 times*
- *Slightly water soluble (0.4% at 20 °C)*
- *Highly flammable and explosive between 4% and 45% (concentration in air)*
- *Solubility changes with water temperature*

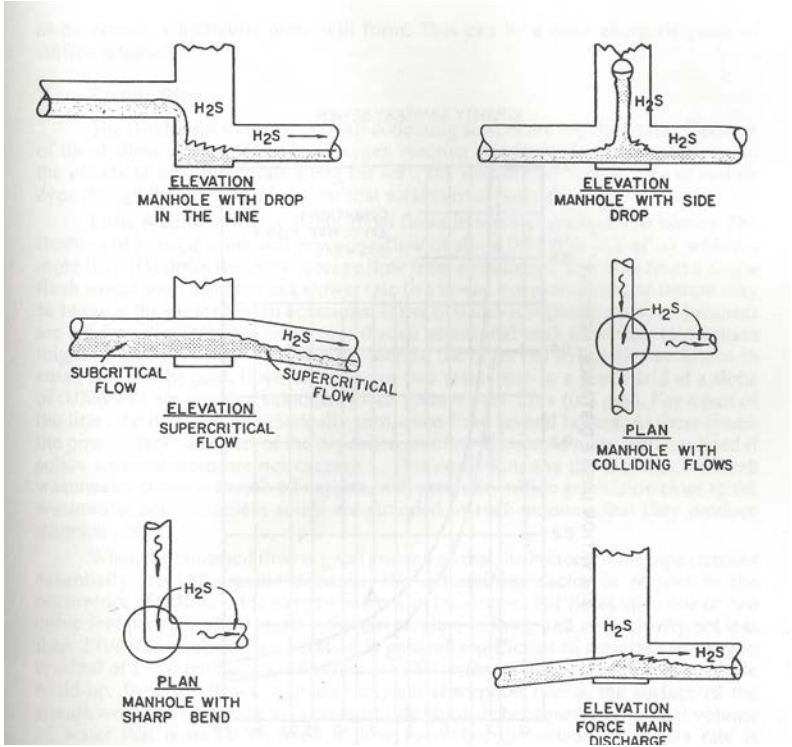
Dissolved H_2S Gas vs Dissolved HS^- Ions? It depends…



H_2S Release Affected by pH, Temperature and Turbulence

- *Lowering pH increases the amount of dissolved gas that can evolve especially in turbulent conditions*
- *Lowering temperature increases H_2S solubility in sewage: 5160 mg/L @ 10 ºC vs 3925 mg/L @ 20 ºC*
- *Increased turbulence improves H_2S release into headspace*

Examples of turbulent flows releasing H_2S



Source: ASCE Manual 69

Hierarchy of Action Levels

Criteria	Description	Threshold
Olfactory detection	Offensive smell	as low as 0.5 ppb
Sewer bylaws	Prohibited substance	0
Sewer bylaws	Restricted substance	Dissolved sulphide <1 ppm in effluent
ACGIH (CUPE)	8-hour Threshold Limit Value (TLV)	1 ppm
ACGIH (CUPE)	15-minute Short-Term Exposure Limit (STEL)	5 ppm
Alberta OH&S Regulation 87-2009	8-hour Occupational Exposure Limit (OEL)	10 ppm
Alberta OH&S Regulation 87-2009	15-minute ceiling (OEL)	15 ppm
Respiratory Distress	Irritation nose, throat, lungs	50 ppm
National Institute for Occupational Safety and Health (NIOSH)	Immediate Danger to Life of Health (IDLH)	100 ppm
Lethal	Cardiac arrest	1000 ppm

Key Considerations for Managing Safety

- *Identify potential sources of H_2S especially anaerobic digestion of organic matter*
- *Identify downstream conditions that can affect releases especially chemical addition, turbulence, change in pH, change in temperature*
- *Address upset conditions that disturb equilibrium of system*
- *Provide adequate detection: both process and personal*
- *Implement engineering controls to prevent generation*
- *Adopt operating protocols to react immediately*

H_2S Treatment Options

- *Technology Selection Depends Upon Desired Outcome:*
  - *meeting effluent discharge criteria*
  - *odour elimination*
  - *occupational health and safety*
  - *reduce damage to infrastructure*
- *Technology types:*
  - *physical-mechanical*
  - *chemical*
  - *biological*
  - *combinations*

