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DRILLING AND OPERATING OIL, GAS, AND GEOTHERMAL WELLS IN AN H₂S ENVIRONMENT





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DRILLING AND OPERATING OIL, GAS, AND GEOTHERMAL WELLS IN AN H2S ENVIRONMENT

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Foreword

The development of oil, gas, and geothermal resources in a hydrogen sulfide (H_2S) environment can be hazardous unless adequate safety precautions are taken. H_2S gas may be emitted from geothermal wells and power plants and from oil and gas wells, gas plants, and sweetening units during drilling, workover, production, injection, gathering, handling, storage, and transmission operations. H_2S gas is toxic to humans and very corrosive to metals, including high-strength steel.

The best protection against H_2S -related accidents is knowing where H_2S environments are likely to be found and being well-informed about safe drilling and operating methods within them. It is to these ends that the present manual has been prepared.

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I. H₂S

TEST YOUR KNOWLEDGE

Poisoning by inhalation is the principal threat to human life from H_2S gas.	True or False
When people are overcome by H_2S gas, immediately rush to their aid.	True or False
You can rely on smelling the odor of rotten eggs when H_2S gas is in the vicinity.	True or False
Cal/OSHA has set 10 ppm as the Permissible Exposure Limit (PEL) of H_2S in the air.	True or False
H ₂ S gas released at a well site disperses evenly around the site.	True or False
(Answers: True, False, False, True, False.)	
	CHARACTERISTICS
H ₂ S is a colorless, acidic gas, almost as toxic as hydrogen cyanide and between 5 and 6 times more toxic than carbon monoxide. H ₂ S gas may be present in crude oil and natural gas produced from oil or gas wells, and in hydrothermal fluids produced from geothermal wells.	Life threatening
The principal threat of H_2S gas to human life is poisoning by inhalation. Whenever H_2S gas is present, respiratory protection is of extreme importance.	

The sense of smell cannot be relied upon to indicate either the presence or the concentration of H_2S gas.

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Toxicity Taste and Odor

§ 5155 Cal/OSHA **TITLE 8**

GENERAL INDUSTRY SAFETY ORDERS

(Register 81, No. 2-1-10-81) (p. 432.270.11)

TABLE AC-2 **EXCURSION EXPOSURES**

Skin (*)	Substance		<u>TL</u> ^(b) mg/M ^{3(d)}	Excursion Limit	Excursion Duration ^(*)	Ceiling Limit
Hy	drogen sulfide	10	15	20 ppm	10 min/8 hrs	50 ppm

 (a) Refer to Section 5155(d) for the significance of the Skin notation.
 (b) For the definition and the application of the Permissible Exposure Limit (PEL), refer to Section 5155(b) and (c) (1). (c) Parts of gas or vapor per million parts of air by volume at 25° C and 760 mm Hg

(c) and of get of vapor per mining parts of all by volution at 20 C and 760 mm Hg pressure.
(d) Milligrams of substance per cubic meter of air at 25° C and 760 mm Hg pressure.
(e) Exposures to concentrations above the "excursion limit", but not exceeding the "ceiling limit", are permitted for a time period not to exceed the "excursion duration".

According to the California Occupational Safety and Health Administration (Cal/OSHA), the Permissible Exposure Limit (PEL) of hydrogen sulfide for an employee in an 8 hour work period is 10 ppm. If an employee is exposed to a concentration of hydrogen sulfide above 20 ppm but never above 50 ppm for a maximum period of 10 minutes during an 8 hour work period, these exposures must be compensated for by exposures to hydrogen sulfide concentrations less than 10 ppm during the same work day such that the permissible exposure limit of 10 ppm is not exceeded.

Lower concentrations

Lower concentrations of H₂S gas have a sweet taste, and the odor of rotten eggs can be detected. However, prolonged exposure to lower concentrations can cause injury or death.

Higher concentrations

Upon exposure to higher concentrations of H₂S gas (100 ppm or above), the sense of smell is impaired in 2 to 15 minutes due to paralysis of the olfactory nerve (National Safety Council). In addition, death from exposure to still higher concentrations of H₂S gas can occur from lung paralysis before any odor is detected.

H,S pom	0-2 Min	2-15 Min.	15-90 Min	30 Min I Hr	t a Htr	4—8 H	8 : ?) Hr
50-100				Mild, Con- junctivitin, res- piratory tract irritation.			
100-150		Coughing: imi- tation of eyes, loss of serve of smell	Disturbed res- piration, pain in eves, sleep- ness	Throat irrita tion	Salivation and mucous dis charge; sharp pain in eyes, coughing	Increased symp toms."	Hemorrhage and death.*
1%0-200		LOSS of sense of smell	Threat and eve writatum	Throat and eye Widataso	Difficult breath- ing, blurned vision; light shy	henows unital- og effect *	Hemorrhage and death *
250-350		irritation of eves, iosi of sense of smell	irreation of eyes.	PaintLI secre tion of tears wear news	Light shy, na sal catardi, pain in eyes, difficult briath- ing: con- junctivitis	Hemorrhage and death *	
)50 450		Irritation of eves, loss of sense of smell.	Difficult respi- ration; cough ing: initiation of eyes.	Increased inn- tation of eyes and nasal tract, dull pain in bead; weati- ness, light shy	Dizziness, weakness, in- creased inita- tion, death	Death *	
500600	Coughing, col- lapse and un- consciousness =	Respiratory dis- turbances: in- ritation of eves: collapse.*	Serrous eye in- ntation light shy, palpita tion of heart, a few cases of death	Severe pain in eyes and head, dziziness; trembling or extremities, great weak- ness and death f			
600-1,500	Collapse;" un- consciousness," death.	Collapse," un- consciousness," death					

*Data secured from experiments on dogs, which have a susceptibility similar to men National Safety Council data sheet D chem. 16

NOTE:

Hydrogen sulfide concentration is expressed in two ways:

- (a) By ppm in liquid by weight, and
- (b) By ppm in vapor by volume.

There is a significant difference between the two measurements, and under certain controlled conditions, this difference can become extreme.

Chemists have measured a deadly concentration of 7,000 ppm in the vapor stream coming out of an opening of a tank being topped off with crude oil that contained only 70 ppm of H_2S as measured in the liquid. It is vitally important to remember that a hydrocarbon liquid such as sour crude oil containing 50 ppm of H_2S gas can release vapors at much higher and sometimes lethal concentrations.

 $\rm H_2S$ gas becomes less soluble in water as the water temperature increases.

 H_2S gas is heavier than air. Because of this, H_2S gas becomes concentrated close to the ground, accumulating in low areas such as well cellars and ditches.

Special precautions must be taken to prevent spontaneous ignition fires when vessels that have contained hydrogen sulfide are opened. Ignition is caused by the reaction of *iron sulfide* with air to form *iron oxide*. The conversion of the sulfide to oxide generates enough heat to ignite flammable vapors.

To prevent these spontaneous fires, iron sulfide on container surfaces or sulfide sludge inside the tanks or vesssels must be kept wet, with water, until the vessels are gas-free.

 H_2S gas burns with a blue flame, producing sulphur dioxide (SO_2) gas that is very irritating to the eyes and lungs. SO_2 gas is less hazardous than H_2S because the odor is so pungent at nonfatal concentrations that humans cannot stand to be around it. However, like H_2S gas, SO_2 gas can cause serious injury as well as death to persons exposed to it.

TOXICITY OF SO1 GAS FOR HUMANS

1 ppm	Pungent smell may cause respira- tory changes.
5 ppm	Safe for eight-hour exposure. Nor- mally, a person can detect the gas in this concentration range.
12 ppm	Throat-irritating cough, constric- tion of the chest, tearing of the eyes.
150 ppm	So irritating that it can only be en- dured for a few minutes.
500 ppm	Causes a sense of suffocation, even with first breath.
1,000 ppm	Will cause death with short-term exposure.

Boiling point: -76°F

Water solubility ratio: 4 volumes gas to 1 volume water at 32°F

Heavier than air (H₂S specific gravity = 1.192^{-2} Air specific gravity = 1.0)

Ignition temperature: 500°F (Highly flammable)

Explosive range: 4.3% – 45.5% by volume ² (Forms explosive mixtures with air or oxygen)

Blue flame; SO₂ produced

² Superior figures refer to entries in a list of references at the end of the report.

II. Drilling and Operating Oil, Gas, and Geothermal Wells

Many oil, gas, and geothermal wells have been drilled and operated successfully in an H₂S environment. No mishaps occurred when wells were properly planned and safe drilling and operating methods for H2S areas were used.

While drilling and operating a well, safety meetings should be held routinely to review H₂S safety practices and to train personnel to use detection equipment and air breathing equipment.

