

# Hydrogen Sulfide Management

Mitigation options in petroleum refining, storage and transportation





Hydrogen sulfide ( $H_2S$ ) is a naturally occurring gas contained in many of the world's crude oils. It is also formed in the refining process by the degradation of sulfur-containing compounds in crude at high temperatures. New market demands globally are expanding hydrocarbon processing and the distribution infrastructure. At the same time, the average sulfur content of crude oils being processed in the world's petroleum refineries continues to increase (Fig. 1).

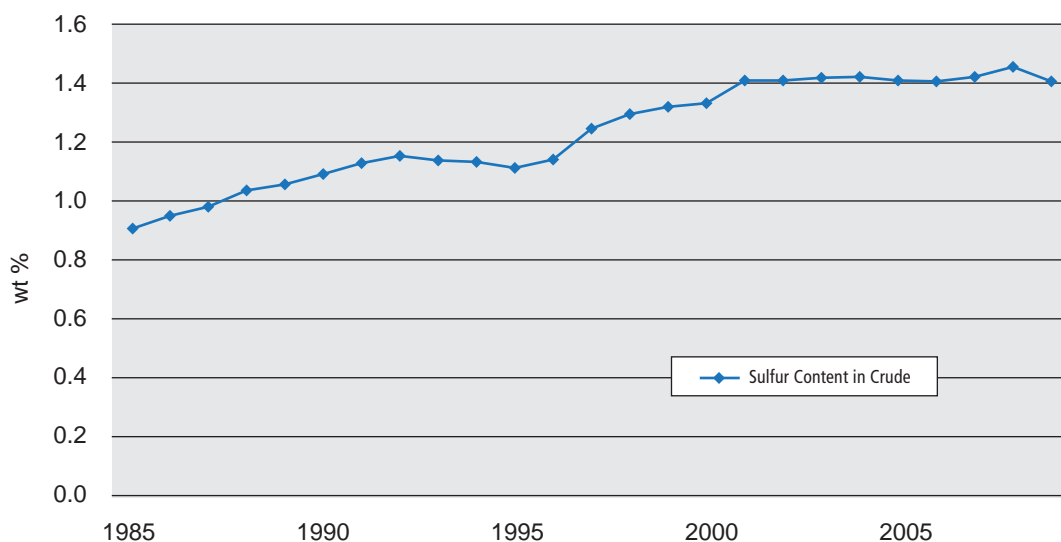


Fig. 1. Average Sulfur Content of U.S. Refinery Crude Oil Inputs

\* Source: Petroleum Navigator, U.S. Energy Information Administration, June 2009

The expansion of hydrocarbon volumes is matched by real problems that relate to higher concentrations of reactive sulfur compounds such as  $H_2S$ . Although many of the challenges posed by high levels of reactive sulfur in crude oil and refinery products are known, the growth of processing, transportation and storage infrastructure can result in hazards and operational concerns. A review of the significant dangers and operating problems posed by  $H_2S$  creates a better understanding of available mitigation options as well as how those options can be tailored to meet particular needs. Proper treatment of  $H_2S$  with an appropriate  $H_2S$  scavenger will improve safety, environmental compliance, product quality and process integrity management.

### Hydrogen sulfide concerns

Increasing world demand for crude oil coupled with the increasing concentration of  $H_2S$  in the oil and products formed from processing hydrocarbon is placing greater emphasis on the safety, environmental and operational concerns associated with hydrocarbon management. Refineries and storage facilities, such as tank farms, are likely to encounter problems specific to the handling of crude oils, intermediates and refined products that contain or generate  $H_2S$ . Heavy oils, including crude oil, residual

fuel and gas oil, tend to have large concentrations of  $H_2S$ . This becomes a concern if these products are to be stored for an extended time or transported. Lighter products leaving the refinery may also be contaminated with  $H_2S$  that distills into them during the refining process. While safety remains the primary concern when dealing with  $H_2S$ , other  $H_2S$ -related issues can create additional challenges for these facilities.

In addition to the risk of direct harm to exposed personnel, products and equipment, environmental considerations such as odor and emissions control must also be addressed. Changing demographics mean that more communities may be susceptible to nuisance odors from nearby facilities. Depending on specific local and national regulations, penalties and fines can result from exceeding either  $H_2S$  or sulfur oxide ( $SO_x$ ) emissions standards.

