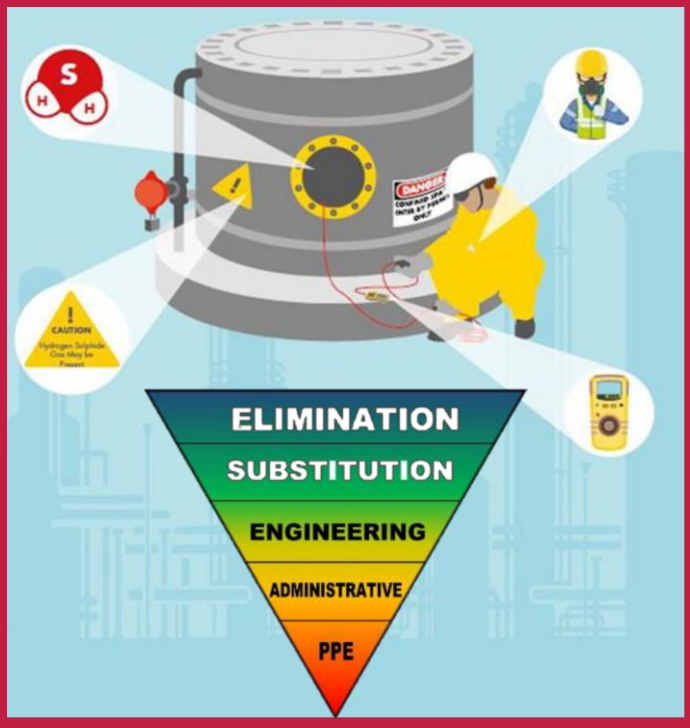
An AIChE Technology Alliance

CCPS

Center for Chemical Process Safety

Golden Rules of Process Safety for:

Hydrogen Sulfide



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Core Team Members:

Denise Chastain-Knight, Chair	Exida
Della Mann	Vice Chair
Warren Greenfield	CCPS Consultant
Denise Albrecht	3M
Kevin Campbell	Shell
Walt Frank	CCPS Emeritus
Anil Gokhale	CCPS Staff
Mike Hazzan	Acutech
Ng Ern Huay	Petronas
Pete Lodal	D&H Process Safety
Frank Renshaw	CCPS Emeritus
Louisa Nara	CCPS Staff
Linda Bergeron	CCPS Emeritus
Jeff Fox	CCPS Emeritus
Curtis Clements	Chemours

Sub Team Hydrogen Sulfide Golden Rule Team Members:

Della Mann, Lead	CCPS Emeritus
Gary Amideneau	CCPS Staff
Andy Crerand	Shell
Andrew Moulder	Inter Pipeline
Jason Vercher	Arkema

The collective industrial experience and knowledge of the team members make this guideline especially valuable to those who develop and manage process safety programs and management systems.

Before publication, all CCPS guidelines are subjected to a peer review process. CCPS gratefully acknowledges the thoughtful comments and suggestions of the peer reviewers. Their work enhanced the accuracy and clarity of this guideline.

Peer reviewers for the Golden Rules of Process Safety for Hydrogen Sulfide:

Steven Betteridge	Shell
Danielle Brown	Buckeye Partners
Andrew Goddard	Arkema
Rizal B Harris Wong	Petronas

Although the peer reviewers provided comments and suggestions, they were not asked to endorse this guideline and did not review the final manuscript before its release.

The Center for Chemical Process Safety was established by the American Institute of Chemical Engineers in 1985 to focus on the engineering and management practices to prevent and mitigate major incidents involving the release of hazardous chemicals and hydrocarbons. CCPS is active worldwide through its comprehensive publishing program, annual technical conference, research, and instructional material for undergraduate engineering education. For more information about CCPS, please call (+1) 646-495-1371, e-mail ccps@aiche.org, or visit www.aiche.org/ccps

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Golden Rules for Hydrogen Sulfide (H_2S)

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Golden Rules for Hydrogen Sulfide (H_2S)

Golden Rule #1: Always understand and respect the hazardous properties of H_2S

Golden Rule #1: Always understand and respect the hazardous properties of H_2S

❖ Why:

1) H_2S is toxic at extremely low concentrations.
2) H_2S is flammable [1].
3) The presence of H_2S is hard to detect, as the gas is colorless.
4) H_2S smells like rotten eggs but at high H_2S concentrations, people will lose their ability to smell the gas as it deadens the sense of smell.
5) H_2S is heavier than air, and it will accumulate in low-lying areas.
6) When H_2S burns, it gives off sulfur dioxide (SO_2), which is toxic.
7) H_2S can result from the reaction of some sulfur-bearing compounds in contact with acidic solutions.
8) H_2S can combine with water to form sulfuric acid (H_2SO_4) which is a corrosive acid [2].
9) Rust (iron oxide) converts to iron sulfide when in the presence of H_2S. Iron Sulfide can spontaneously ignite to produce a fire (i.e., it is pyrophoric).
10) H_2S is a very aggressive form of hydrates (i.e., H_2S readily forms one of the highest temperature hydrates in the presence of water). In the production, processing, or transportation of sour oil or gas, flow restrictions can occur due to the formation of H_2S hydrates [3].
11) A false sense of safety can exist, for example when:
    a) Employees, contractors, and visitors have little to no experience with H_2S.
    b) The potential for H_2S exposure is not understood.
    c) Previous experiences with H_2S did not result in injury. This can marginalize the potential hazard and harm from H_2S.
12) Incident History:
    a) On the evening of October 26, 2019, a pump inside a pump house failed, resulting in the release of water containing H_2S. An employee drove to the facility to address a pump oil level alarm. After entering the pump house, the employee was overcome by H_2S gas. Around 9:30 p.m., having not heard back from her husband for a few hours, the employee's wife drove to the pump house with their two children in her personal vehicle to check on him. It appears she entered the pump house to look for her husband and then she was overcome by H_2S gas. Emergency responders, arriving later, noticed two children in the back seat of the wife's car. An emergency responder put on protective gear, including a self-contained breathing apparatus (SCBA) and entered the pump house. The H_2S gas exposure was fatal for both the employee and his wife [4]. The emergency responders rescued the two children from the car.

       The learning from this incident relevant to this Golden Rule is that management and staff did not understand the H_2S hazard as evidenced by:
       (1) Failure to wear required personal protective equipment (i.e., failure to wear the company-provided personal H_2S detector)
       (2) Ineffective lockout / tagout
       (3) Inadequate mechanical ventilation design leading to H_2S confinement in the pump house
       (4) Non-functioning H_2S fixed detectors and alarm system
       (5) Deficient site security

(6) Inadequate signage/comprehension of the situation and potential harm in a pump house where there was equipment that contained H_2S, see Figure 1 for appropriate signage.

Figure 1 Be aware of the toxic hazards of H_2S before you take action

Source: Shutterstock.com

b) On December 23, 2003, at 9:55 pm, a gas well blew out resulting in a natural gas and toxic H_2S gas cloud extending 30m high. This cloud covered 25 square kilometers (10 square miles) and resulted in 234 fatalities, over 1000 injuries, and hundreds of livestock fatalities. There was a delay of around 1.5 hours before safety officials were informed. Mountainous topography led to the heavy H_2S collecting in populated low-level locations. Figure 2 shows the area affected. Overall, 60,000 people were evacuated. Specialist teams arrived in the affected areas on the fourth day. On the fifth day the release was brought under control, and one day after that people started returning home [5].

