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### Hydrogen Sulphide Strategy in Oil and Gas Field. Review

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#### ABSTRACT

Hydrogen sulphide ( $H_2S$ ) is one of the most hazardous substances in oil and gas production fields when it comes to the risks posed by its presence.  $H_2S$  is a naturally occurring gas found within oil, gas reservoirs, and sewage water. Chemically the gas is extremely toxic, flammable, and corrosive to different materials.  $H_2S$  can strongly cause material cracking and environmental pollution and a reduction in oil quality. Thus, prevention measures are very important to produce gas containing even low levels of  $H_2S$ . The prevention requires chemical treatment to remove  $H_2S$ or convert the gas to an acceptable compound. Therefore, a big challenge was faced to develop a new technological method to manipulate  $H_2S$  problems. This review evaluates strategies for crude oil desulfurization by reviewing desulfurization literature. In addition, the effects of hydrogen sulfide on metals and metal protection will be outlined. Finally, some perspectives on the effects of  $H_2S$  on personnel health and safety will be discussed.

#### 1. Introduction

Numerous businesses and environmental regulatory authorities have expressed worry about the rising sulfur content of crude oil over time. Hydrogen Sulphide chemically contains one sulfur atom and two hydrogen atoms, the distance between the sulfur atom and hydrogen atom is 133.6 pm, while the angle between hydrogen atoms is 92.1 degrees (Figure 1).<sup>[1]</sup> Hydrogen sulphide has many names, such as acidic gas, sour gas, rotten egg gas, stink damp, swamp gas, manure gas, and hydrosulfuric acid.<sup>[2]</sup> Recently, reports have found a significant increase in H<sub>2</sub>S in the environments.<sup>[3]</sup>



Figure (1): The structure of hydrogen sulphide with bond distance and angle

H<sub>2</sub>S specification is a colorless, flammable gas with an unpleasant and pungent odor, similar to the smell of rotten eggs. Since H<sub>2</sub>S has a density heavier than air, typically usually found in lower places.<sup>[4]</sup> Hydrogen sulfide is chemically considered a moderate reducing agent and it plays a significant role in the normal qualitative analysis as it precipitates some metals in the form of sulfides that are insoluble in water in the presence of an acidic medium such as Cu, Hg, Cd, Bi, Sb, Sn and others.<sup>[5]</sup> H<sub>2</sub>S has many applications used in the manufacture of some medicines and is widely applied in chemical analysis.<sup>[6, 7]</sup> H<sub>2</sub>S when burn in the air, gives off a faint blue flame. Based on H<sub>2</sub>S soluble in water and ethanol (see Table 1).<sup>[6, 8]</sup>

Table (1): shows chemical information of H<sub>2</sub>S

Formula	H <sub>2</sub> S
Density	1.36 kg/m <sup>3</sup>
Molecular mass	34.0809 g/mol
Boiling point	-60 °C(-76 F; 213 K)
Melting point	-82 °C(-116 F; 191 K)
Solubility	water, ethanol

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#### 1.1 H<sub>2</sub>S gas sources

Hydrogen sulphide is naturally present in different proportions it is found in high proportions in natural gas and oil and comes out of volcanoes with other gases and in some water wells.<sup>[9]</sup> It is produced from the decomposition of biomass due to its fermentation and mildew a product of the processes of decomposition of corpses as well as the decomposition of garbage, as happens with the formation of coal, or the decomposition of tree branches in swamps, or the fermentation of human waste, which leads to the generation of gas.<sup>[10]</sup> It is generated because of the interaction of acidic water with components of an underground water tank that contains sulfur compounds, and it is formed when certain types of bacteria that use iron and manganese as part of their food release it, sometimes known as iron bacteria.<sup>[11]</sup> Moreover, the gas typically spreads near sewage treatment plants, water pumps, and treatment plants, trucks transporting sewage and chemicals, but it may be emitted from groundwater wells, particularly in areas near oil fields or where wells penetrate limestone layers.<sup>[12]</sup> Usually, H<sub>2</sub>S gas is extracted from the associated petroleum gas and separated by heat, treated, and condensed to facilitate its transportation as it is exported abroad. The crude is sweet with a sulfur content of 0.5% or less, and it is sour or bitter with a sulfur content greater than that. Nowadays 60% of the oil traded in the world markets is a heavy acid type that contains sulfur.[13, 14]