From an operational standpoint, off-spec products can lead to difficulties in meeting customer commitments and in accumulation of unsalable inventory. Moreover,  $H_2S$  is highly corrosive and can degrade both process and storage equipment, potentially reducing throughput and increasing the difficulty and cost of integrity management programs.







## Safety

Safety for personnel and for the community is the foremost consideration when dealing with crudes or other hydrocarbons containing large amounts of  $H_2S$ .

$H_2S$  is especially insidious because it deadens the sense of smell at concentrations as low as 30 parts per million (ppm). Death can occur within a few breaths at low concentrations of 700 ppm. Hydrocarbons containing even a few ppms of  $H_2S$  can produce headspace concentrations in excess of these levels.

$H_2S$  is a gas at typical storage temperatures and equilibrates between liquid and vapor phases. Distressed cargoes containing high  $H_2S$  levels can easily generate percent levels (parts per hundred) of  $H_2S$  in storage tank and transport vessel headspaces. Certain tank conditions (increased liquid volume, agitation and high temperatures) cause deterioration of this already hazardous situation by changing

the partition coefficients (the ratio of  $H_2S$  in the liquid and vapor phases of the hydrocarbon). For example, as a tank fills with  $H_2S$ -laden oil, the volume of headspace decreases, increasing the relative concentration of  $H_2S$  in the headspace. Fig. 2 shows the effect of tank level on headspace  $H_2S$  content for one hydrocarbon storage tank.

Fig. 3 illustrates the measured effects of temperature on tank headspace  $H_2S$  levels. A crude oil tank with 450 ppm of  $H_2S$  in the vapor phase at 120°F (49°C) can have nearly 1,500 ppm at 300°F (149°C). In fact,  $H_2S$  can be generated by thermal cracking of higher molecular weight sulfur compounds at temperatures as low as 200°F (93°C).

In summary, small concentrations of  $H_2S$  can be deadly to exposed personnel. Other factors such as temperature and tank-filling practices affect  $H_2S$  concentrations and can create a more hazardous situation.

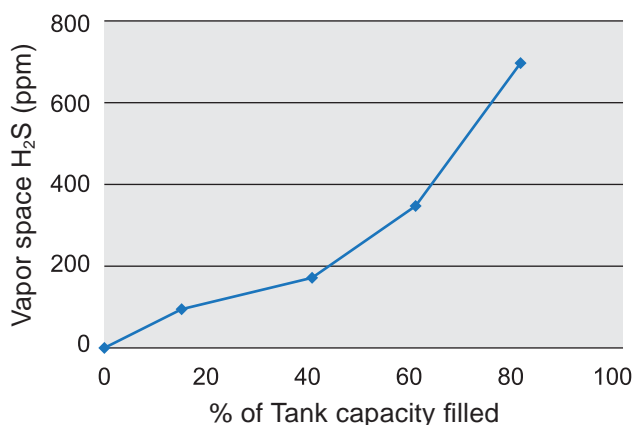


Fig. 2.  $H_2S$  content vs. tank liquid level

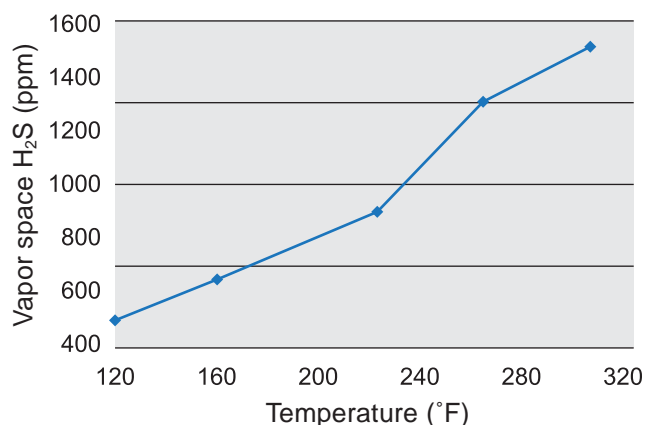


Fig. 3. Effect of temperature on  $H_2S$  partitioning



### Environmental and regulatory concerns

In recent years, residential communities and hydrocarbon storage facilities have become closer in proximity. At the same time, fugitive emission/ environmental regulations in many areas have become more prevalent.