The learning relevant to this Golden Rule is that there was no understanding nor respect for the hazards of H_2S. Each of the following shortcomings would not have existed if these hazards had been understood:

(1) At the time, regulations did not consider the extent of the H_2S hazard and allowed houses to be built within 30 m (98 feet) of the well.
(2) Operational procedures were not followed.
(3) The incident was reported too late for effective emergency response.
(4) Emergency response was initially carried out with little knowledge and a lack of equipment.

Golden Rules for Hydrogen Sulfide (H_2S)

Golden Rule #1: Always understand and respect the hazardous properties of H_2S

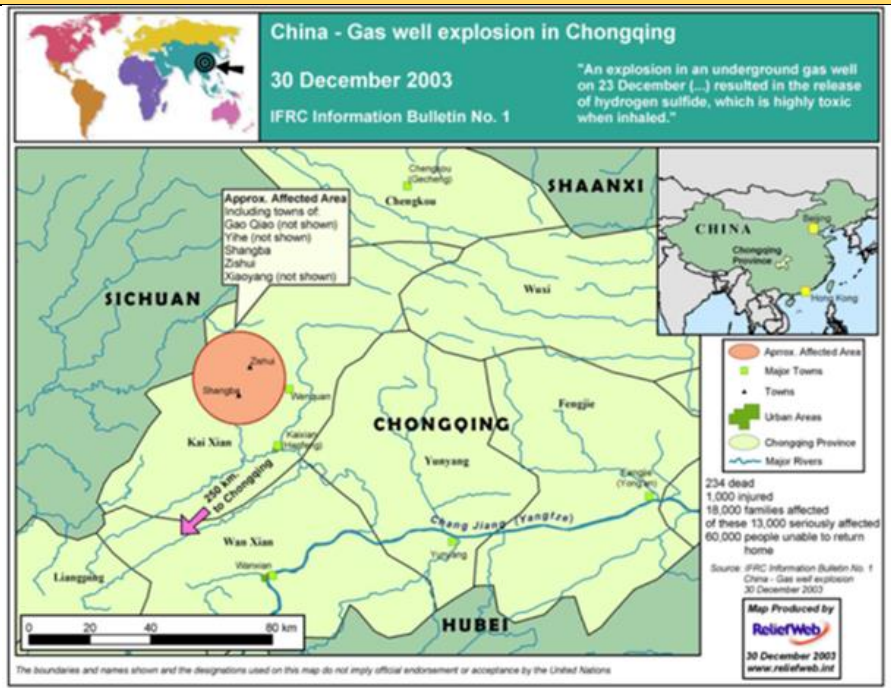

Figure 2 Significant area of impact from an H_2S release to atmosphere

Source: [5]

❖ How – All Users:

1) Know if you can be potentially exposed to H_2S in your area by taking adequate training [6] to understand H_2S hazards including:
   a) H_2S is toxic.
   b) The general levels of concern for H_2S. Short-term health effects can occur at low concentrations, while personnel can quickly be incapacitated at moderate levels, as shown in Table 1.
   c) H_2S can deaden your sense of smell.
   d) H_2S is flammable, as shown in Table 2.
   e) H_2S can accumulate in low areas because it is heavier than air.
   f) H_2S is colorless.
   g) H_2S is soluble in water and in hydrocarbons.
   h) H_2S releases can drift significant distances.

Table 1 Hydrogen Sulfide Hazards - OSHA

Health Hazards

Hydrogen sulfide gas causes a wide range of health effects. Workers are primarily exposed to hydrogen sulfide by breathing it. The effects depend on how much hydrogen sulfide you breathe and for how long. Exposure to very high concentrations can quickly lead to death.

Short-term (also called acute) symptoms and effects are shown below:

Worker Exposure Limits
NIOSH REL (10-min. ceiling): 10 ppm
OSHA PELs: General Industry Ceiling Limit: 20 ppm General Industry Peak Limit: 50 ppm (up to 10 minutes if no other exposure during shift) Construction 8-hour Limit: 10 ppm Shipyard 8-hour limit: 10 ppm
NIOSH IDLH: 100 ppm
IDLH: immediately dangerous to life and health (level that interferes with the ability to escape) (NIOSH) **PEL:** permissible exposure limit (enforceable) (OSHA) **ppm:** parts per million **REL:** recommended exposure limit (NIOSH)

Concentration (ppm)	Symptoms/Effects
0.00011-0.00033	Typical background concentrations
0.01-1.5	Odor threshold (when rotten egg smell is first noticeable to some). Odor becomes more offensive at 3-5 ppm. Above 30 ppm, odor described as sweet or sickeningly sweet.
2-5	Prolonged exposure may cause nausea, tearing of the eyes, headaches or loss of sleep. Airway problems (bronchial constriction) in some asthma patients.
20	Possible fatigue, loss of appetite, headache, irritability, poor memory, dizziness.
50-100	Slight conjunctivitis ("gas eye") and respiratory tract irritation after 1 hour. May cause digestive upset and loss of appetite.
100	Coughing, eye irritation, loss of smell after 2-15 minutes (olfactory fatigue). Altered breathing, drowsiness after 15-30 minutes. Throat irritation after 1 hour. Gradual increase in severity of symptoms over several hours. Death may occur after 48 hours.
100-150	Loss of smell (olfactory fatigue or paralysis).
200-300	Marked conjunctivitis and respiratory tract irritation after 1 hour. Pulmonary edema may occur from prolonged exposure.
500-700	Staggering, collapse in 5 minutes. Serious damage to the eyes in 30 minutes. Death after 30-60 minutes.
700-1000	Rapid unconsciousness, "knockdown" or immediate collapse within 1 to 2 breaths, breathing stops, death within minutes.
1000-2000	Nearly instant death

Footnote: The exact concentration and exposure time at which different physiological effects occur is not known precisely and different industry bodies use slightly different boundary levels to categorize the physiological effects including fatality. The table published by OSHA should therefore only be used as an approximate guide to manage the H_2S hazard, especially at higher concentration levels. Source: OSHA [7]

Golden Rules for Hydrogen Sulfide (H_2S)

Golden Rule #1: Always understand and respect the hazardous properties of H_2S

Table 2 Hydrogen Sulfide International Chemical Safety Card

Hydrogen sulfide	**Formula:** H_2S	**CAS#:** 7783-06-4	**RTECS#:** MX1225000	**IDLH:** 100 ppm
Conversion: 1 ppm = 1.40 mg/m^3	**DOT:** 1053 117			
Synonyms/Trade Names: Hydrosulfuric acid, Sewer gas, Sulfuretted hydrogen				
Exposure Limits: **NIOSH REL:** C 10 ppm (15 mg/m^3) [10-minute] **OSHA PEL†:** C 20 ppm 50 ppm [10-minute maximum peak]			**Measurement Methods (see Table 1):** **NIOSH** 6013 **OSHA** ID141	
Physical Description: Colorless gas with a strong odor of rotten eggs. [**Note:** Sense of smell becomes rapidly fatigued & can NOT be relied upon to warn of the continuous presence of H_2S. Shipped as a liquefied compressed gas.]				