Drilling and operating wells safely in an H₂S environment is not possible without proper well site design. To design a safe site, these factors must be known: weather conditions Safe Drilling of Wells Containing Hydrogen Sulfide. The API has requested including wind speed and direction; terrain; site space avail- that "Section 1, Scope," of publication RP49 be reprinted here, as well.) able; and whether the site is in an urban or a rural area.

SAFETY FIRST

WELL SITE PLANNING

(Many suggestions in this section are taken from API publication RP49,

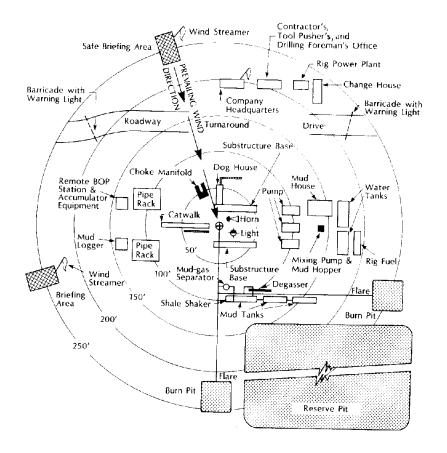
SECTION I, SCOPE

1.1 Drilling operations where hydrogen sulfide may be encountered should include provisions to use the safety guidelines outlined in this publication. These guidelines should be administered where there is a reasonable expectation that hydrogen sulfide gas-bearing zones will be encountered that could potentially result in atmospheric concentrations of 20 ppm or more of hydrogen sulfide. These are requirements for deep, high pressured wells located in or near a populated area.

1.2 Several factors, including but not limited to hydrogen sulfide content, potential surface pressure, potential flow characteristics, and geographical location, may dictate modifications or exceptions to the recommendations set forth herein. These safety recommendations have been developed, considering land locations with unconfined areal boundaries, to safeguard personnel at the rig site and surrounding area and to minimize risk exposure to rig equipment. Recognizing that there are many locations with confined boundaries (such as locations found in marsh, marine, urban, and mountainous areas), attention should be given to safety recommendations resulting from these geographical limitations. Additional safety guidelines for these confined locations are set forth under Section 4. "Location".

1.3 Recommended safety procedures on rank wildcat drilling operations should be initiated immediately after setting of the intermediate casing string. On development wells or wells where knowledge of formation type allows good correlation, recommended safety procedures should begin well in advance of reaching a depth where hydrogen sulfide may be encountered.

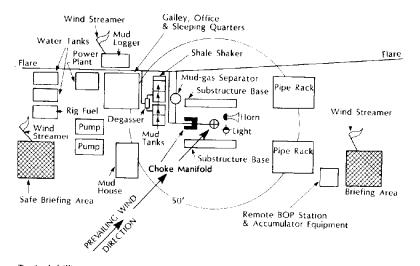
Site size	A well site planned for an H ₂ S environment should be larger than usual, i.e., larger reserve pits, turnaround room, etc. The extra room allows for a greater margin of safety in well site activities.
Access routes	Two access routes to the well site are needed so safe site entrance and exit routes are always available. Access routes to the well site should be planned so they can be barricaded if H ₂ S emergency conditions arise.
Passageways	Unobstructed passageways are needed between well site areas, including easy access between the rig floor and the drill stem test head if a drill stem test is made.
Ventilation	Drilling rig ventilation
	The drilling rig should be placed so that prevailing winds blow across the rig towards the reserve pits.
	Allow for adequate ventilation on the rig floor. In addition, take down the rig curtains and windbreakers when drilling approaches sour gas production zones. Remove all can- vasses at drill stem testing time and make use of blower fans at the rotary and shale shaker.
	Use every precaution to prevent the escape of gas into the air.
	Wind streamers
	Erect at least three sets of wind streamers on streamer poles to give wind directions at tree top level, draw works level, and at a level 8 feet above the ground.
	All wind streamers should be visible from the rig floor and illuminated at night.
	Bug blowers
	There should be three, explosion–proof bug blowers:
	 One blowing across the cellar area towards the pits; One blowing across the rotary table; and One blowing on the derrick work board to remove gas fumes near the derrickman.
Well site buildings	Well site buildings should be located on rises when the terrain is uneven. All buildings should be placed upwind from the well bore or any anticipated gas source.
Well cellars	In areas such as Santa Maria where highly toxic H_2S gas is produced with crude oil, operators should eliminate well cellars whenever possible. Any new cellars should not be more than 2 ½ feet deep.
Mud tanks	Place mud tanks away from the substructure to maximize the movement of fresh air around the cellar. This will lessen the danger if any gas breaks out of the mud.



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Typical drilling equipment layout—unconfined location. After API publication RP49. Reprinted with permission.



Typical drilling equipment layout—confined location. After API publication RP49. Reprinted with permission,

BOP equipment	The prevailing wind directions should be identified. Con- trols to operate blowout prevention equipment should be placed upwind, a safe distance from the well.
	An auxiliary closing unit should be provided that can be activated when the primary controls are not accessible.
	The installation of the BOPE choke manifold system, includ- ing pipe and choke, should be planned carefully. The choke should be located far enough from the rig to remain opera- tional if trouble develops. Before all piping, collars, flanges, and valves are placed in the system, care must be taken to see that they are made of proper materials.
	BOPE choke manifolds should be supported and anchored to withstand pressure and vibration. Flow lines laid with 90 degree turns and sharp bends create the most serious haz- ards. Be sure the flow lines are anchored properly and not plugged with mud.
	Conduct BOPE drills. When each crew member knows how to handle a task, the training pays off in an emergency.
	The warning signs for wells in H_2S areas are similar to signs occurring when any gas is encountered:
	 Drilling breaks; Pit mud gains; Mud weight decreases; and Wells trying to flow.
Briefing areas	Two or three, cleared, briefing areas should be designated that are at least 225feet from blowout prevention equipment so they offset prevailing winds perpendicularly (or at a 45° angle if wind direction tends to shift in the area). Self- contained breathing equipment for the crew and on-site personnel should be kept in each of the briefing areas so equipment would not have to be moved with shifts in the wind.
	The briefing area most upwind is designated as the "Safe Briefing Area". In an emergency, personnel must assemble at this upwind area for instructions from their supervisor.
Logging units	Consider terrain and prevailing wind when locating logging units. Place logging units away from the shale shaker mud tank and at least 125 feet from BOPE areas to eliminate congestion and increase safety for all.
Electrical generators	Locate electrical power generators at least 150 feet from BOP equipment to reduce the danger of an explosion and to allow the generators to be used under conditions when they otherwise would be shut down because combustible gases are present.
Flare areas and flare lines	Depending on the environment, it is usually safer to burn H_2S gas than to let it blow into the atmosphere. Primarily, burning H_2S gas produces sulfur dioxide (SO ₂). The heat carries the SO ₂ and H_2S gases high into the air, mixing them with a greater volume of air, thereby lowering the concentration of the H_2S .



Photo 1. Flare gun used to ignite H_2S flared at the well site. Upon ignition, the H_2S is converted to SO_2 . *Photo by Murray Dosch.*

Two flare areas should be located 90 degrees from each other. The flare areas should be at least 150 feet from the rig and other installations to protect workers during testing and trouble periods. The ground should be cleared around flare areas to prevent brush and grass fires.

Two flare lines should be installed with proper valves so the flow can be transferred from one pit to the other at any change in wind direction. Install flare lines to the burn pits from the degasser, choke manifold, and mud/gas separator. The diameters of the flare lines should be large enough to allow easy, unrestricted flow of H_2S .

Flow lines and flare lines should be targeted with running tees and staked securely. Flow lines to flare areas should be as long (150 feet, minimum) and as straight as possible, free from 90 degree turns. After installation, flare lines should be tested with air, natural gas, or butane to ensure proper operation.

Every effort should be made to keep H_2S flare lines lighted at all times. This may be done with burning pots or a propane pilot light. Special flare gun shells are a relatively safe means of lighting a flare. A combustible gas indicator should be provided for identifying the presence of an H_2S gas mixture.

Lay a kill line of ample strength to a point from which fluid can be pumped into the well safely.

Place emergency relief valves and vent lines a safe distance from work areas. When venting into the atmosphere is unsafe, the H_2S gas should be disposed of inside a closed system.

All lines, fittings, valves, etc., should be installed and maintained in a manner that eliminates all gas and oil leaks.

All electrical wiring, devices, and lights should be vapor proof to reduce the possibility of explosion.

The use of ground level tank gauges, automatic custody transfer units, and vapor recovery systems reduces the exposure of personnel to H_2S gas.