These factors result in an increase in the number of complaints about odors issued to terminals by residents. An increase in the use of higher-sulfur crudes will compound this problem. Nuisance odors are caused by many types of sulfur- and nitrogen-containing volatile compounds that are present in

these crudes stored at terminals. These compounds can be present in very small quantities or within the safety level for the particular compound and still be unpleasant to workers and neighbors (see table below).



### Olfactory detection limits of hazardous materials

Hazard	Detection Level (ppm)	Hazard	Detection Level (ppm)
Hydrogen sulfide	0.0047	Carbon disulfide	0.21
Methyl mercaptan	0.0021	Methyl alcohol	100
Ethyl mercaptan	0.001	Kerosene	1
n-Propyl mercaptan	0.00075	Ammonia	46.8
n-Butyl mercaptan	0.001	Sulfur dioxide	3.0

Source: *Hazardous chemicals data book*, G. Weiss (1980)

Government agencies have implemented many regulations on terminals, refineries and ports that cap the amount of  $H_2S$  a product or a storage vessel headspace may contain. These rules may stem from emissions concerns or may be

driven by air pollution legislation. Of recent interest, many U.S. refinery flare gas systems are affected by environmental regulations that limit  $H_2S$  content in fuel gases sent to combustion devices. For example, the New Source

Performance Standards (NSPS) for Petroleum Refineries, Subparts J and Ja, 40 C.F.R. 60.100 limits the permissible  $H_2S$  in gas burned in a flare to 160 ppm  $H_2S$  on a rolling three-hour average.



### Operational issues

Facilities that process or store hydrocarbons containing  $H_2S$  often face a number of operational challenges. Two such considerations are contamination of intermediates and finished products with  $H_2S$ , and the effects of  $H_2S$ -induced corrosion on terminal facilities.

Contamination of hydrocarbon products with  $H_2S$  can cause products to be off-specification. Even when there is not an overt limit on  $H_2S$ , its presence can render the contaminated product off-specification on a number of other product quality checks. Unfortunately, costs associated with demurrage, out-of-service tanks tied up with off-specification product, reprocessing fees, and product downgrades can quickly add up. Product quality issues relative to specific hydrocarbon products are discussed in the next section.

In addition to impacting product quality,  $H_2S$  can have a significant effect on storage tank corrosion.  $H_2S$  readily dissolves in condensed water to form the bisulfide ion, which is corrosive to carbon steel. Storage tanks used to store hydrocarbons with large concentrations of  $H_2S$  are therefore very susceptible to  $H_2S$ -induced corrosion. Moreover, the resulting iron sulfide deposits adhere to storage tank walls and can act as cathodic sites that induce severe pitting corrosion. Hydrogen embrittlement and sulfide stress cracking have also been observed. The rates of corrosion are often severe enough to significantly shorten the useful lifespan of a storage tank.

The rate at which  $H_2S$  corrodes storage tanks is influenced by a number of factors. The concentration of  $H_2S$  is important, but oxygen, water, locale and turnover frequency should also be

considered. For instance, storage tanks that show the highest corrosion rates are those which are loaded and unloaded frequently with crude oil containing  $H_2S$  and are located in humid coastal regions. Large amounts of oxygen and water (often salt water) are introduced during tank turnovers and during normal tank breathing. The combination of  $H_2S$ , oxygen, salt and moisture produces a very aggressive corrosive environment.

### Hydrocarbon streams and associated $H_2S$ issues

Nearly every hydrocarbon product entering or exiting the refinery, from flare gas and liquefied petroleum gas (LPG) to crudes and resids, is subject to  $H_2S$  contamination and its corresponding problems. Mitigation is critical to ensure the safety of personnel as well as environmental compliance, product quality and equipment integrity.





### Flare gas

Flare gas is often limited by government regulations on the amount of  $H_2S$  it can contain. Refineries produce  $SO_x$  emissions when  $H_2S$ -laden gases are flared. The process of flaring converts  $H_2S$  to  $SO_x$ . For refineries to reduce  $SO_x$  emissions and avoid noncompliance issues, it is now more common to treat the flare gas to reduce the amount of  $H_2S$  it contains.