H	**Chemical & Physical Properties:**	**Personal Protection/Sanitation (see Table 2):**	**Respirator Recommendations (see Tables 3 and 4):**
	MW: 34.1 **BP:** -77°F **Sol:** 0.4% **Fl.P:** NA (Gas) **IP:** 10.46 eV **RGasD:** 1.19 **VP:** 17.6 atm **FRZ:** -122°F **UEL:** 44.0% **LEL:** 4.0% Flammable Gas	**Skin:** Frostbite **Eyes:** Frostbite **Wash skin:** N.R. **Remove:** When wet (flamm) **Change:** N.R. **Provide:** Frostbite wash	**NIOSH** **100 ppm:** PaprS/GmFS/Sa*/ScbaF **§:** ScbaF:Pd,Pp/SaF:Pd,Pp:AScba **Escape:** GmFS/ScbaE

Incompatibilities and Reactivities: Strong oxidizers, strong nitric acid, metals	
Exposure Routes, Symptoms, Target Organs (see Table 5): **ER:** Inh, Con **SY:** Irrit eyes, resp sys; apnea, coma, convuls; conj, eye pain, lac, photo, corn vesic; dizz, head, lass, irrity, insom; GI dist; liquid: frostbite **TO:** Eyes, resp sys, CNS	**First Aid (see Table 6):** **Eye:** Frostbite **Skin:** Frostbite **Breath:** Resp support

Source: [8]

❖ How – Operators, Mechanics, and Technicians:

1) Be aware of all properties of H_2S.
2) Understand the nature of the H_2S hazards.
3) Understand the personal protective equipment (PPE) requirements for H_2S (See Figure 3) including personal H_2S detectors
4) Understand the alarm notification system for H_2S releases.
5) Develop and/or help develop the Operating Procedures that address the H_2S hazard.
6) Understand proper response procedures for H_2S exposures.
7) Include consideration of exposure to H_2S in the Permit to Work and Job Task Hazard Analysis where there is a potential H_2S hazard.
8) Follow the H_2S decontamination and gas-freeing procedures when removing equipment that contained H_2S.
9) Be aware of the potential for the presence of pyrophoric iron sulfide that may develop when H_2S is in contact with iron. Use caution when opening such equipment.
10) Observe the H_2S practices of coworkers and provide positive/constructive feedback to encourage good H_2S behaviors.

Golden Rules for Hydrogen Sulfide (H_2S)	
Golden Rule #1:	**Always understand and respect the hazardous properties of H_2S**

Normal PPE inadequate to respond to an H_2S release

Application of short duration Breathing Apparatus for escape

Application of Breathing Apparatus to respond

Application of Breathing Apparatus and protective chemical suit to respond

Figure 3 Choosing the correct PPE

Source: Images 1, 2 and 3: Shutterstock, Image 4: CSB

❖ How – Management:

1) Provide adequate training for all workers potentially exposed to H_2S.
2) Assure H_2S hazardous properties are documented in your Process Safety Information/Process Knowledge Management database.
3) Define and enforce safety expectations for all workers around H_2S hazards.
4) Ensure qualitative/quantitative studies such as Quantitative Risk Assessment/Process Hazard Analysis/Hazard Identification (QRA/PHA/HAZID) are completed by competent people with an understanding of H_2S hazards and the correct level of understanding for the system under review.
5) Establish and document a site-wide H_2S policy that specifies which standards and regulations will apply along with any company requirements that might exceed those standards and regulations.
6) Implement policies for risk management of intentional H_2S releases, where other methods of disposal are not possible/appropriate. This very rare situation warrants thorough risk analysis.
7) Do not tolerate the odor of H_2S in a workplace, even if the H_2S concentration is at or below the permissible exposure level. See Supplemental Reading, "Toxicological Profile for Hydrogen Sulfide and Carbonyl Sulfide" [9] for more information.

❖ How – Engineers and Designers:

1) Seek adequate training if you potentially can be exposed to H_2S or are involved in H_2S-related designs.
2) Follow relevant H_2S design standards.
3) Provide signage across the site where an H_2S hazard exists.
4) Provide visual and audible alarms to alert people of an H_2S release.

5) Review and record H_2S process composition information, including possible side reactions. These side reactions should include the credible scenarios that may bring H_2S in contact with other materials present at the site even though it may be unlikely.
6) Participate in/support qualitative/quantitative studies (such as QRA/PHA/HAZID) that address H_2S hazards.

❖ How – Emergency Responders:

1) Know that water sprays can be used to disperse an H_2S cloud.
2) Use caution with handling and storage of runoff water. The hazard of H_2S solubility in water should be known to responders since water containing H_2S could pose a health hazard.
3) Due to the dynamic nature of emergency situations and the toxicity of H_2S, always be prepared to wear the highest level of protection (see Golden Rule 4) when responding to an H_2S release event.

❖ Supplemental Reading:

- API RP 55 Recommended Practice for Oil and Gas Producing and Gas Processing Plant Operations Involving Hydrogen Sulfide [3]
- Small, Portable Oil & Gas Production Facilities: Recommended Solutions for Design and Operation (Safety Guide) [6]
- OSHA : Hydrogen Sulfide – Hazards [7]
- Toxicological Profile for Hydrogen Sulfide and Carbonyl Sulfide [9]
- Killer Gas Bulletin CH026, Government of Alberta [10]
- Risk Based Process Safety, Chapters 8 and 9 [11, pp. 169-244]
- API 49 Recommended Practice for Drilling and Well Servicing Operations Involving Hydrogen Sulfide [12]
- Environmental Health Criteria 19 Hydrogen Sulfide [13]
- API STD 2015 Requirements for Safe Entry and Cleaning of Petroleum Storage Tanks [14]
- Lethal Service – Quick Guide [15]
- ASME, Section VIII Boiler and Pressure Vessel Code Division 1 Section UW-2 [16]
- Toxicological Review Of Hydrogen Sulfide [17]
- Substance Information – Hydrogen Sulphide [18]
- H_2S Release Rate Assessment and Audit Forms [19]

Golden Rule #2: Always know where the H_2S hazard exists or can be produced

❖ Why:

1) Knowing where H_2S may exist or can be produced is critical to risk management.
2) Lack of knowledge can be caused by poor H_2S hazard awareness, recognition, or assessment.
3) H_2S exists in nature and in a very wide range of industries/locations, including leather tanning, pulp and paper, chemical, dye, decomposing organic material, wastewater plants, stagnant seawater systems, hot springs, mineral extraction and oil and gas production [20]. Many incidents have occurred where people did not prepare for the H_2S hazard because they did not know where H_2S could exist or where H_2S could be produced:
    a) People did not know the reactions that produce H_2S. Reaction scenarios can be created by intentional mixing (e.g. chemical cleaning using a hydrochloric acid wash on a vessel containing water with H_2S), mixing of chemicals out-of-sequence, or by inadvertent mixing [21] [22] [23].
    b) People were unaware that H_2S could accumulate in low areas. People had poor process safety knowledge that a chemical reaction had occurred and generated H_2S.
    c) People had a lack of awareness of work happening in an adjacent area, (e.g., simultaneous work at different elevations). The dispersion of an H_2S release may not be easily apparent as it can migrate in/out of buildings or in/out of adjacent locations [24].
    d) People responded to assist succumbed victims, without recognizing that they were exposing themselves to an H_2S hazard. Many have an innate spontaneous reaction to assist succumbed victims. People have an automatic reaction to help others first (before securing their own safety).
    e) People had poor awareness of the H_2S cloud due to its invisibility.
    f) People were unprepared for upset conditions leading to an H_2S release.
4) By knowing if H_2S is or could be present, management, engineering, operations, maintenance, and emergency responders can take proactive steps to prevent H_2S-related process safety incidents. See also Golden Rule #3 and Golden Rule #4.
5) Incident History:
    a) Contract construction employees were working at a pulp and paper mill. On January 15, 2002, sodium hydrosulfide (NaSH) was unloaded at the tank truck unloading station. The unloading station pad drained into a collection pit that collected rainwater, condensate, and occasionally spilled chemicals (e.g., NaSH) from the unloading operation. The pit could be drained to a sewer, see Figure 4 Figure 4. However, due to environmental concerns, the drain valve from the pit to the sewer was typically locked closed. On the day of the incident, January 16, 2002, the pit contained an appreciable quantity of NaSH solution diluted by water. To avoid having the construction crew stand in the fluid-filled pit, an operator unlocked and opened a valve to drain the contents of the pit into the sewer. After 5 minutes, the valve was closed and re-locked.

        On the day of the incident, sulfuric acid was added to the sewer to control the pH in the downstream effluent treatment area. The sulfuric acid reacted with the NaSH in the sewer, producing H_2S. A gap in the seal of sewer manway allowed the release of the H_2S gas, which drifted into the area of the construction workers. Two construction workers near the manway were fatally injured by H_2S poisoning. Further, seven construction workers and one truck driver were injured due to H_2S exposure [25].

The learning relevant to this Golden Rule is that that there was a potential for the creation of H_2S when the isolation between the pit and the sewer was compromised.

(1) The company did not communicate to the workers involved in the delivery, unloading, and handling of NaSH that mixing with acid creates H_2S.
(2) H_2S was not identified as a hazard in the immediate area of the mill where the incident occurred. For this reason, there were no monitors, alarms, or warning signs in the area.
(3) The design engineers did not evaluate the potential for generating H_2S when they tied the unloading station drain into the plant's acid sewer system [26].
(4) The maintenance staff were not aware of the importance of maintaining a tightly closed acid sewer system

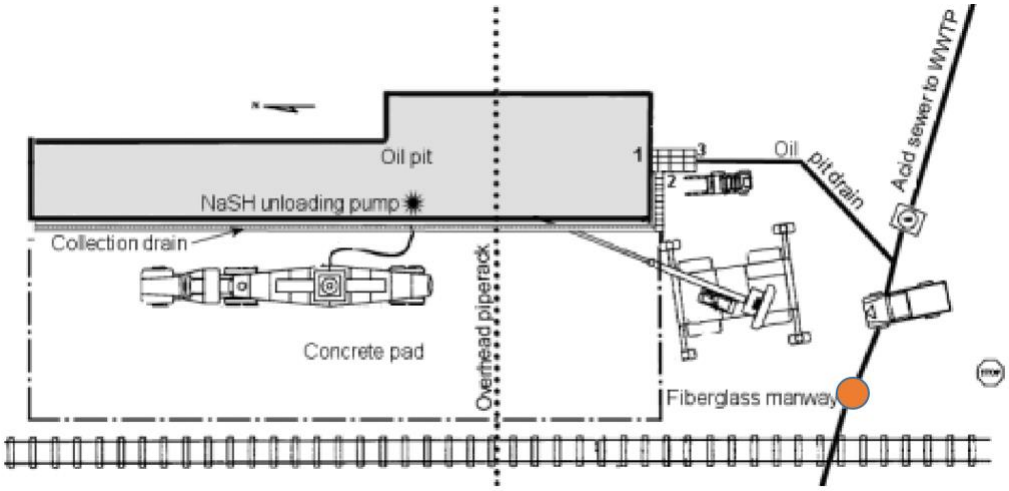

Figure 4 Acid sewer system safety critical equipment failure- non-sealed manway cover which exposed 9 people to H_2S gas
Source: U.S. Chemical Safety and Hazard Investigation Board [25]

❖ How – All Users:

1) Be aware of the possible locations of H_2S in your local area or when visiting a new area. For example,
   a) in the leather industry, H_2S can exist in the pre-tanning of raw hides
   b) in stagnant seawater systems, H_2S can be produced by the action of certain types of bacteria
   c) in sewer systems where H_2S can be produced by the decay of organic matter
   d) in a refinery, H_2S can exist in many units
   e) at a H_2S production site, H_2S exists throughout the site
2) Follow signage instructions. Do not enter H_2S-restricted areas without permission.
3) Ask where H_2S can be present.
4) Attend any training or awareness presentation provided to assure an understanding of all H_2S hazards, potential exposure locations, and emergency response procedures.
5) Understand and be aware of all alarms provided to signal an H_2S release.
6) Be aware of designated evacuation routes and assembly/muster point requirements.

7) Understand the use of and comply with requirements for personal protective equipment. For example, some sites will require that personnel carry emergency evacuation respirators when working in or vising areas with a particularly high potential for H_2S releases.

❖ How – Operations & Maintenance:

1) Attend advanced training for Operations, Mechanics, and Technicians associated with H_2S hazards, the H_2S locations, and the potential for exposure, including the emergency response procedures.
2) Report all observations of H_2S releases and communicate potential hazards that may not be well understood to others.
3) When changing the operating status of the process, always walk through the process lineup to know if it is in an H_2S-safe state for the transition, especially when process boundaries are involved. A marked-up drawing may assist in identifying key H_2S isolation locations. This will allow for knowledge of where H_2S exists [27] [28].
4) When maintenance work is required on H_2S-containing equipment, ensure the job task analysis is approved and that there is a risk analysis for this situation [29].
5) Due to the hazards of H_2S, use caution when a deviation from procedural steps is required. Incident history has shown that unwanted chemical reactions can take place. Follow Management of Change with a Process Hazard Review, if applicable. See Supplemental Readings "Guidelines for Writing Effective Operations and Maintenance Procedures" and "Human Factors for Process Plant Operations: A Handbook" from CCPS for more information [30] [31].
6) Ensure operating and maintenance procedures adequately address where H_2S exists or can be produced.
7) Consider the potential presence of H_2S when establishing maintenance programs. See also Golden Rule #3.

❖ How – Management:

1) Establish risk-based security measures to prevent public access to chemical facilities [32]. This may include toxic chemical warning signs, video surveillance, or perimeter fencing.
2) Provide awareness training to workers who could be exposed to H_2S. They must be aware of the hazards of their workplace. [33]
3) Sponsor a multi-disciplined group to participate in a hazard identification and evaluation of the processes to identify where H_2S can exist or can be produced, including potential unintended chemical reactions that create H_2S.
4) Broadly communicate the H_2S hazard source locations along with the characteristics of H_2S and the emergency response procedures associated with H_2S.
5) Mandate an appropriate level of H_2S detection and warning systems in the areas where a significant potential for H_2S release exists. As well, mandate that these systems always be maintained in a functional state.
6) Establish mandatory work permit system, if not already in place, which addresses the risk of H_2S exposure and creates an awareness of H_2S risks and potential exposure locations.