Emergency relief valves and vent lines

Miscellaneous equipment



Photos 2a and 2b. Emergency equipment: stretcher, rope, safety harness, resuscitator with an oxygen tank, fire blanket, and first aid kit. *Photos by Ed Hickey and Murray Dosch.*

Heaters used on the rig floor and in the doghouse should be flame proof and MUST BE TURNED OFF when $\rm H_2S$ is first encountered.

At least five 30-pound dry-chemical fire extinguishers should be located at strategic positions at the drill site.

Wall-type first aid kits with standard contents should be mounted at the safe briefing areas and in the trailers.

Two 500-foot rolls of 400 pound-test, soft, fire-resistant rope should be provided to use as safety lines.

Fire extinguishers

Other emergency equipment

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A rigid, body-fitting litter should be in a location accessible from the work area.

Telephone or radio communication should be available at the rig. Each employee should know how to contact the nearest doctor and hospital. Post these numbers near the telephone or radio.

"Warning", "Keep Out", and "Keep Off Rig Floor" signs should be hung at the well site and at well site approaches to keep unauthorized people away from well sites and to warn others unfamiliar with the dangers of H_2S gas.

"No Smoking" signs should be placed in areas adjacent to the wellbore, rig floor, and mud pits. Outside communication

Warning signs

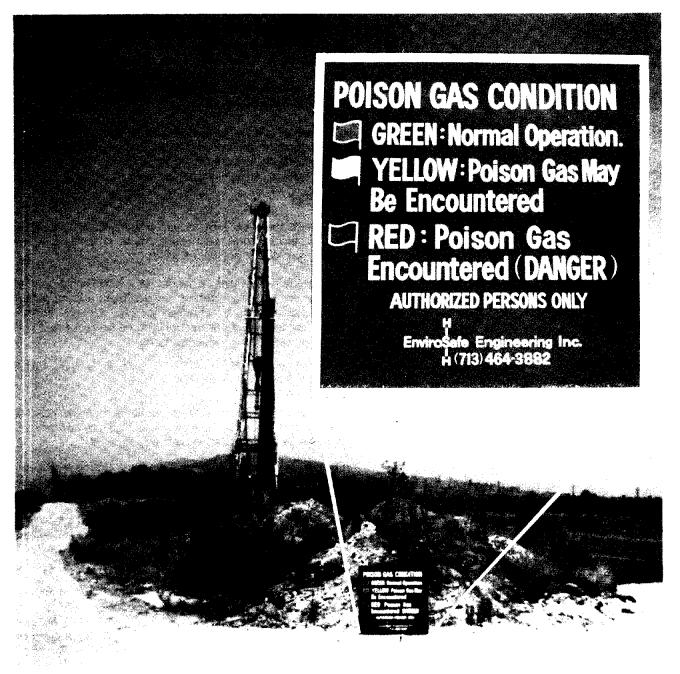


Photo 3. Well site sign describing poisoneous gas conditions. Photo by Murray Dosch.

Radius of exposure

Contingency plan

The locations of all structures within the exposed areas should be noted on a map. It is essential that all occupied buildings be marked and a list compiled of the number and names of the occupants and their telephone numbers.Contact with these people should start once drilling begins, to explain the hazards and the fact that evacuation might be necessary if an emergency develops. Procedures to notify these persons in an emergency should be worked out before drilling begins.

To calculate potential well area toxicity from H₂S emissions,

it is necessary to know the volume of oil or gas produced and the concentration of the hydrogen sulfide in the oil or

From these data, the radius from the source to the 300 ppm and 100 ppm– H_2S concentration units can be determined on scales as shown in the examples. Potential sources of toxic gas emissions include wells and production, treat-

The most stringent safety precautions must be undertaken in the areas with the highest concentrations of H_2S .

ment, processing, and storage facilities.

Because of high-pressure dispersion, the probability of a lethal concentration of H_2S extending beyond a 1-mile radius is unlikely, except on a dead-calm day with a tremendous release of heavily concentrated vapors.

Livestock

1. 2.

3.

gas.

Livestock must be moved out of pastures in hazardous zones before a drill stem test is made. Animals are overcome quickly by poisonous gases.

Before equipment from a service or workover rig enters a

well where H₂S was present, the wellhead, casing, tubing,

and gauges should be checked for H_2S damage. Furthermore, the following information should be requested from

In addition to these steps, the procedures recommended for drilling and operating a well in an H_2S environment, as

the exploration or production company:

outlined in this chapter, should be followed.

Date of the last H₂S test;

Who tested the well; and

Test results.

SERVICE OR WORKOVER RIG OPERATIONS

Facilities inspection

PRODUCTION Warning signs

Danger signs should be posted at all production tank batteries where the thief hatch reading for H_2S has reached or could exceed Cal/OSHA standards. The sign should say:

DANGER

HYDROGEN SULFIDE

Self-contained breathing equipment must be worn when opening tank hatches.

Regular preventative maintenance and safety inspections should be made to detect leaks and prevent malfunction of equipment. Inspected items should include tank hatch seals, tank vent lines, and relief valves.

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Use the Pasquill–Gifford equation to determine the location of the 100 ppm radius of exposure:

 $X = [(1.589) \text{ (mole fraction} H_2S) (Q)]^{(.6250)}$

Where:

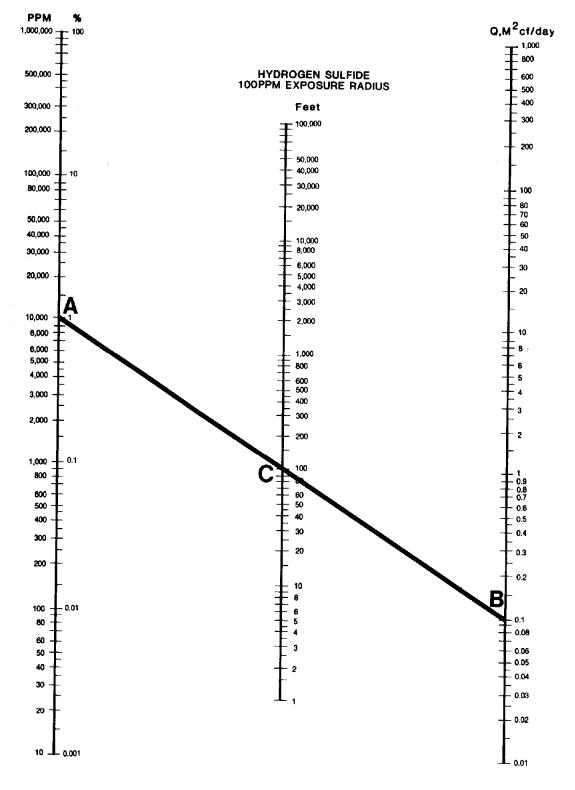
- X = radius of exposure in feet
- Q = maximum volume determined to be available for escape in cubic feet per day
- H₂S = mole fraction of hydrogen sulfide in the gaseous mixture available for escape

In making dispersion calculations, the values used in the equation shall be specific well or facility ones and not averaged lease figures.

Calculation of volume of produced gas:

The volume used as the escape rate in determining the radius of exposure shall be that specified below, as is applicable:

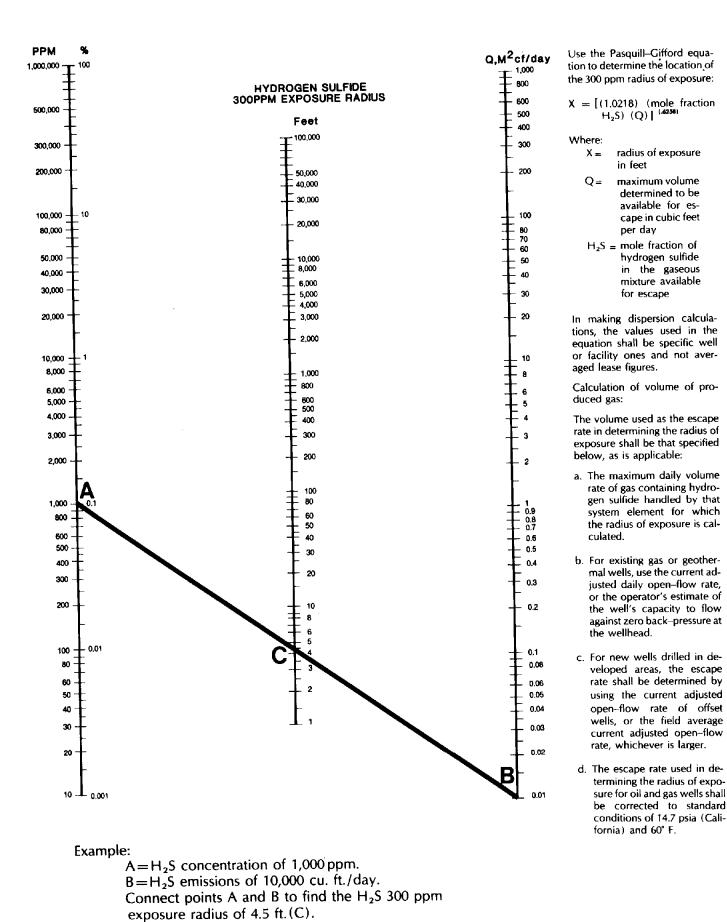
- a. The maximum daily volume rate of gas containing hydrogen sulfide handled by that system element for which the radius of exposure is calculated.
- b. For existing gas or geothermal wells, use the current adjusted daily open-flow rate, or the operator's estimate of the well's capacity to flow against zero back-pressure at the wellhead.
- c. For new wells drilled in developed areas, the escape rate shall be determined by using the current adjusted open-flow rate of offset wells, or the field average current adjusted open-flow rate, whichever is larger.
- d. The escape rate used in determining the radius of exposure for oil and gas wells shall be corrected to standard conditions of 14.7 psia (California) and 60° F.