In these applications, consideration of the injection technique and system operational factors are as important as the selection of the best chemical additive. Residence time, temperatures, pressures and other variables should be considered, as should the separation and disposal of spent scavenger. These applications have the potential to save refiners millions of dollars by maintaining desired throughput, by reducing capital expenditures, and by avoiding unplanned shutdowns, fines and penalties.



### LPG

LPG may also be contaminated with  $H_2S$ . Most LPG specifications require a fuel to be noncorrosive to copper because of the copper and copper alloys used in fuel systems. This corrosion is most often caused by  $H_2S$  remaining in the LPG after a unit upset. In addition to  $H_2S$ -related copper corrosion in LPG systems, the presence of  $H_2S$  is also a potential health hazard to consumers. In the case of an LPG leak in a residence or workplace, the hazard is much greater when the LPG is contaminated by  $H_2S$  than if the leak consisted of LPG alone. Finally,  $H_2S$  in LPG can corrode ferrous metal surfaces within storage and piping systems, and compromise the integrity of the metal. LPG that contains  $H_2S$  could be handled by reprocessing or by blending it off; however, these methods can tie up storage and take time.

The use of  $H_2S$  scavengers is usually an economical and reliable way to resolve these issues. Water-soluble scavengers are generally recommended because they will separate completely from the hydrocarbon and prevent contamination of the LPG with materials of lower volatility. The presence of lower-volatility components in LPG is undesirable because these materials do not burn as well and could cause injector plugging and fouling on burner tips.

### Other finished fuels

Similar to LPG, finished fuels such as gasoline, kerosene and diesel are required to be noncorrosive to copper. Moreover, gasoline is required to be noncorrosive to silver and to pass ASTM D4952, Qualitative Analysis for Active Sulfur Species in Fuels and Solvents (doctor test). Finished fuels can fail such final specifications when  $H_2S$  is present. While there are many chemical programs that will readily react with  $H_2S$ , including caustic, peroxides, nitrites and many types of amines, most of these are neither suitable nor effective for finished products because they will alter important fuel properties such as viscosity, flash point, pour point and ash content. Oil-soluble, nonreversible  $H_2S$  scavengers are typically the product of choice because they will not adversely affect critical fuel properties and will not add water (and possibly a haze) to a finished fuel.



### Crude oil and heavy fuel oil

Crude and heavy residual oils can contain significant concentrations of  $H_2S$  as a natural component and/or as a result of thermal cracking processes that break apart high molecular weight sulfur-containing compounds to generate  $H_2S$ . These products often have to be treated with an  $H_2S$  scavenger before transport to the refinery, when entering storage, or when being transferred between facilities to meet port, terminal, or refinery specifications. Since both of these materials can undergo further processing, the impact of any scavenger or scavenger- $H_2S$  reaction byproduct on equipment and processes should be considered. For example, certain amines can distill into crude towers and overhead condensing systems, contributing to salt fouling and related corrosion activity. In these instances, scavengers with noncorrosive reaction products that do not distill overhead are preferred. Because reformer catalysts are typically sensitive to nitrogen content, non-nitrogen or water-soluble scavengers are preferred to minimize the nitrogen content of the hydrocarbon streams processed in the reformer.

### Asphalt

Asphalt is the heaviest of the products coming out of the refinery and typically the product in which sulfur compounds concentrate. Because of the high viscosity of asphalt, it must be stored at high temperatures (300 to 400°F). These temperatures promote cracking of sulfur-containing compounds and formation of  $H_2S$ . For these reasons, asphalt contains extremely high levels of  $H_2S$ , often exceeding 1% (10,000 ppm). Moreover, asphalt has a high vapor:liquid partition coefficient (400:1), meaning that  $H_2S$  tends to collect in the vapor phase. The combination of high temperatures, high  $H_2S$  concentrations, and high viscosity makes asphalt challenging to treat. It is especially critical to lower the  $H_2S$  content because asphalt is shipped by rail car and tank truck, and exposure of personnel and consumers is a real concern. Because of the elevated temperatures of asphalt applications, water-soluble scavengers generally are not suitable; rather, oil-soluble carriers for scavengers are preferred.