Golden Rules for Hydrogen Sulfide (H_2S)

Golden Rule #2: Always know where the H_2S hazard exists or can be produced

❖ How – Engineers and Designers:

1) Attend process hazard analysis (PHA) studies, especially those with knowledge of the process with respect to H_2S. These engineers will understand the normal and abnormal situations that can create H_2S. PHA studies should be archived and communicated in a manner that enhances process safety knowledge of where the H_2S hazard exists or can be produced [11, pp. 169-244].
2) Asset Integrity Engineers must be aware of where H_2S exists and can be produced and assess the potential impact of H_2S on the mechanical integrity of the containment equipment. See Supplemental Reading "Guidelines for Mechanical Integrity Systems" [34].

   For example, the combined effect of H_2S and tensile stress can cause sulfide stress cracking corrosion (SSC) of metallic material. Asset Integrity Engineers can provide forecasting of known SSC hazards. This is especially true where welding (e.g. fittings) should be done with an approved welding procedure (e.g. avoid excessive manganese and chrome in the welding material, insufficient weld material deposited, or inadequate leg size). Adequate preparation is necessary (e.g. bake-out procedure especially on carbon steel) [35] [36].
3) Use a risk-based approach when relying on check valve(s) for the prevention of H_2S gas or liquid backflow when there is a possibility of an H_2S release to atmosphere. An active (non-passive) positive isolation should be installed unless it can be justified through the risk-based approach [37].
4) Avoid open-to-atmosphere designs when the process involves H_2S. When H_2S exists or can be produced, engineers should evaluate closed (contained) system designs to avoid activities like opening equipment to do pH or level measurements [23] [38].
5) Know the chemistry and the physics of the process (specifically Henry's Law) to determine if and when H_2S may be liberated from a solution. H_2S gas may be liberated directly from the original source or place where it is generated, or in downstream locations due to its solubility in water and hydrocarbons. See Supplemental Reading, "Hazards of Molten Sulfur Storage & Handling [39]" for further information.
6) Higher temperatures and lower pH enhance the release quantity. H_2S gas venting locations should be engineered under all credible operating conditions. For example, a wastewater tank containing dissolved H_2S can liberate H_2S gas with increased temperatures. If an engineered solution is not possible, then use the hierarchical control philosophy (see Figure 5).
7) Determine the criteria and location for H_2S fixed gas detection and associated alarm systems. Considerations may include the potential release locations, the characteristics of H_2S (e.g., heavier than air), and the migration potential of H_2S in the event of a release (e.g., the dominant wind speed, wind direction and distance to downwind sensitive receptors such as people).

❖ How – Emergency Responders:

1) Consider factors such as the wind direction, building ventilation, and terrain when responding to an H_2S release.
2) Use monitoring equipment to know where the presence of H_2S exists or can be produced during emergencies. See also Golden Rule #4.

Golden Rules for Hydrogen Sulfide (H_2S)	
Golden Rule #2:	**Always know where the H_2S hazard exists or can be produced**

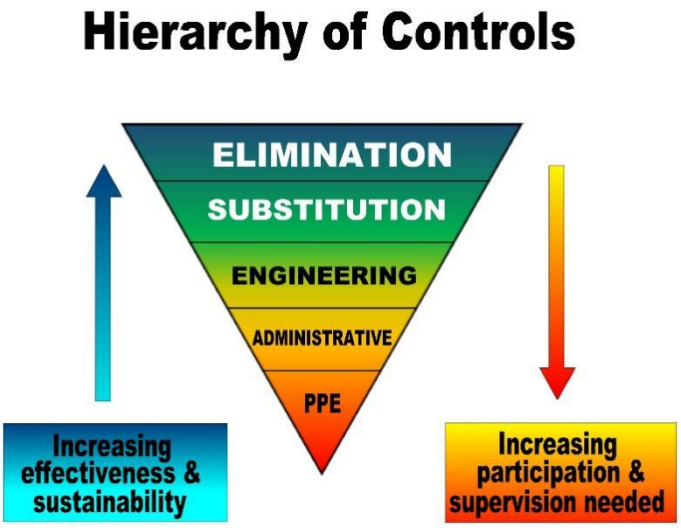

Figure 5 Hierarchy of Controls

Source: Shutterstock.com

❖ Supplemental Reading:

- Toxicological Profile for Hydrogen Sulfide 2016 [9]
- CCPS, Guidelines for Risk Based Process Safety [11, pp. 169-244]
- CSB Georgia-Pacific Corp. Hydrogen Sulfide Poisoning [25]
- Guidelines for Writing Effective Operations and Maintenance Procedures [30]
- Human Factors for Process Plant Operations: A Handbook [31]
- Guidelines for Mechanical Integrity Systems [34]

Golden Rules for Hydrogen Sulfide (H_2S)

Golden Rule #3: Always establish prevention controls against an H_2S release

Golden Rule #3: Always establish prevention controls against an H_2S release

❖ Why:

1) To protect workers and others from toxic gas exposures which can lead to injury and possible fatality [40] [41] [42]
2) To prevent harm to the environment [43]
3) Incident History:
   a) On July 7th 1993, in Grasse France, a release of H_2S occurred during the transfer of waste water from a tank to a tanker truck, resulting in the death of the tanker truck driver. The H_2S produced in the production process was to be neutralized per procedure prior to transfer of the wastewater to the tanker truck. However, the neutralization procedure had not been followed as written because one of the key reactants had been changed. Furthermore, there was no instrumentation to monitor the H_2S concentration in the wastewater and the technician had to rely on his sense of smell to monitor the neutralization reaction. Due to ineffective testing of the neutralization steps, a significant concentration of H_2S remained in the wastewater. As the liquid waste was transferred by vacuum pump, H_2S in high concentrations was released through the exhaust of the pump. The pump exhaust was not expected to handle toxic material, and so it was at an elevation such that the passing driver breathed in the fumes and was fatally injured. [44]

      The learnings relevant to this Golden Rule are:
      (1) The H_2S treatment conditions were not stringently followed with one of the key reactants being changed without analysis of the required amount. The treatment procedure was found to be incomplete and was not supervised at any stage.
      (2) The procedure contained unnecessary details and did not contain the necessary information.
      (3) The H_2S-rich waste stream was not analyzed before the transfer.
      (4) Guidelines and procedures were not followed (I.e., start of operations report was not signed, readings on the waste tank after neutralization were not taken).
      (5) H_2S was known to be a hazard onsite but instrumentation to measure concentrations in liquid steams and emissions were not present.

❖ How – All Users:

1) Always think and practice the ways you can eliminate/substitute/avoid H_2S [45]. As per Figure 5, the hierarchy of controls should start with elimination.
2) Be aware of the H_2S hazards and rigorously follow procedures and other administrative controls to guard yourself from H_2S exposure. For example, ensure that personal H_2S monitors are functional and are maintained, including regular calibration.