Example:

 $A=H_2S$ concentration of 10,000 ppm. $B=H_2S$ emissions of 100,000 cu. ft./day. Connect points A and B to find the H₂S 100 ppm exposure radius of 100 ft. (C).

Scales to determine H_2S 100 ppm exposure radius.

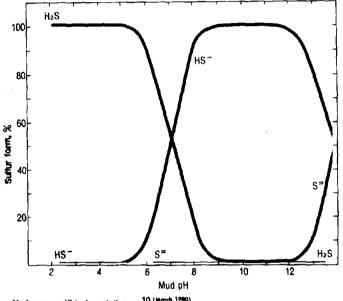


Scales to determine H₂S 300 ppm exposure radius.

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 H_2S gas control in drilling mud means, first, a mud sufficiently alkaline to neutralize the acidic, H_2S gas and to form soluble sulfide salts. The drilling fluid pH level should be maintained above 9.5 at all times.² In some cases, this may mean a pH of 11.5 to prevent a pH reduction below 9.5 while tripping the drill string.

For further H_2S gas protection, heavy metal compounds are added to the mud as scavengers, precipitating the soluable sulfides salts as insoluable metal sulfides.[#]Once, copper compounds were common as scavengers. Today, they are not recommended because of electronic corrosion of copper against iron.¹⁷



Hydrogen	sulfide	in.	solution,	10 (Ma
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Mud types	HzS presence on coupons	Hydrogen embrittlement	Corresion rate (MPY)
1, Invermul	No	No	5.30
(3 lb/bbl lime)			
2. Invermul	No	No	3.99
(8 lb/bbl lime)			
3. Low lime	No	No	3.23
4. High lime	No	No	3.42
5. Non dispersed –	Yes	Yes	26.60
low lime with saturated salt, polymer, starch			
6. Lignite/lignosulfonate (starting pH 9-11)	Yes	Yes	107.47
7. Lignite/lignosulfonate (starting pH 11)	Yes	Yes	70.02

Effect of mud type on corrosion. ¹⁰ (Marth 1990) Series of tests using mild steel coupons and prestressed bearings contaminated with 2.400 ppm H₂S rolled 16 hr at 150°F. MPY = mils/year. (From N.L. Baroid)

Dissolved gas	Decrease from air-endurance limit. %
H₂S	20
CO2	41
CO ₂ + Air	41
H ₂ S + Air	48
HzS + COz	62
Air	65

Corrosion fatigue of steel in brine. 10 (March 1980)

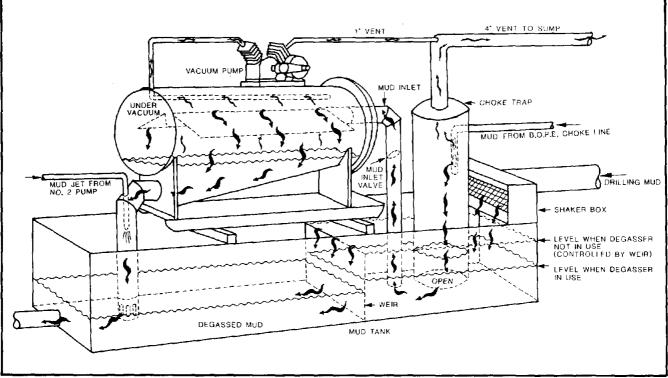
Analyzing drilling mud The iodometric method is one field method of analyzing drilling mud for H_2S gas. This method shows trends of sulfides in strata and allows sulfides to be measured over a 0 to 200 ppm-concentration range.

When gas cutting of drilling mud occurs, the blowout preventers are closed immediately and normal circulation maintained through the choke lines (choke wide open) to the choke trap.

The choke trap is a barrel-like apparatus suspended upside down in the shaker tank with the lower lip of the barrel below normal mud level. The mud and gas flow into the side of the barrel. A four-inch vent line leads from the top of the barrel to a safe distance from the mud stream in the choke trap, and the gas can be vented and flared safely through the four-inch line.

The mud containing residual gas passes out the bottom of the choke trap and enters a degasser installed for separating gas from the drilling fluid between the first and second mud tanks. The degasser operates under a vacuum of 10–20 inches of mercury, extracting virtually all of the remaining gas by allowing the mud to flow over a series of baffles.

Vacuum in the degasser is maintained by a jet on the discharge side of the degasser and by a vacuum pump mounted on the top. The vacuum pump discharge should be vented at a safe distance from the rig and flared, if necessary. A partition in the mud tank, between the intake and the discharge of the degasser, separates the gas-cut mud from the degassed mud. The jet is operated by the standby mud pump.



Hook-up for SWACO degasser and choke trap.

Mud degassers

Adequate ventilation and, where necessary, air blowers are generally employed to keep the rig floor and the area under the rig floor relatively free of any residual H_2S gas. The use of lime mud with a high pH also assists in minimizing the hazards of H_2S by neutralizing the gas in the well bore. Mud additions of 500 to 1,000 pounds of both caustic and lime are frequently employed for this purpose when the mud becomes gas cut.

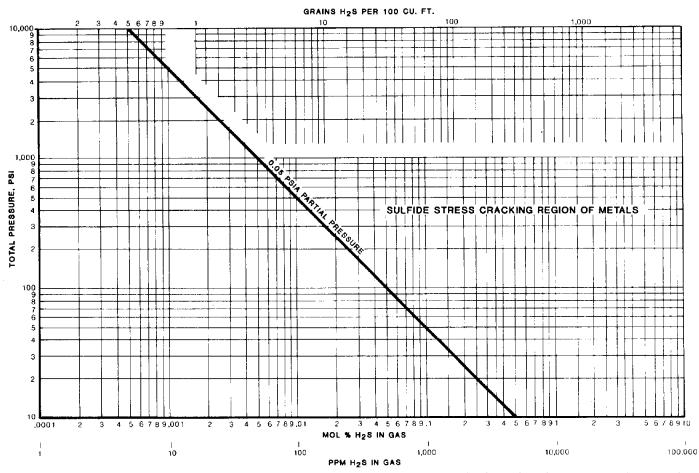
Normally, after circulating for a few hours with the blowout preventers closed, the amount of gas will decrease to the point where the blowout preventers can be opened and drilling operations resumed without using the choke trap.

The degasser will continue to be employed until the mud is gas free. This may take up to one to two days of more-orless continuous operation. If the gas cutting exists for longer periods, usually a small amount of weight material will be added to the mud. Normally, this will eliminate the continuous type of gas cutting, although trip gas still may persist.

Trip gas is handled with the degasser; and, if it is severe, the blowout preventers are closed again and the flow turned through the choke trap for a few minutes.

H₂S gas is very corrosive to metals, including high-tensile

EMBRITTLEMENT



Correlation between partial pressure of H_2S in mole percent and H_2S content in grains per 100 cubic feet with total pressure. From the National Association of Corrosion Engineers Publication No. MR-01-75; *Material Requirements-Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment.*

	steel, which H_2S can embrittle. Drilling mud especially for- mulated for an H_2S environment reduces the reaction of H_2S with the drill string, tool joints, pump fluid ends, choke, and piping.
Minimizing embrittlement	To minimize embrittlement:
	 Select tubular goods, wellhead equipment, and other drilling-related equipment with metallurgical properties most resistive to H₂S embrittlement;
	b. Avoid exposing high strength drill pipe to H_2S gas;
	c. Use drill pipe coated internally with plastic (effective only in preventing exposure of pipe bore to H_2S gas encountered during drill stem testing or drilling);
	d. Maintain mud pH at 9.5 or higher;
	e. Limit periods of drill stem testing with marginally susceptible drill pipe to one hour if gas containing H ₂ S flows at less than 1,000 Mcf per day, or 15 minutes if gas containing H ₂ S flows at more than 1,000 Mcf per day.
	f. Use an inhibitor in the water cushion prior to the drill stem test when H ₂ S exposure is anticipated.
	g. Flush out the drill stem through the pump-out sub fol- lowing drill stem tests and prior to handling the pipe on a trip out of the hole. Use an inhibited mud or solution to clean the pipe as quickly as possible.
	h. Use appropriate inhibitors in the mud system. Although many inhibitors are sold for sulfide-stress corrosion control, the best seem to be the filming-type amines. Both soluble and insoluble types are available for direct application to metal, plug-type addition, and continu- ous addition to the mud system.
	i. Use care in out-of-hole handling of susceptible pipe that has been exposed to embrittling conditions. Special care should be exercised in use of tongs and slips to avoid the introduction of localized high stresses at not- ches.
	j. Minimize down-hole stresses in the drill string.