## Operational and chemical solutions

There are a variety of strategies available that can alleviate the safety, environmental and operational problems caused by the storage and handling of problematic crude oils, refined products, and various other feedstocks and intermediates, such as condensates, naphthas, light distillates, gas oils and residual materials.

### Operating solutions

In a perfect world,  $H_2S$  could be managed by keeping storage temperatures and tank volumes low to minimize the concentration of  $H_2S$  in the vapor phase. Tank-to-tank transfers, venting and air blowing are also methods that help dissipate  $H_2S$  (with appropriate understanding of applicable environmental regulations). However, these practices are often impractical from cost, time and environmental perspectives, and can be unreliable as a means for reactive sulfur removal. Some of these practices may not be permitted by governmental regulations. Alternatively, there are treatment options using chemical scavengers to reduce  $H_2S$ .

## Chemical treatments

There are many chemicals that will readily react with  $H_2S$ , including caustic, peroxides, formaldehyde, nitrites and many types of amines. All of these convert the  $H_2S$  or mercaptans into other sulfur compounds.

### Commodity additives

Oxidizers, such as peroxide, convert  $H_2S$  into elemental sulfur or sulfur oxides. However, oxidizers are not selective for sulfur compounds and will react with other components of the oil, resulting in high chemical consumption and potential degradation of the oil. Amine neutralizers react very quickly with  $H_2S$  and are suitable for certain lower-temperature applications. However, the reaction products are not heat-stable and may regenerate  $H_2S$  under certain conditions.

The use of caustic (sodium hydroxide or a blend of sodium and potassium hydroxide) alone, or as a base treatment in combination with another scavenger, has been practiced. With sufficient agitation, caustic can be effective, but its use increases the sodium and/or potassium content of the treated oil and may lead to deposit formation and high-temperature corrosion in heaters, boilers and turbines. Additionally, caustic embrittlement of refinery rundown lines can occur if caustic is injected above 180°F (82°C).



### Specialty chemical conversion reagents

The preferred method for scavenging  $H_2S$  and mercaptans from hydrocarbon streams is to use a chemical conversion reagent. This type of additive reacts with  $H_2S$  irreversibly to form thermally stable reaction products and does not revert back to  $H_2S$  if exposed to higher temperatures farther downstream. Scavenger programs are selected depending on the nature of the  $H_2S$  problem being addressed and the petroleum product being treated.



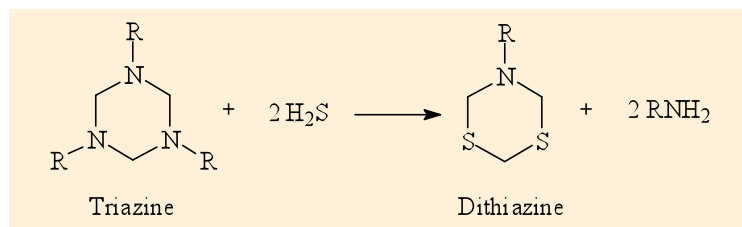


### **Water-soluble scavengers**

Water-soluble scavengers are among the most common scavengers and are often the product of choice for applications at temperatures below 200°F (93°C). Economical costs and fast reaction rates make them attractive options. Moreover, due to their water solubility, they add a minimum amount of nitrogen to the fuel. These are the preferred additives for use in flare gas, LPG, resids and crude oils.

A common type of water-soluble H<sub>2</sub>S scavenger is a triazine-based chemistry. Triazine-based scavengers undergo the basic reaction with H<sub>2</sub>S outlined below.

Triazines made from monoethanolamine (MEA) or methylamine (MA) are the most common commercially available scavengers. MEA-based triazines react more efficiently in the liquid phase than other chemistries and are particularly useful if the immediate reduction of H<sub>2</sub>S is critical; as is the case when ships or barges are loaded with H<sub>2</sub>S-laden product and the safety of the crew is at risk.



Other water-soluble H<sub>2</sub>S scavengers include polymeric, nitrogen-based products, as well as aldehyde-based, non-nitrogen chemistries. These scavengers are typically less likely to cause any fouling and corrosion problems in crude oil distillation units and refinery process equipment.