#### 1.2 The ways to detect hydrogen H<sub>2</sub>S

Due to  $H_2S$  being dangerous, it is not permissible to rely on the sense of smell to detect the presence of hydrogen sulphide gas. There are several ways to detect it and its concentration using such as methylene blue liquid and gas chromatography, flame color, digital gas detectors, and adsorption measuring tubes.<sup>[15]</sup>

#### 2. Danger levels and precautionary

#### measures

Hydrogen sulphide gas is considered a dangerous gas that affects humans according to its concentration. Hydrogen sulphide is very toxic and its toxicity is higher than that of hydrogen cyanide.<sup>[16]</sup> When upon direct exposure to the gas some symptoms occur such as; irritation of the eyes, shortness of breath, disturbances in the nervous system, headache, dizziness, sweating, fatigue, body fatigue, paralysis in the breathing area of the brain, and finally loss of consciousness and sometimes death occur (see Table 2).<sup>[17, 18]</sup>

Table (2): shows the safety information of H<sub>2</sub>S

Concentration		Effects on	The level
mg/m <sup>3</sup>	ppm	humans	of risk
1000-2000	1400-2800	Immediate collapse with fatal respiratory paralysis	Fatal
530-1000	530-1000	Central nervous system cell damage, respiratory paralysis leading to death	Very high
320-530	450-750	Acute pulmonary with a high risk of death	High
150-250	210-350	Loss of smell	Moderate
50-100	70-140	Perceived eye damage	Low
10-20	15-30	Eye sensitivity	Normal



Figure (2): Safety sign for H<sub>2</sub>S

### **3.** Effect of H<sub>2</sub>S gas on equipment in the oil field

Hydrogen sulphide can be dissolved in water and becomes acidic which will be increasing pH, which influences the amount of corrosion damage, resulting in electrochemical corrosion, localized pitting, and pipeline perforation(Figure 3).<sup>[19]</sup>



Figure (3): pipeline corroded by H<sub>2</sub>S

The hydrogen atoms generated in the corrosion process will be absorbed by the steel and enriched in the metallic defects of the tube, which can lead to the embrittlement of the steel and the initiation of cracks, which leads to cracking (Figure 4).



Figure (4) H<sub>2</sub>S tendency to attack the metal even corrosion inhibitors are used.

Hydrogen sulphide gas reacts with steel in the presence of water, leading to the formation of iron-sulfur and the release of hydrogen. The iron-sulfur resulting from the reaction will be deposited on the surface of the metal, forming a crust that leads to the formation of a galvanic cell, in which the deposited iron-sulfur plays the role of the cathode (negative), while the steel plays the role of the anode (positive). As a result, several forms of corrosion occur on the metal, the hydrogen atoms released from this reaction penetrate the pores, where these atoms unite with each other to form hydrogen molecules a size larger than the size of the hydrogen atoms (Figure 5). It is necessary to take preventive measures to reduce corrosion as it causes direct and indirect economic losses to oil and gas equipment in the fields.<sup>[20]</sup>



Figure (5): Corrosion mechanism on metal by H<sub>2</sub>S enhanced with CO<sub>2</sub>.

#### 4. Roles of H<sub>2</sub>S gas in corrosion

The majority of pipeline damage is caused by the  $CO_2$ and  $H_2S$ -dominated conditions in the oil and gas industry. Since many of the world's oil fields contain  $H_2S$ gas, understanding the roles of  $H_2S$  gas in corrosion issues is crucial for predicting pipeline corrosion. The impact of  $H_2S$  gas in the system has been the subject of much research. It is challenging to estimate  $H_2S$ corrosion processes, due to the complicated chemistry and mechanism of the corrosion process. Combinations of responses between the rates of corrosion and film formation may occur during the corrosion process.

#### 4.1 H<sub>2</sub>S chemistry in aqueous solution

Corrosion processes can occur under a variety of pipeline environments, and they usually: <sup>[21]</sup> Fe +  $H_2S \longrightarrow FeS + H_2$ 

$$Fe + CO_2 + H_2O \longrightarrow FeCO_3 + H_2$$

 $2Fe + O_2 + 4H^+ \longrightarrow 2Fe^{2+} + H_2 + 2 H_2O$ 

In the pipeline that includes hydrogen sulfide, several chemical processes are taking place, which are mildly acidic when dissolved in water. The chemistry is as follows: <sup>[22, 23]</sup>