· · ·

III. Detection Devices and Protective Equipment

A quantitative, electronic hydrogen sulfide monitor has been designed for permanent 24-hour-a-day operation in a fixed location on oil, gas, and geothermal rigs and production facilities. It can have from 1 to 12 channels on which sensors are attached. The sensors are positioned around the rig in low areas, including the bell nipple, shale shaker, rig floor, and mud pits. The monitor is placed in a conspicuous place and monitors the channels separately. The monitor has a needle indicator that gives a continuous readout, in parts-per-million, of H₂S concentrations. The system is usually equipped with a strobe light that activates at a certain gas concentration, and an audio alarm that automatically sounds when higher concentrations are present. The monitor must be calibrated and checked periodically to ensure proper functioning.

The paper used in paper H_2S detectors has been impregnated with lead acetate that , when exposed to H_2S , forms lead sulfide. Lead sulfide changes the paper color to shades of brown, depending on the concentrations of H_2S .

Badge- or spot-type detectors can be worn or carried by workers, and the paper can be changed after exposure.

Photo 4. Electronic H_2S monitor. The 4- channel monitor, built by Texas Analytical Controls, Inc., measures H_2S concentrations between 0 and 50 ppm.

H₂S DETECTION METHODS

Related material: Entry No.10 in Selected References.

Hydrogen sulfide monitor

Paper detector

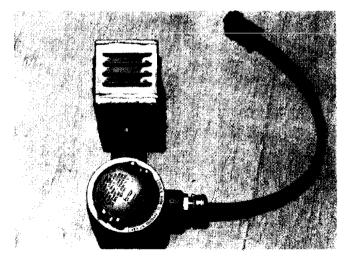


Photo 5. Sensor head for an H_2S monitoring system. Sensor heads should be placed at the bell nipple, shale shaker, mud pits, and rig floor. *Photo by Ed Hickey.*



Photo 6. H_2S sensor head is mounted, photo center, above the shale shaker. Photo by Ed Hickey.

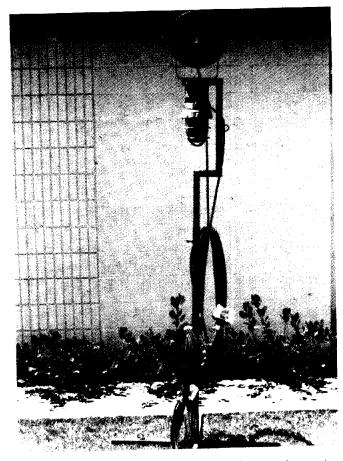


Photo 7. Portable audio and visual alarm, with a siren alarm and a flashing strobe light. *Photo by Murray Dosch*.

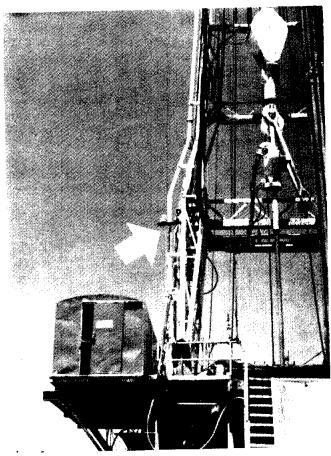


Photo 8. Portable audio and visual alarm mounted on the rig at photo center, to the right of the dog house. *Photo by Ed Hickey*.

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Three to 5 minutes are needed to record a reaction on a paper detector, a possibly dangerous time lapse when large concentrations of H_2S are encountered. Therefore, paper detectors are used mainly to indicate when H_2S is present and not to determine the concentration of the gas, although the detector has an approximate range of 0 to 20 ppm H_2S .

A capsule detector is made of glass filled with granules and covered with a nylon sheath. To use, the capsule is broken and attached to clothing with a string. When hydrogen sulfide contacts the granules, they turn brown.

This type of detector is used to indicate the presence of H_2S , but the maximum concentration of the gas that can be measured is 20 ppm. Use life is 6 days.

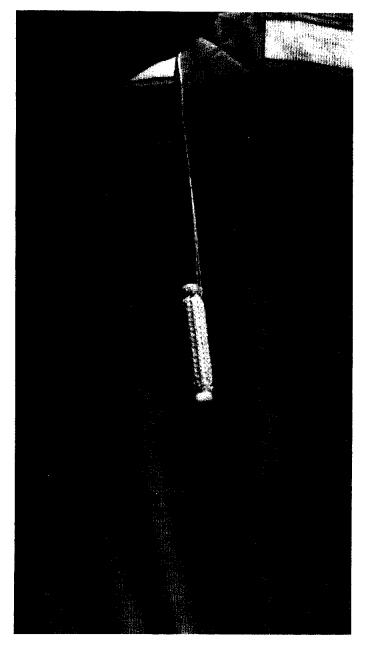
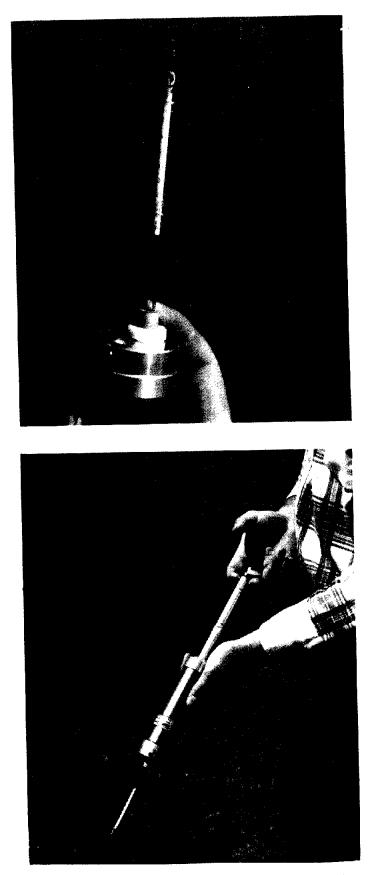


Photo 9. Glass capsule H_2S detector, covered with a nylon sheath. Photo by Ed Hickey.

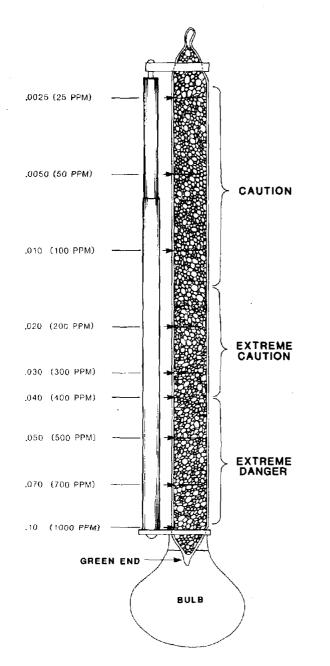
Capsule detector



Photos 10a and 10b. Bendex-Gas Tec. H_2S pump-style detectors. *Photos by Ed Hickey*.

Pump detectors are comprised of glass tubes and hand pumps. The sealed tubes are filled with granules impregnated with a chemical. To use, a tube is broken on both ends and attached to a hand pump or bulb that is operated to draw in an air sample. For samples of low H₂S concentration, it may take 10 strokes on the pump to get an adequate sample; for samples of high H₂S concentration, it may take only one stroke. The H₂S gas reacts with the granules, and the concentrations can be read directly from tube calibrations.

Tubes with different concentration ranges can be used after the tips are broken (as long as no indication of H_2S is present). Detector accuracy depends on the experience of the user; concentrations between 1 and 1,000 ppm can be measured.