H_2S Treatment Technologies: High Water Volume

Technology	Description
Modular Stripper-Polisher	5-stage process (1) inlet separator (2) natural gas mixer (3) flash vessel (4) polishing chemical (5) off-gas to recovery or flare
Conventional Stripper (Debolt)	5-stage process (1) inlet separator (2) degassing tower (3) stripping tower (4) polishing chemical (5) off-gas to incinerator
Oxidation: Hydrogen peroxide H_2O_2 (Permian)	5 stage process (1) oxidant addition (2) reactor (3) filtration (5 µm) (4) residual scavenger (5) elemental sulfur disposal
Oxidation: Chlorine dioxide ClO_2 (Permian)	5-stage process (1) oxidant addition (2) reactor (3) filtration (5 µm) (4) residual scavenger (5) elemental sulfur disposal
Oxidation: ozone (Permian)	4-stage process (1) hydrodynamic cavitation (2) ozonation (3) acoustic cavitation (4) electrochemical oxidation
Scavenger (Permian)	4-stage process (1) gas scrubber (2) scavenger (3) tank scrubber (4) sweet water disposal/recycle
Triazine (Common)	Direct injection or contactor tower.

H_2S Treatment Technologies: Low Volume

Technology	Description
Chlorine dioxide ClO_2	Prevent formation of H_2S (water). Applied at high doses to remove biofilm layer without forming colloidal sulfur.
Sodium Nitrate $NaNO_3$	Prevent formation of H_2S (water). Applied to retard septicity by providing alternative source of oxygen to anaerobic microorganisms rather than sulfate. $BOD + NO_3^- \rightarrow N_2 + CO_2 + biomass$
Sodium Chlorite $NaClO_2$	Remove H_2S (water). Selectively oxidizes H_2S without reacting with ammonia or forming chlorinated organics. Used for remote sites for long duration control. $2H_2S + NaClO_2 \rightarrow 2H_2O + NaCl$
Hydrogen Peroxide H_2O_2	Remove H_2S (water). Oxidizes H_2S and decomposes into O_2 and H_2O. $H_2S + H_2O_2 \rightarrow S^o + 2H_2O$ ($pH < 8.5$) $H_2S + 4H_2O \rightarrow SO_4^{2-} + 2H_2O$ ($pH > 8.5$)
Nitrate NO3	Removal (water). Bacteria utilize nitrate for bioxidation of H_2S. $8NO_3^- + 5H_2S \rightarrow 5SO_4^{2-} + 4N_2$
Iron Salts: Ferrous Fe^{2+} Ferric Fe^{3+}	Removal (water). React with dissolved H_2S to form precipitate. $Fe^{2+} + HS^- \rightarrow FeS + H^+$ $2Fe^{3+} + 3HS^- \rightarrow Fe_2S_3 + 3H^+$
Iron Sponge	Removal (gas). React with H2S to produce water and ferric sulfide. $FeO_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O$
Carbon Absorption	Impregnated with sodium hydroxide (NaOH) or potassium hydroxide (KOH) to increase affinity for H_2S
Scrubbing	Liquid packed bed or misting system in which foul air is mixed with pH-controlled water or vapour

Variety of Treatment Applications

Beverly Hills WTP

Horn River Flowback

Produced Water and Flowback

Detection Methods

- *Gas detection tubes: colorimetric test in which H_2S reacts with lead acetate coated beads (Gastec, Matheson-Kitagawa)*
- *Passive sampler badges (Morphix)*
- *Electrochemical handheld (Odalog, Jerome)*
- *Electrochemical fixed (Cti)*
- *Tunable diode laser fixed (Galvanic)*
- *Tape-based fixed (Galvanic)*
- *Open path laser fixed (Boreal)*

Due Diligence Factors

- *H_2S Alive Training*
- *Engineering Controls*
- *Detection Equipment*
- *Personal Protective Equipment*

Lessons-Learned

- *Identify conditions that generate H_2S*
- *Understand how changes in water chemistry alter availability: pH, T and turbulence*
- *Understand how changes in air flow distribute H_2S*
- *Address root causes of potential problems with engineering controls*
- *Ensure sufficient treatment capacity is in place to deal with upsets*
- *Ensure personal monitors in place where there is still a risk of exposure*
- *Evacuate first: ask questions later*

Questions or Suggestions

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