H <sub>2</sub> S dissolution
$H_2S_{(g)} \longrightarrow H_2S_{(aq)}$
H <sub>2</sub> S dissociation
$H_2S_{(aq)} \longrightarrow HS_{(aq)}^- + H^+_{(aq)}$
HS <sup>-</sup> dissociation
$HS^{-}(aq) \longrightarrow H^{+}(aq) + S^{-}(aq)$
H <sub>2</sub> S reduction
$2 H_2 S_{(aq)} + 2 e^- \longrightarrow H_{2(g)} + 2HS_{(aq)}^-$
FeS formation by precipitation
$Fe_{(S)} + S^{2}_{(aq)} \longrightarrow FeS_{(s)}$

The pH has an impact on how  $H_2S$  reacts in water. The molecular  $H_2S$  is the most prevalent form of the sulfide species at low pH (acidic solutions).<sup>[22]</sup> This persists until the bisulfide ion is present in large proportions at a pH of around 6. Greater amounts of bisulfide will develop with any pH rise.<sup>[22]</sup> The molecular and bisulfide forms are present in equal proportions at a pH of a little around 7. The concentration of the bisulfide ion is around ten folds greater than that of the molecular  $H_2S$  at a pH of eight. For pH values higher than 8, <sup>[22, 24, 25]</sup> the bisulfide ion is the predominant hydrogen sulfide species iron sulfide can develop in three distinct ways:

I) The dissolution of iron causes a visible black solid film on the surface. The cathodic reaction occurs at the sulfide film/solution interface, and it is constrained by the passage of ferrous ions and electrons through the film.

**II**) Ferrous ions dissolve in the solution and interact with sulfide ions, preventing the formation of a corrosion product coating on the surface.

**III**) A mixture of both where ferrous ions react both in solution and on the surface. Iron sulfides form a porous layer as a result.

The cathodic reaction and iron anodic dissolution are made possible by the porous surface.<sup>[22]</sup>

### 5. Factors enhanced the corrosion rate of H<sub>2</sub>S

Many factors can enhance hydrogen sulphide tendency to attack the metals such as the following:

I) **Presence of chlorine ions**: Chlorine ions contribute greatly to the continuation of the corrosion process when they are present with hydrogen sulfur and water.

II) **Humidity**: Humidity negatively affects the corrosion of metals with hydrogen sulphide gas, and if moisture is absent, hydrogen sulphide does not affect metals, so drying the gas leads to a significant reduction in the rate of corrosion.

III) **Concentration**: The corrosion rate increases with the increase in  $H_2S$  concentration resulting from the increase in the acidity of the medium which the pH increase.<sup>[26]</sup>

IV) **Pressure**: The increase in pressure directly affects the rate of corrosion because it increases the concentration of  $H_2S$  in one volume, and here severe corrosion is observed even at low pressures. At a partial pressure of 0.05Psia of hydrogen sulphide it causes corrosion to steel alloys.<sup>[27]</sup>

V) **Temperatures**: In the gaseous medium, heat affects the rate of corrosion inversely. Corrosion occurs with hydrogen sulphide gas at temperatures of (-6,49) °C.<sup>[28, 29]</sup>

VI) **Time**: In the beginning, a layer of iron-sulfur is formed that plays a protective role, and with the passage of time its structure changes, leading to an increase in the rate of corrosion.<sup>[30]</sup>

### 6. Methods of protecting metals from H<sub>2</sub>S aggressive

There are many methods to protect the metals used in oil and gas fields from corrosion chemical and nonchemical methods such as a) Good equipment design, b) Treating the surrounding medium, c) Covering, including metallic sheathing (electrochemical nickelcobalt plating...etc.) or organic coverage (polyethylene epoxy), d) Injection of corrosion inhibitors, e) Cathodic protection and sacrificial anode. On the other hand, the hydrogen sulphide scavenger is a remarkable method to remove hydrogen sulphide from systems, as well as corrosion allowance, which must be considered by engineering design.<sup>[31, 32]</sup>

#### 7. Removal of hydrogen sulfide (H<sub>2</sub>S)

Removal of hydrogen sulfide  $(H_2S)$  released from various source processes is crucial because this compound can cause corrosion and environmental damage even at low concentration levels.