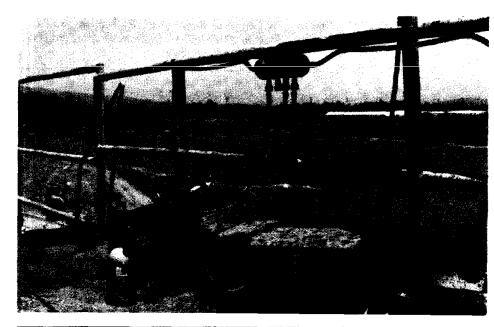
MSA H₂S gas detector-bulb type.

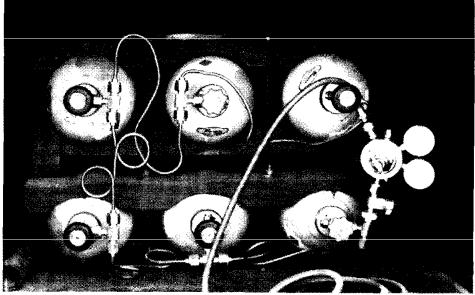
Belt type

The belt-attached, hydrogen sulfide detector is a batteryoperated electronic device with an audible alarm. The detector has a sensor head that will detect H_2S gas and measure concentrations between 0 to 50 ppm. The detector is usually preset to respond at 20 ppm. Response time is about 35 seconds. This detector must be calibrated and checked periodically to ensure proper functioning.



Photos 11a and 11b. Scott air pac. Tank holds a 30 minute supply of air. When 78 percent of the air has been used, an alarm sounds, warning the wearer to leave for a safe-breathing area. *Photos by Ed Hickey*.





12b

Types of self-contained air breathing equipment range from short-term escape units to long-term work units.

Regulations on the selection, type, use, and maintenance of respirators are in the following publications:

- 1. Occupational Safety and Health Administration (OSHA): Occupational Safety and Health Standards for General Industry, 29 CFR 1910 (1978) 128.
- 2. OSHA: Table Z-2(a)(3), 29 CFR 1910, Table 2, p. 1001.
- 3. Department of Health, Education, and Welfare (DHEW); National Institute for Occupational Safety and Health (NIOSH): Criteria for a Recommended Standard for Occupational Exposure to Hydrogen Sulfide, publication No. 77–158.



Photos 12a, 12b, and 12c. Well cascade system designed for workers on the rig floor. Air is supplied from a battery of tanks, such as those in photo 12b. Each tank holds a 3 hour supply of air.

The workers wear small containers of air, such as the Scott 5 minute-escape air tank, to use when they must escape from the rig. Notice the breakaway valve released in photo 12c. *Photos by Ed Hickey*.

AIR BREATHING EQUIPMENT

4.	DHEW:	A Guide to Respiratory Protection, 30 CFR,
		Part II (1976) 52. A table from this guide has
	been reprinted below.	

been reprinted below.					
	DHEW Respirator Selection Guide for Hydrogen Sulfide ¹⁰				
H ₂ S Concentration		Respirator type approved under provisions of 30 CFR II			
Less than or equal to 70 mg/cu meter (50 ppm)	2007	Any supplied-air respirator with full facepiece. Any self-contained breathing apparatus with full facepiece.			
Greater than 70 mg/cu meter (50 ppm)		Self-contained breathing apparatus with full faceplece operated in pressure-demand or other positive- pressure mode. Combination Type C supplied-air respirator with full faceplece operated in pressure-demand or other positive-pressure or continuous-flow mode and auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressue mode.			
Emergency (entry into area of unknown concentration for emergency purposes, e.g., firefighting)		Self-contained breathing apparatus with full facepiece operated in pressure-demand or other positive- pressure mode. Combination Type C supplied-air respirator with full facepiece operated in pressure-demand or other positive- pressure or continuous-flow mode and auxiliary self-contained breathing apparatus operated in pressure-demand or other positive-pressure mode.			
Escape (from an area of unknown concentration)		Any self-contained breathing apparatus. Any gas mask providing adequate protec- tion against hydrogen sulfide (not to be used in confined spaces).			
pressure from the tank to demand mode in which mask under slight vacuu in which the regulator al mask. The main differen	o th im, llov ce l	ne respirator that reduces the air ne mask. There are two types, the ne wearer draws the air into the and the pressure-demand mode vs a slight pressure buildup in the between the two is that once a ode type would leak inward and			
The pressure demand n taminates being drawn i it is required to be use (tolerance limit value) is being exceeded. Som	noc nto ed i cor e u	le limits the possibilities of con- the mask, and this is the reason in atmospheres where the TLV incentration for hydrogen sulfide nits are equipped with a bypass			

When to	o use	self-contained
air brea	thing	equipment

Regulators

Use self-contained air breathing equipment:

(MESA).

1. When Cal/OSHA H_2S standards are or could be exceeded (see page 2).

valve that allows partially regulated air to be delivered to the mask in case of regulator failure. A mask with a full face piece must be used and the respirator must be approved by the National Institute for Occupational Safety and Health (NIOSH) and the Mine Enforcement Safety Administration

2. While rescuing a person overcome by H₂S.

Persons with a perforated ear drum *should never* work in an H_2S environment with concentrations above 10 ppm, even with self-contained breathing equipment, because gas can enter the lungs through a damaged ear passageway. For this reason, physical examinations of crew members should include ear examinations. When *not* to use self-contained air breathing equipment

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VI. Hazard Levels and Safety Procedures *

Potential Danger H₂S gas concentration 0 to 20 ppm Minor gas breakout from mud or equipment. **Probable occurrence** As a drill show, trip gas, or lost circulation. **General action** The procedures outlined in this section, or similar procedures, should be implemented whenever a concentration over 10 ppm of H₂S gas is detected. 1. The driller should shut down mud pumps and continue to rotate the drill pipe. 2. If the well attempts to flow, the driller should stop rotating the drill pipe and close the blowout preventers. The following personnel must immediately put on their breathing equipment with the mask in a ready position: a. All personnel on the rig floor. b. All personnel at the mudpits, and c. All personnel required to work below and down wind of the rig. Check all gas monitoring devices and increase gas monitoring activities. 5. Immediately begin to ascertain the source of the H₂S and take steps to suppress the H2S. Drilling should not proceed until the source is determined and the well is

circulated. Rig floor and mud pit personnel should wear breathing equipment while monitoring this circu-

3.

4.

lation.

Characterized by

CONDITION I:

^{*}Procedures have been adopted from many sources, including the SOHIO Petroleum Company, cited as Number 20 in the list of Selected References.

- 6. The mud engineer should run a sulfide determination of the flowline mud.
- 7. The drilling foreman and the drilling rig tool pusher should be notified.
- 8. The drilling foreman should alert all personnel that Condition I exists. The drilling rig tool pusher should be prepared to shut off the forced air circulating system.
- 9. The drilling rig tool pusher should make sure all nonessential personnel are out of potentially dangerous areas such as the mud pit area, mud shack, and mud storage room. All persons who remain in potentially dangerous areas should utilize the buddy system.
- 10. All personnel should ensure that their safety equipment is working properly and is in the proper location.
- 11. Protective breathing apparatus should be worn by all working personnel. Personnel with perforated eardrums should be evacuated from the site. Nonworking personnel should go to the SAFE BRIEFING AREA, taking their breathing equipment.

20 ppm–50 ppm
Moderate gas breakout from mud or equipment.
As trip gas, well kick, or lost circulation.
If the H_2S concentration reaches 50 ppm, the following steps must be taken:
 Order evacuation of local residents if gas threatens their safety. Request help from local authorities if required, but do not delay evacuation of persons in the Danger Area.
Set up roadblocks and minimize personnel movements.
2. All nonessential personnel or all personnel, as appropri- ate, shall remain in the SAFE BRIEFING AREA.
3. The driller should shut down the pumps and continue to rotate the drill pipe.

- 4. If the well attempts to flow, the driller should stop rotating the drill pipe and close the blowout preventer.
- 5. The driller should notify the drilling foreman and the drilling rig tool pusher and all other persons on the emergency telephone list.
- 6. The drilling rig tool pusher should alert all personnel that the dangerous situation exists and be sure the forced air circulation system is shut off.
- 7. Always put on a portable air breathing mask before proceeding to assist anyone affected by the gas or before entering areas of possible contamination; utilize the buddy system. If the affected person is stricken in a high concentration area, put on a safety belt with 50 feet of tail line and obtain standby assistance before entering the area.

CONDITION III: Extreme Danger H₂S concentration

Characterized by

Probable occurrence

General action

Over 50 ppm

Full-scale blowout (or) poisonous gas concentrations above hazardous limits.

Complete loss of well control during drilling.