❖ How – Operations & Maintenance:

1) Write/follow proper operating and maintenance procedures which include
   a) Highlighting procedures where the H_2S hazard exists
   b) Highlighting critical steps where preventive monitoring/control of H_2S is needed
   c) Verification / assurance that these procedures are clear and are current [30]
2) Write/follow H_2S equipment decontamination procedures, which may include use of steam or an oxidizer such as potassium permanganate ($KMnO_4$) [46].

3) Write/follow line-breaking procedures. This should include, at a minimum, the first break performed and the requirements for personnel protection (including respiratory protection up to and including pressure demand self-contained breathing apparatus (SCBA) for unknown concentrations of H_2S).
4) Participate in Operational Readiness Reviews, including Pre-Startup Safety Reviews, when H_2S service equipment is returned to service and when H_2S service equipment has undergone a change [40]. Some examples include:
    a) Walking the line to ensure that manual valves are in proper operating position and open-ended lines are not present.
    b) Ensuring that all process instrumentation are in good working order including fixed H_2S detectors.
5) Follow a Work Permit Program that addresses activities commonly associated with H_2S equipment including, but not limited to:
    a) General Work
    b) Hot Work [47]
    c) Confined Space [48]
    d) Lock Out Tag Out [49]
6) Conduct a field level risk assessment / job hazard assessment in the Work Permit Program that prompts a review for hazards such as H_2S.
7) Prioritize maintenance work orders where the functionality of safety critical functions is impaired.

❖ How – Management:

1) Establish a policy that all H_2S release and near misses undergo a process incident investigation, and mandate that key findings are shared throughout organization [50]. Understanding H_2S releases and near-miss investigation findings may allow organizations to develop future prevention measures. Also refer to Golden Rule #5.
2) Establish a Management of Change program that includes H_2S service equipment [40]. The program should include a review of the H_2S prevention controls to assure the changes are acceptable.
3) Ensure that the dangers of H_2S are reflected in management systems therefore promoting a sense of vulnerability for potential high severity H_2S release events. This may include the engineering standards, the emergency response program, and the onboarding orientation. Refer to Golden Rule #1.
4) Create performance indicators to assure maintenance work orders where the functionality of safety critical functions is impaired are addressed in a timely manner.
5) The identification of root cause factors of the failures requiring work orders is paramount to prevent recurring safety critical equipment failures [51].

Golden Rules for Hydrogen Sulfide (H_2S)
Golden Rule #3: Always establish prevention controls against an H_2S release

❖ How – Engineering & Projects:

1) Establish a design basis that includes H_2S-related information so that it will be apparent that changes in H_2S composition are appropriately flagged for Change Management analysis. For example, changes in the feedstock.
2) Write and follow internal engineering standards that address H_2S hazards, including:
   a) Design H_2S units with an inherently safer design (ISD) approach per Figure 5. For example, engineers can:
      (1) Eliminate H_2S hazards downstream by combining H_2S with caustic soda (NaOH), which would alter the downstream hazards to a resulting NaSH (or Na_2S) solution (liquid). This may be easier to safely transport than H_2S (gas).
      (2) Provide a fail-safe design such as depressurization valves to 'fail to the open' position to flare systems
      (3) Simplify piping designs to prevent cross contamination
      (4) Design for the treatment of sour natural gas with a scavenger to eliminate / reduce H_2S from the downstream equipment, such as a pipeline network
   b) Perform facility siting for H_2S hazards by determining consequence (or risk) contours to determine separation distance and layout design. Calculate areas of H_2S impact and use this data for risk decisions addressing safe havens, facility siting, and emergency response planning including offsite impacts [52] [53] [54]. The H2S hazards include its toxic and flammable properties.
   c) Follow proper recognized and generally accepted good engineering practices (RAGAGEP) in specifying the inspection, testing, and preventive maintenance tasks and frequencies, especially for sour water service. This can be an area requiring close Preventive Maintenance (PM) monitoring due to its potential for increased corrosion. [55] [56]
   d) Provide specifically-designed ventilation for occupied buildings in H_2S hazard zones [57]
3) Follow lethal service standards in designing equipment in H_2S service. [58]
4) Specify proper materials of construction in H_2S-containing services to reduce / eliminate corrosion. For instance, brass and copper must be avoided in H_2S service. [59]
5) Minimize leak sources, (e.g., do not allow small or screwed fittings in H_2S-containing services).
6) Perform routine Process Hazard Analyses with the emphasis on leak prevention and assessing the adequacy of the safeguards. [60]
7) Design for means to isolate and ventilate H_2S-containing equipment so as it can be entered and/ or removed from service. Take care to re-establish a non-H_2S environment after any prolonged periods of time as conditions may have changed (e.g., due to slow leaking valves that were thought to have been fully closed).
8) Be aware of your responsibilities (including material and equipment selection, process design, chemical reaction and side reaction, etc.) that could lead to an H_2S incident or near miss.

❖ Supplemental Reading:

- CCPS, Guidelines for Process Safety Documentation [61]
- CCPS, Guidelines for Engineering Design for Process Safety 2nd Ed [62]
- WHO, H_2S Human Health Aspects [63]

Golden Rule #4: Always develop mitigation measures in the event of an H_2S release

❖ Why:

1) Early warning of an H_2S release increases the likelihood that people can take effective mitigative action.
2) Provisions to limit an H_2S release increase the likelihood of minimizing injuries and fatalities.
3) Practiced emergency response plans and appropriate PPE to aid escape increase the likelihood of minimizing injuries and fatalities.
4) Provision of safe locations increases the likelihood that people are protected from the release.
5) Incident History:
   a) An oil worker, operating a valve, collapsed when exposed to H_2S. The foreman tried to rescue him and was overcome, as was a third rescue worker. Neither of the would-be rescuers had H_2S gas monitors nor wore respiratory protection. Remaining crew members, wearing self-contained breathing apparatus, finally removed the injured workers from the area. The third worker was revived, but the first worker and the foreman were fatally injured [64].

      The learning relevant to this Golden Rule is that:
      (1) Responding without appropriate personal protective equipment (PPE) and training can result in rescuer(s) becoming victim(s). See Figure 3.

   b) Two workers were investigating an H_2S leak of unknown origin or magnitude in a building. The workers entered the building without respiratory protection to conduct air quality tests. One worker's personal H_2S alarm went off at the entrance to the building, and both workers left the area. One worker returned with a monitor on a broom handle and measured 250 ppm H_2S (more than twice the Immediately Dangerous to Life and Health (IDLH) concentration in the problem area). Both workers sought medical attention [64].

      The learnings relevant to this Golden Rule are:
      (1) If the building had appropriate gas detection installed, then personnel would have had an earlier warning and would not have been at risk to investigate an area with high levels of H_2S present.
      (2) There would also not have been the need to return to the area with a makeshift testing arrangement that increased the risk to the personnel.
      (3) H_2S leaks should only be investigated when workers are using SCBA or equivalent supplied air. This reduces the risk to personnel, especially if the extent of the leak has changed / worsened since it was first reported.

   c) Please read the Why incident in Golden Rule #2.
      Seven of the injured contractors were driven in private vehicles to the regional medical center, and Emergency Medical Services (EMS) transported three other victims (including the two fatally injured) to different hospitals. The clothing of one victim was completely removed and placed in a bag; the clothing of the other two victims was not removed. The EMS paramedics who transported the victims reported symptoms of H_2S exposure; however, the two paramedics who removed the clothes of the patient reported milder symptoms. All of the paramedics were medically evaluated and then released.