### **Oil-soluble scavengers**

Oil-soluble scavengers are used in high-temperature applications or when water tolerance of the hydrocarbon is an issue. These products are typically amine-based and perform as effectively as water-soluble additives. These products react with H<sub>2</sub>S irreversibly to form a thermally stable, oil-soluble alkyl sulfide. They can be applied at a wide range of temperatures, from ambient up to 350°F (177°C), and are often the product of choice for viscous heavy oils and resids. They are also preferred by many users over

water-soluble additives in finished fuels to avoid any possibility of haze formation.

### **Metal-based scavengers**

Metal-based scavengers answer the specific needs of very high-temperature and high-H<sub>2</sub>S concentration applications. These additives can be used at temperatures in excess of 350°F (177°C) to form thermally stable products and are able to provide H<sub>2</sub>S reduction levels that other H<sub>2</sub>S scavengers cannot achieve. While these products are typically used to treat asphalt, other applications can be envisioned. These scavengers and reaction products remain in distillation column bottoms and could be used in refinery applications that are not sensitive to metal content. The increased reactivity with H<sub>2</sub>S gives these products a favorable cost-performance ratio relative to other H<sub>2</sub>S scavengers.





### Scavenger system controls H<sub>2</sub>S in flare gas

A refinery involved Baker Hughes in a custom H<sub>2</sub>S scavenging program to be used when the H<sub>2</sub>S content of flare gas threatened to exceed acceptable levels; reduction rates for SO<sub>x</sub> were set to less than 200 pounds a day and H<sub>2</sub>S levels to less than 4,000 ppm. After a thorough survey, a four-nozzle injection system was used in existing flare gas process lines.

Field trials were conducted to verify that all customer requirements could be met. SO<sub>x</sub> emissions were reduced from over 500 to less than 70 pounds a day. H<sub>2</sub>S levels were reduced from over 18,000 to 900 ppm (Fig. 4).

This program will allow the refinery to maintain compliance with government regulations and avoid possible fines or penalties. The refinery was also able to avoid installation of a multi-million dollar processing unit. Finally, the refinery will not have to decrease throughput to remain in compliance.

### H<sub>2</sub>S scavengers help control tank roof corrosion

In a study conducted by Baker Hughes, the corrosion rate of the roof of a storage tank located in a coastal region was monitored for one year using metal coupons and electrical resistance probes attached to the tank roof. This particular tank contained a residual fuel with liquid phase H<sub>2</sub>S levels of 15 to 25 ppm. The H<sub>2</sub>S content of the vapor phase ranged from 100 to 600 ppm during the study period. When the H<sub>2</sub>S content of the vapor space increased, a corresponding increase in the rate of corrosion was recorded (Fig. 5). In this location, corrosion rates had been high enough to reduce the lifetime of storage tank roofs to less than five years.

Implementation of an H<sub>2</sub>S scavenger program helped to control tank roof corrosion. By reducing the concentration of H<sub>2</sub>S in storage tank headspace, use of an H<sub>2</sub>S scavenger reduced corrosion rates measured on the tank roofs from nearly 14 to < 1 mils per year (0.36 to 0.0254 mm per year).

### Off-spec propane treated in cavern

A products pipeline system that uses underground salt caverns to store propane prior to shipment had several caverns containing propane off-specification on the ASTM D1838 Copper Strip Corrosion Test. While H<sub>2</sub>S was the suspected culprit, the pipeline company needed assistance in identifying and resolving the problem. The Baker Petrolite PREPARED TO RESPOND services program offered prompt and effective remediation.

After the pipeline consolidated 42,000 barrels of the off-specification propane into a 100,000-barrel capacity cavern, Baker Hughes applied SULFIX™ 9272 scavenger over a three-hour period via an inlet to a 4-in. steel pipe that serves to circulate the cavern contents. The propane in the cavern was circulated for 12 hours and allowed to settle for an additional 10 hours. Adequate settling time is necessary to allow the water-soluble H<sub>2</sub>S scavenger to separate from the hydrocarbon phase. The treated propane passed the copper strip corrosion test with a "1" rating; furthermore, no H<sub>2</sub>S was detected after treatment.

The treatment and its responsiveness enabled the client to minimize the amount of money lost as a result of missed shipments and lack of storage capacity.