- 1. Stay in the SAFE AREA if you are not working to correct or control the situation.
- 2. Follow all instructions of the supervisor in charge.
- 3. Order evacuation of local people within danger zone.
- 4. Assign someone to notify the company and the California Division of Oil and Gas.
- 5. Set up roadblocks and prevent entry of unauthorized persons.
- 6. Request help from local authorities to evacuate people and to control traffic in the threatened area.
- 7. The driller should shut down mud pumps and continue to rotate the drill pipe.
- 8. If the well attempts to flow, the driller should stop rotating the drill pipe and close the blowout preventer.
- 9. It may be necessary to ignite the gas. Once the gas is ignited, burning H₂S gas will be converted to SO₂ gas that is less toxic. Continue to observe emergency procedures.
- 10. Conduct all operations with a minimum of personnel.

DRILLING AND OPERATING OIL, GAS, AND GEOTHERMAL WELLS IN AN H₂S ENVIRONMENT

V. First Aid

The sheriff, ambulance, hospital, and nearby doctors should be contacted after drilling begins in an H_2S area. These people should be alerted to the situation and to what could happen in an emergency. Most doctors have not treated H_2S inhalation cases, and operators should offer to give doctors pertinent information.

Every person working in an H_2S environment should know the effects of inhaling H_2S in toxic concentrations and rescue and first aid procedures to use when this occurs. Specifically, each person at the drill site needs to know about:

- 1. Self-contained air breathing equipment;
- 2. The buddy system;
- Rescue breathing techniques (cardiopulmonary resuscitation if possible);
- 4. The resuscitator (Pneolator); and
- 5. Additional first aid techniques.

Remember, speed is essential in rescuing a victim and in administering proper first aid.**

- Don breathing apparatus before entering danger area to rescue a victim of H₂S inhalation. You, too, can become a victim if this is not done. Work with a partner on a lifeline, when possible.
- 2. Move victim to fresh, pure air at once.
- 3. Let *someone else* get the resuscitator and *someone else* call a physician.

**The following first aid procedures represent practices recommended by the Workmen's Compensation Board, Alberta, Canada, and the American Heart Association.

INFORM LOCAL HEALTHCARE PERSONNEL

RESCUE TECHNIQUES*

^{*}First aid techniques for H_2S victims should be posted in a place close to the work site such as a crew change room or driller's station.



If you find a collapsed person, determine if victim is conscious by shaking the shoulder and shouting "Are you all right?" If no response, shout for help. Then open the airway. If victim is not lying flat on his back, roll victim over, moving the entire body at one time as a total unit.

To open the victim's airway, lift up the neck (or chin) gently with one hand while pushing down on the forehead with the other to tilt head back. Once the airway is open, place your ear close to the victim's mouth:

Look – at the chest and stomach for movement.

Listen – for sounds of breathing.

Feel – for breath on your cheek.

If none of these signs is present, victim is not breathing.

If opening the airway does not cause the victim to begin to breathe spontaneously, you must provide rescue breathing.



The best way to provide rescue breathing is by using the mouth-to-mouth technique. Take your hand that is on the victim's forehead and turn it so that you can pinch the victim's nose shut while keeping the heel of the hand in place to maintain head tilt. Your other hand should remain under the victim's neck (or chin), lifting up.

Immediately give four quick, full breaths in rapid succession using the mouth-to-mouth method.



After giving the four quick breaths, locate the victim's carotid pulse to see if the heart is

*© 1977 American Heart Association. Reprinted with permission.

beating. To find the carotid artery, take your hand that is under the victim's neck and locate the voice box. Slide the tips of your index and middle fingers into the groove beside the voice box. Feel for the pulse. Cardiac arrest can be recognized by absent breathing and an absent pulse in the carotid artery in the neck.

For Infants and Small Children

Basic life support for infants and small children is similar to that for adults. A few important differences to remember are given below.

Airway

Be careful when handling an infant that you do not exaggerate the backward position of the head tilt. An infant's neck is so pliable that forceful backward tilting might block breathing passages instead of opening them.

Breathing

Don't try to pinch off the nose. Cover both the mouth and nose of an infant or small child who is not breathing. Use small breaths with less volume to inflate the lungs. Give one small breath every three seconds.

Check Pulse

The absence of a pulse may be more easily determined by feeling over the left nipple.

- 7. If you <u>CAN</u> find the pulse, continue rescue breathing until victim revives or the resuscitator is readied. (Exercise care due to possible lung congestion.) According to the American Red Cross rescue breathing instructions, you should:
 - Repeat breaths about 12 times a minute for an adult or 20 times a minute for a child.
 - Establish a rhythm.
 - If victims's stomach rises, press it gently to remove air.
 - As patient revives, watch closely. Treat for shock.
- 7. If you <u>CANNOT</u> find the pulse, the victim needs CPR, Cardiopulmonary Resuscitation. CPR should be administered ONLY by a person properly trained and certified. It is too complicated to be taught from printed pages alone.

Free CPR courses are offered by the American Heart Association and the American Red Cross.

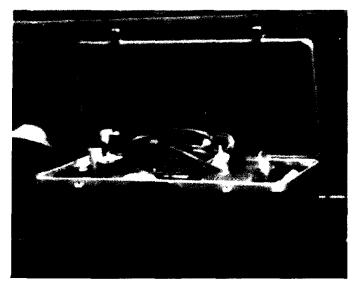


Photo 13. A resuscitator. Photo by Murray Dosch.

choice in restoring breathing.

The resuscitator (Pneolator) 8. The Pneolator is an instrument that performs artificial respiration with an automatic, predetermined pressure on inhalation, and without suction on exhalation. This most nearly represents normal respiration and has been selected by medical authorities as the method of

Once the patient is breathing, the Pneolator becomes an effective oxygen inhalator by a simple adjustment. If the air passage is obstructed by mucous or foreign material, a warning is immediately given by a chattering of the cycling valve, and the Pneolator provides an aspirator for removing the obstruction. The Pneolator can be taken with a victim to the hospital.

NOTE: The small oxygen bottles carried by most ambulances are not the type required for a Pneolator. The 21 cubic foot bottle of oxygen in the Pneolator should be checked and filled to capacity *before* all well testing operations. Furthermore, it is strongly recommended that an extra supply of oxygen (a commercial tank) be kept on hand as a "standby" supply.

> This large oxygen cylinder can be hooked up to the resuscitator while it is being used to increase the volume of oxygen that is available for use should there be more than one victim overcome.

Victim position

Physician visit

- 9. Keep victim warm and quiet, but never unattended.
- 10. A person who has been overcome by H_2S gas and revived could go into shock. Because of this, take the victim to a doctor at once. Patients should be kept under medical observation until the doctor declares them fit to return to work.

- 11. A patient breathing normally may be given stimulants such as tea or coffee. (Alcohol is a depressant).
- 12. If eyes are affected by H_2S , wash them thoroughly with clear water. For slight eye irritation, cold compresses will help.
- 13. Once a victim is removed to fresh air and normal respiration restored before heart action ceases, rapid recovery may be expected.

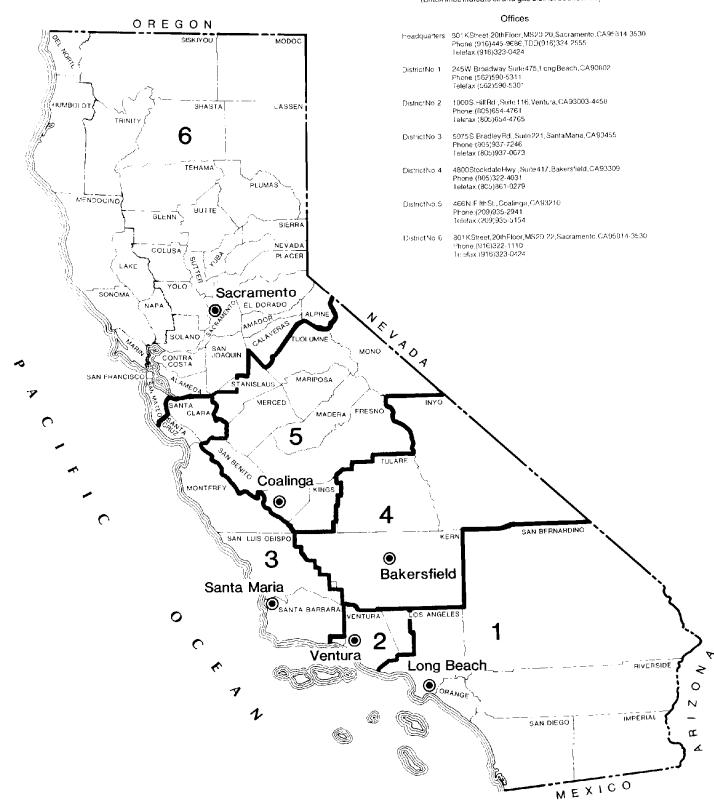
In cases of slight or minor exposures, where the worker has not been totally unconscious and wants to return to work after a short rest period, it is recommended that duty be postponed until the following day. Reflexes may not have returned to normal, and the person could be subject to injuries from other work hazards. Stimulants