Golden Rules for Hydrogen Sulfide (H_2S)

Golden Rule #4: Always develop mitigation measures in the event of an H_2S release

The learnings relevant to this Golden Rule are:

(1) The victims were removed from the incident scene and taken to the mill's first-aid station prior to setup of the incident command system without being decontaminated at the scene. Mill guidelines did not require decontamination at the scene nor at the first-aid station.

(2) The clothing of one of the three victims transported to hospitals was removed, which was not the case with the other two victims. The paramedics were exposed to H_2S due to contamination on the clothing.

(3) The local authority's medical management guidelines did not recognize that clothing of victims of H_2S gas exposure may release H_2S which could pose a medical risk to responders [25]

❖ How – All Users:

1) Always be aware of the locations onsite where H_2S is present or may be generated and the means to detect and raise an alarm for an H_2S release.
2) Attend training on the dangers (including flammability and toxicity) of H_2S.
3) Carry an escape respirator when stipulated by site procedures.
4) Actively engage in all emergency response drills to know how to escape when an H_2S alarm is sounding; (e.g., escape crosswind and apply escape respirator (when provided)). [10]
5) Follow the instructions of emergency response personnel.
6) Do not attempt to rescue H_2S affected personnel unless you are trained to do so and are wearing appropriate personal protective equipment, including a SCBA.

❖ How – Operations & Maintenance:

1) Maintain fixed and portable gas detection systems following manufacturer's specifications such as periodic calibration (which is usually a monthly or bi-monthly task as specified by the manufacturers).
2) Regularly test the gas detection and audible alarm systems.
3) Inspect, maintain, and function test H_2S detector-triggered interlock shutdowns.
4) Inspect and maintain all escape respirators and self-contained breathing equipment present on-site.
5) Maintain the H_2S-safe locations across the site to be effective against H_2S gas ingress.
6) Discuss H_2S hazards applicable to work permits prior to field work including H_2S hazard mitigation on any equipment first disconnections. This will prepare personnel to mitigate the H_2S hazards in the event of a H_2S release.
7) In the event of an H_2S release, be prepared and trained in mitigation measures including emergency shutdown of the process.
8) Be prepared with mitigation measures including escape when entering process areas and other locations where H_2S may be present.
9) Be able to communicate appropriate information to any emergency response (ER) team regarding potential for exposure.

❖ How – Management:

1) Establish H2S-safe locations on or off site depending on the emergency situation
2) Confirm that site training on the hazards (including flammability and toxicity) of H_2S is being conducted across all levels of the organization. Set appropriate training levels for all personnel who could be on-site (e.g., visitors, contractors, non-operating staff, administration staff).

3) Ensure the site conducts a risk assessment to define the appropriate escape/breathing equipment for all personnel who could be exposed to H_2S.
4) Confirm that protective equipment does not create a hazard to worker's health and safety. For example, do not use an escape bottle/pack for a rescue operation
5) Ensure site-wide emergency response plans are available and that periodic drills and exercises are conducted, documented, and critiqued.
6) Provide ER teams with the correct equipment for responding to an H_2S incident.
7) Ensure that the site H_2S policy includes mitigation and preventative measures.
8) Ensure coordination, as appropriate, with community authorities, included emergency response agencies.

❖ How – Engineering & Projects:

1) Design and install appropriate detector coverage with fixed H_2S gas detection, following company, regulatory, and/or industry guidance on alarm set points [65].
2) Design and install an appropriate level of alarms (visible and audible) following company standards, regulatory requirements, and best practice guidance. Always automate the alarms to avoid any potential delay since H_2S releases can disperse quickly [66].
3) Design any enclosures with a method to alert people external to the enclosure of an internal H_2S release (e.g., gas detection linked to external audible and visual alarm).
4) Design controls to reduce the H_2S hazard in the indoor/outdoor workplaces.; For example, increased ventilation or automatic closure of HVAC to protect building occupants
5) Design H_2S-safe locations onsite based on the possible release scenarios, prevailing wind direction, and concentrations to be effective against H_2S gas ingress. Ideally, more than one safe location should be provided in case the wind is not along the prevailing wind direction.
6) Design for remotely operated emergency isolation valves on H_2S containing equipment. This may include a defined threshold quantity or high leak locations.

❖ How – Emergency Responders:

1) Specify appropriate breathing equipment based on the concentration of H_2S present onsite. Use full face pressure demand self-contained breathing apparatus for emergency response. Never use escape packs or rebreathers for emergency response [64] [66] [67].
2) Develop emergency management plans for credible H_2S releases from all identified locations onsite.
3) Conduct Emergency Response exercises for these scenarios including practical exercises with SCBAs.
4) Complete emergency response (ER) and first aid training specific for the hazards associated with H_2S.
5) When entering an enclosure, use air monitoring equipment to characterize the internal atmosphere to avoid entering an toxic atmosphere [66].
6) When responding to an H_2S release, follow the established Emergency Response Plan (ERP) including the constant monitoring of the wind direction.
7) Be cautious of the potential for a large zone that could be significantly affected when H_2S is released. This zone could extend offsite and therefore should be included in the site and local authority ERP.
8) Do not attempt to rescue any person where there has been an H_2S release unless you have been trained in the use of SCBA. The buddy system can be adopted [4] [64].

9) Move personnel affected by H_2S to a safe location (e.g. to fresh air). If a victim is having trouble breathing or is not breathing, start assisted ventilation using a protective mask with a one-way valve (such as a Pocket Mask), and add oxygen to the mask if available. If the worker has no pulse, begin cardiopulmonary resuscitation (CPR). Because the body rids itself of H_2S if removed from the exposure, it is critical to continue to give the victim assisted ventilation with oxygen until medical aid arrives [64].
10) Take measures to protect against exposure to H_2S that may have contaminated the victims' skin or clothing. This may include removing the victim's clothing in a ventilated space to help protect the victim and the emergency responders.
11) Have a coordinated plan to access community resources with equipment that assists in the treatment of H_2S exposure, such as hyperbaric oxygen equipment [68].
12) Evaluate the incident emergency response (both drills and actual events) for improvement opportunities.

❖ Supplemental Reading:

- Rethink your refuge [69]
- Shelter-in-place. Reducing Risk from Toxic Impacts [70]
- 29 CFR. 1910.119 Occupational Safety and Health Administration [71]
- CCPS Guidelines for Technical Planning for On-Site Emergencies [72]
- CCPS Guidelines for Post Release Mitigation Technology in the Chemical Process Industry [73]

Golden Rules for Hydrogen Sulfide (H_2S)
Golden Rule #5: Always investigate H_2S incidents to improve management systems

Golden Rule #5: Always investigate H_2S incidents to improve management systems

❖ Why:

1) The root causes of many incidents have been linked to a management system deficiency.
2) H_2S incident and near miss investigations provide valuable learnings that, properly applied, can reduce the possibility of recurrence of similar incidents in the future.
3) Incident investigation learnings provide the opportunity to strengthen management systems and company culture, including other process safety elements.
4) Incident investigation learnings from other company sites or from elsewhere in industry may provide valuable insights for improving site management systems [74].
5) Incident History:
   a) On December 11, 2002, an incident resulted in an employee collapsing due to H_2S exposure as he entered a wastewater treatment room (Refer to Figure 6). The employee went into the room to retrieve a tool. He noticed the smell of "rotten eggs" and felt pressure in his lungs that made it difficult to breathe. He attempted to evacuate but collapsed in the room. Colleagues pulled him to safety.