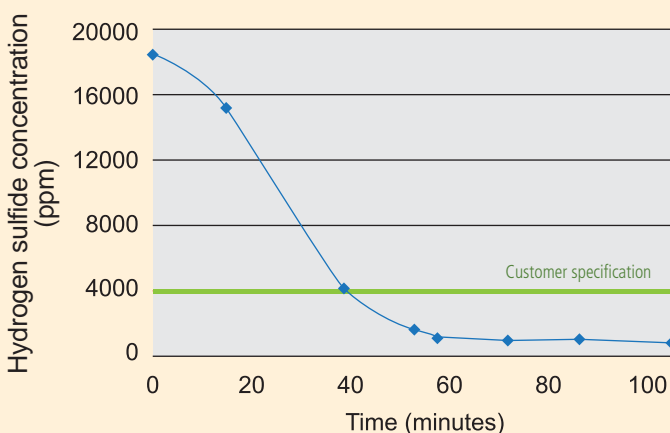


Fig. 4. Flare gas treatment with SULFIX™ H<sub>2</sub>S scavenger

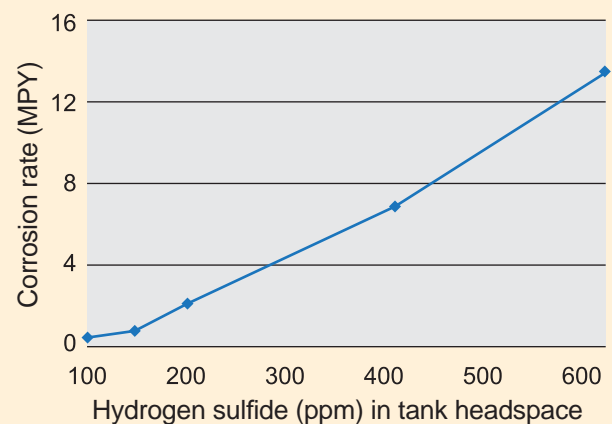


Fig. 5. Tank roof corrosion rates related to H<sub>2</sub>S concentration





### Speed of mitigation

In many cases, tank farm or terminal operators have very little time in which to correct H<sub>2</sub>S-related problems. These could impact operations (personnel safety issues) or profitability (product transport/transfer issues) in a time-critical manner.

Baker Hughes offers unique PREPARED TO RESPOND™ services that are focused on quickly remediating distressed feedstocks. The services include product selection, mobilization of chemicals, injection equipment and experienced personnel that can all arrive on site within 24 hours in most major refining and fuel transportation centers worldwide to safely and effectively bring cargos back on specification, thereby increasing safety and profitability.

### Effective removal yields clear benefits

H<sub>2</sub>S scavengers are industry-proven methods to remediate dangerous conditions that present safety and regulatory issues. Additional issues caused by H<sub>2</sub>S contamination include corrosion problems, odor concerns and product degradation.

Experience demonstrates that proper selection and application of these proven classes of chemicals are critical to successful H<sub>2</sub>S-abatement programs. The combination of effective products and application expertise results in a successful program that can maximize safety, minimize or eliminate corrosion, and improve profit margins.

## Contact



Baker Hughes  
12645 West Airport Boulevard  
Sugar Land, Texas 77478-6120

Tel +1 800 231 3606  
Fax +1 281 275 7218

SULFIX and PREPARED TO RESPOND are a trademark of Baker Hughes Incorporated.

The information and recommendations contained herein are believed to be accurate and reliable as of the date hereof; however we do not warrant or represent their accuracy or reliability.

Baker Petrolite Corporation and its affiliates (BPC) disclaim all warranties or representations express or implied, including any implied warranties of merchantability or fitness for a particular purpose or to the accuracy, correctness or completeness of such information herein or that reliance on such information will accomplish any particular result. All such information is furnished "as is" and by using such information the user is assuming all liabilities for the use or reliance on such information. BPC SHALL NOT BE LIABLE FOR ANY INDIRECT, SPECIAL, PUNITIVE, EXEMPLARY OR CONSEQUENTIAL DAMAGES OR LOSSES FROM ANY CAUSE WHATSOEVER INCLUDING BUT NOT LIMITED TO ITS NEGLIGENCE.

[www.bakerhughes.com/sulfix](http://www.bakerhughes.com/sulfix)

© 2011 Baker Hughes Incorporated. All rights reserved. 28859