Eyes affected by H₂S

Minor exposure

OIL AND GAS DISTRICT BOUNDARIES

(Black lines indicate oil and gas district boundaries)



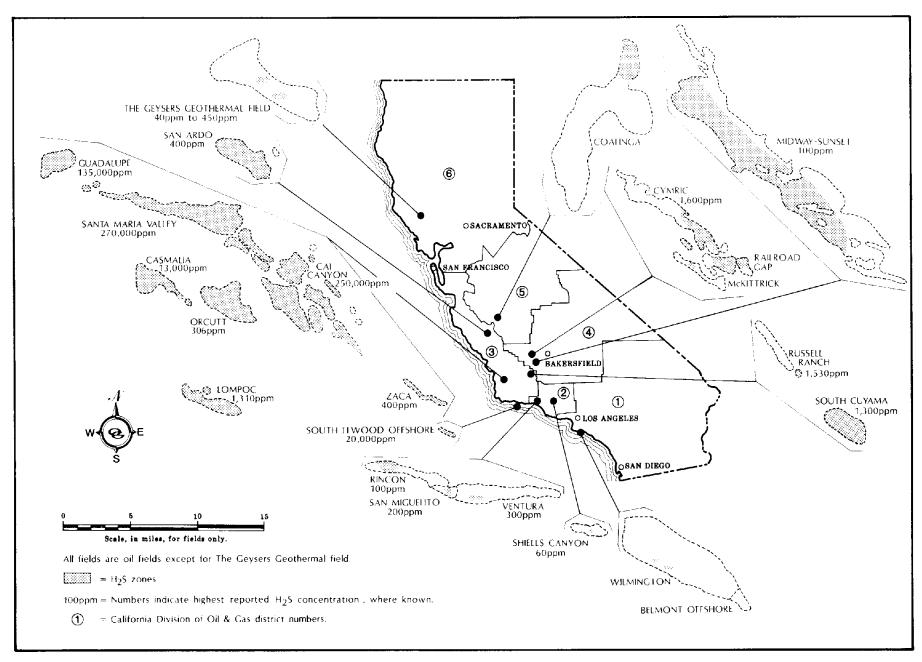
VI. H₂S in California Oil, Gas, and Geothermal Fields

 H_2S in various concentrations is found in oil, gas, and geothermal fields throughout California. Some of the fields are included on maps in this chapter. Where known, the H_2S concentrations are noted, as well.

Any operator requesting a well permit from the California Division of Oil and Gas for well operations in a known H_2S area will be notified of this hazard on the permit (P-Report) issued by the division.

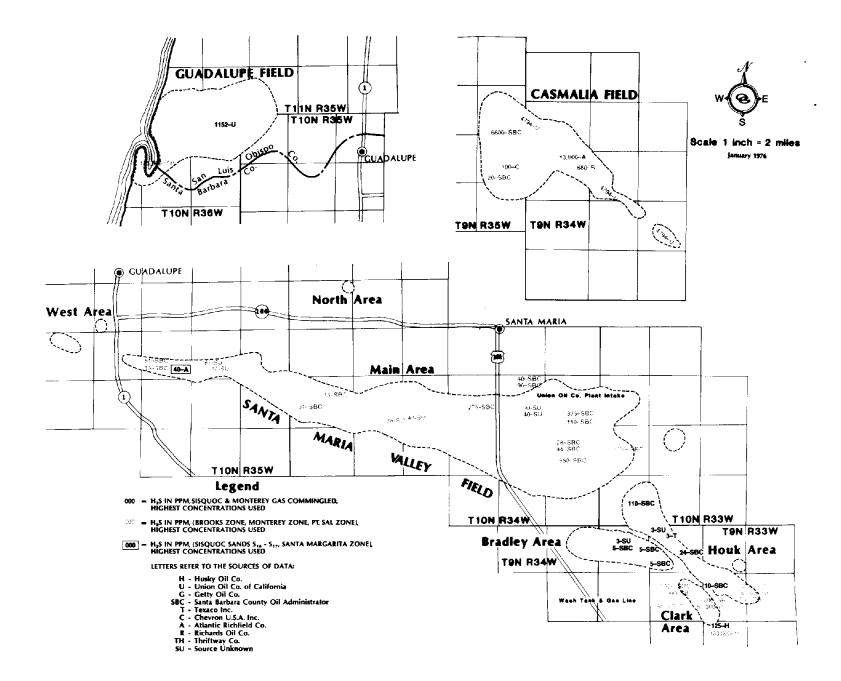
Oil and Gas District	Fields with H₂S Concentrations of 100 ppm or above	Fields with H ₂ S Concentrations under 100 ppm	Fields with H2S Odor, but with Concentrations Unknown	
1	1 _		Wilmington, Huntington Beach, Newport, Torrance , Brea Olinda	
2 Rincon, 100 ppm San Miguelito, 200 ppm Ventura, 300 ppm		Shiells Canyon 60 ppm	Aliso Canyon, Bardsdale, Big Moun- tain, Del Valle, Las Llajas, Oak Park, Oakridge, Ojai, Piru, Santa Paula, Santa Susana, Simi, South Mountain, Tapo Canyon So., Temescal, Torrey Canyon, and West Mountain	
3	Casmalia, 13,000 ppm Cat Canyon, 250,000 ppm Cuyama So., 1300 ppm Elwood So., Offshore, 20,000 ppm Guadalupe, 135,000 ppm Lompoc, 1,310 ppm Orcutt, 306 ppm Russell Ranch, 1,530 ppm San Ardo, 400 ppm Santa Maria Valley, 270,000 ppm Zaca, 400 ppm	-	Capitan Onshore, King City Four Deer	
4 Midway Sunset, 100 ppm Cymric, 1,600 ppm			North Belridge, South Belridge, Blackwells Corner, Edison, Northeast Edison, Kern River, Lost Hills, McKittrick, Mount Poso, Poso Creek Railroad Gap, and Wheeler Ridge	
5		-	Coalinga	
6		**		
Geothermal District				
G3	The Geysers, 40–450 ppm	* **		

H₂S in some California oil and geothermal fields. Data compiled in September 1976. (Data in the first two columns are on the map following this figure.)



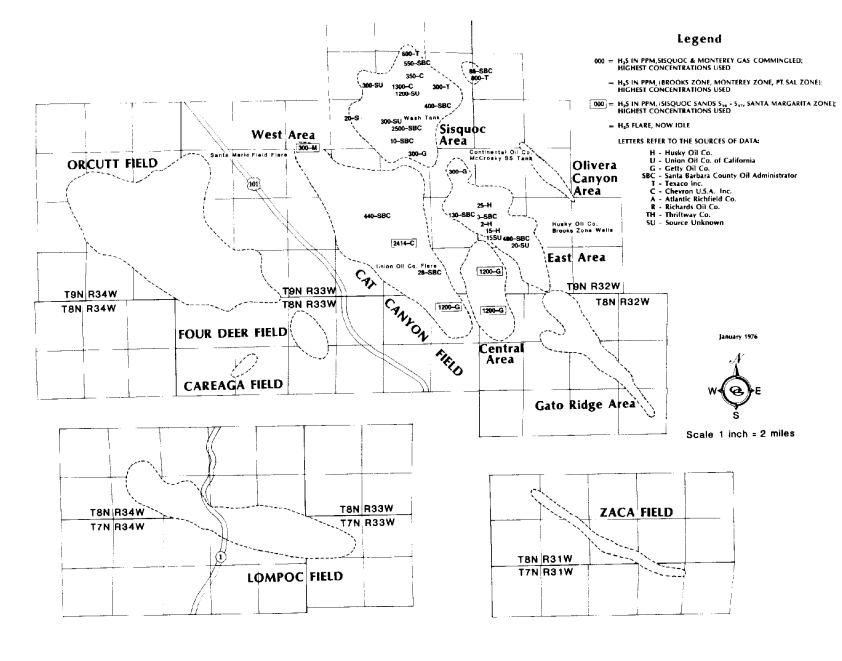
Parts per million of H₂S gas in some California oil and geothermal fields. Data compiled in September 1976.

40



Parts per million of H₂S gas in some California oil fields. Data compiled in 1976.

4



Selected References

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- American Petroleum Institute, 1974, API recommended practices for safe drilling of wells containing hydrogen sulfide: American Petroleum Institute, Dallas, Texas, API RP 49, 11 p.
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- 24. Workman's Compensation Board, Alberta, Canada.

See pages 25 and 26 for additional references to regulations on the selection, type, use, and maintenance of respirators.

M10 (9/97/DWRR/1M)