      The facility had experienced a previous H_2S incident, which resulted in an external investigation by city officials and a written abatement order. In response, an H_2S detector was installed, but required procedures were not developed nor was required training implemented to ensure employees understood the H_2S hazards and controls associated with the wastewater treatment process.

      The learnings relevant to this Golden Rule are that:
      (1) Weak H_2S Management Systems provide an avenue for incident occurrence. The company did not have robust systems to manage H_2S hazards and to keep their employees safe through effective hazard identification and management.
      (2) The company lacked a formal system for investigating and communicating incidents. Failure to learn from previous company incidents left opportunity for incident recurrence. Lessons were not adequately learned and management systems were not improved sufficiently after the prior incident.
      (3) There was a lack of formal procedures and training for operating the wastewater treatment area. This incident might have been avoided had the unit operator been aware of the possible reactions that can generate H_2S.
      (4) Normalization of deviance led to complacency and acceptance that offensive odors were a usual part of operating the facility and the employees were accustomed to smells such as "rotten eggs." Not everyone was familiar with the dangers associated with H_2S.
      (5) During the Chemical Safety Board (CSB) investigation, it was further found that the incident was the result of wastes that were chemically treated in a vessel not designed for such. [75].

Golden Rules for Hydrogen Sulfide (H_2S)
Golden Rule #5: Always investigate H2S incidents to improve management systems

Figure 6 The location where the workers were normalized to H2S odors.

Source: Chemical Safety Board [75]

❖ How – All Users:

1) Participate in the incident and near miss reporting and investigation program for events involving H_2S and help implement the program consistently across the organization.
2) Use the knowledge from H_2S training and incident and near miss training to Identify H_2S incidents and near misses requiring investigation. Refer to Golden Rule #1.
3) Use appropriate techniques to investigate incidents and near misses [50]
4) Whenever possible, ensure that investigations go beyond the physical and/or human factors that allowed the incident to occur, so that management system-level causes can be identified. This allows for an understanding of why the physical and human factors were present, so that future incidents can be prevented more broadly and effectively.
5) Evaluate the effectiveness of layers of protection and identify deficiencies requiring improvement based upon incident findings.
6) Participate in documenting and sharing incident and near miss investigation results.
7) Follow through on the results of investigations to resolve recommendations. This includes implementation, training, and management system updates as they relate to the recommendation.
    a) Track incidents and associated root cause(s) to identify recurring incidents and near misses that require further investigation to identify potential recurring causal factors.
    b) Continuously improve management systems to reduce the potential for incidents and near misses.
    c) Recognize that not all incidents represent the "worst case" event. Just because the event only resulted in minor consequences does not mean a more significant event is not possible.

d) Ensure that "corporate memory" of incidents remains effective and that lessons learned are shared regularly with new and existing employees.
e) Use a cross-industry (within the same industry and across different industries) approach to gathering lessons learned from incidents

❖ How- Operators and Maintenance:

1) Understand how to identify H_2S incidents and near misses that require investigation. Refer to Golden Rule #2.
2) Understand roles in implementing the investigation program.
3) Report H_2S incidents and near misses for investigation.
4) Participate in investigations (as team member or witness) as requested.
5) Maintain awareness of H_2S incident and near miss learnings and how operations and maintenance can use these learning to continuously improve work processes regarding H_2S safety.
6) Help implement investigation recommendations.
7) Be aware of your actions that could lead to an incident or near miss, including actions in response to abnormal conditions.
8) Be aware of, and implement where feasible, actions that could be taken to prevent escalation of incident consequences.
9) Share your experience or knowledge of incidents when applicable to help others learn and gain awareness of real events that have occurred involving H_2S; e.g., when participating in a process hazard analyses.

❖ How - Management

1) Develop and implement a documented incident and near miss incident investigation program.
2) Provide training on the investigation program.
3) Provide reinforcement to encourage the reporting of incidents and near misses.
4) Provide the resources required to assure a cross-industry approach to lessons learned is applied.
5) Establish and reinforce expectations of compliance with the investigation program.
6) Ensure incident investigations are initiated promptly, and that data collection (including physical evidence, witness observations, and electronic data) begins before and/or during cleanup activities.
7) Provide the resources and availability of trained and experienced lead investigators and call in outside experts as necessary.
8) Ensure the investigation team is composed of personnel who can provide an objective investigation.
9) Require that the investigation team include personnel who understand H_2S properties (refer to Golden Rule #1), H_2S processes, and the location's management system (policy, standards, and procedures).
10) Provide sufficient resources and priority to ensure the investigation team is able to conduct a quality investigation.
11) Provide resources to allow timely resolution of investigation recommendations.
12) Share learnings with other facilities and the industry.
13) Monitor for trends in H_2S incidents causation to identify and address any systemic problems.

14) Monitor performance of, and compliance with, the investigation program. This includes monitoring timely completion of investigations and timely implementation of recommendations.
15) Ensure that the boundary of the incident investigation includes the incident response activity within the timeline. There are times where the investigation of the incident response activity is separated from the main timeline

❖ How - Engineers and Designers:

1) Understand how to identify incidents and near misses that require investigation. Refer to Golden Rule #2.
2) Understand roles in implementing the investigation program.
3) Participate in investigations (as lead investigator, team member, or witness) as requested.
4) Provide access to process data (digital event logs, instrumentation records, system status, etc.) for use in developing the incident timeline.
5) Maintain awareness of incident and near miss history.
6) Help implement investigation recommendations and, where appropriate, implement solutions that eliminate the root cause(s) of previous incidents.
7) Assist in providing training on investigation learnings to personnel.
8) Report incidents and near misses for investigation.
9) Review previous incidents for how Engineers can better design H_2S facilities.

❖ How - Emergency Responders:

1) Understand roles in implementing the investigation program.
2) Participate in investigations (as team member or witness) as requested.
3) Report any operational changes that the emergency responders made during the incident response to the investigation team (e.g., opening or closing of valves, relocation of items).
4) Review previous incidents for how to improve the Emergency Response plan

❖ Supplemental Reading:

- CCPS, Guidelines for Risk Based Process Safety, Chapters 8 and 9 [11, pp. 169-244]
- CCPS, Guidelines for Investigating Process Safety Incidents 3rd Edition [50]
- CCPS, A Practical Approach to Hazard Identification For Operations and Maintenance Workers [76]
- CCPS, Guidelines for Implementing Process Safety Management Systems [77]
- CCPS, Guidelines for Process Safety Metrics [78]
- CCPS, Guidelines for Preventing Human Error in Process Safety [79]
- CCPS, Driving Continuous Process Safety Improvement from Investigated Incidents [80]

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