#### 7.1 H<sub>2</sub>S scavenger

H<sub>2</sub>S scavengers are widely used in hydrocarbon and chemical processing facilities to remove H<sub>2</sub>S with low capital cost.<sup>[33]</sup> Triazines and Glyoxal are commonly used as H<sub>2</sub>S scavengers in oil and gas production. In offshore plants, triazines are directly injected into the gas streams, while in onshore plants triazines will be injected in contactor towers. Moreover, one mole of triazine can scavenge two moles of hydrogen sulfide.<sup>[34]</sup> Glyoxal (C<sub>2</sub>H<sub>2</sub>O<sub>2</sub>) is a hydrogen sulfide scavenger that does not contain nitrogen, which given the glyoxal advantage does not cause corrosion problems in refineries. However, the disadvantage of using glyoxal are; first glyoxal is acidic and it has a low pH that can cause the water phase to have a low pH and result in corrosion at any location, while reaction with H<sub>2</sub>S at low temperatures is less efficient, second glyoxal is a slowacting scavenger and may be corrosive to mild steel.<sup>[35,</sup> 36] Moreover, Ethanol amines have been used extensively to remove H<sub>2</sub>S from gas streams in sweetening towers while Diglycolamine [2-(2-Aminoethoxy) ethanol] has been used since 1965 for the industrial removal of hydrogen sulphide and /or carbon dioxide from gas streams[37, 38]. Acrolein (C<sub>3</sub>H<sub>4</sub>O) has been used as an H<sub>2</sub>S scavenger in these instances; Acrolein is an effective scavenger but an extremely toxic substance. On other hand, H<sub>2</sub>S reacts with aldehydes across the C=O double bond in a reversible process[39]. The most common use of formaldehyde. Zinc oxide and zinc carbonate are also used as H<sub>2</sub>S scavengers because it has a high to reduce the production of sulphur compounds.<sup>[40]</sup> Recently the development and field application of a new Hydrogen Sulfide (H<sub>2</sub>S) Scavenger in oilfield mixed production applications is presented.<sup>[41]</sup> However, there is disadvantages using H<sub>2</sub>S scavenger; the first trail must be done to choose a suitable H<sub>2</sub>S scavenger, the second H<sub>2</sub>S scavenger maybe reacts with other chemicals such as corrosion inhibitors and demulsifiers.

#### 7.2 Solid bed H<sub>2</sub>S scavengers unit

Hydrogen sulfide is mostly removed from associated gas in oil fields using solid bed H<sub>2</sub>S scavengers. To protect people and downstream equipment from dangerous and extremely corrosive hydrogen sulfide, the solid-state H<sub>2</sub>S removal technology is the best option for gas processors to reduce the quantity of hydrogen sulfide and the outlet pipeline (Figure 6).<sup>[42, 43]</sup>



#### 7.3 Claus process

In 1883, the first process to extract and produce sulfur from hydrogen sulphide was invented by the chemist Carl Friedrich Claus. Based on this, the Claus process, which recovers elemental sulfur from gaseous hydrogen sulfide, where the input gas is burnt, is still the most significant gas desulfurizing method. Claus furnaces frequently sustain temperatures beyond 1050°C.<sup>[44]</sup> In general, hydrogen sulfide is converted to elemental sulfur in two steps; The first involves the oxidation of a portion of hydrogen sulfide to sulfur dioxide with air oxygen, and then in the second step by conducting a coproportional reaction between hydrogen sulfide and sulfur dioxide as follows:

 $2H_2S+3O_2 \rightarrow 2 SO_2 + 2 H_2O (\Delta H = -518 \text{ kJ mol}^{-1})$ 

The reaction is a strongly exothermic free-flame total oxidation of hydrogen sulfide generating sulfur dioxide that reacts away in subsequent reactions.<sup>[45]</sup> The most important one is the Claus reaction is:

 $2H_2S + SO_2 \rightarrow 3 S + 2 H_2O$ The overall equation is:  $2H_2S + O_2 \rightarrow 2 S + 2 H_2O$ 

#### 8. H<sub>2</sub>S corrosion monitoring

H<sub>2</sub>S Corrosion monitoring has the potential to be a significant asset as part of comprehensive corrosion management since H<sub>2</sub>S corrosion affects oil construction.<sup>[46]</sup> There are different classical monitoring methods have been various traditional monitoring techniques that employed, including:

#### 8.1 Corrosion coupons

Corrosion coupons can be used in vessels, tanks, and pipes. Corrosion coupons usually can be manufactured in different sizes and shapes. Corrosion coupons are closer resemblance to actual condition, and reliable information for future designs (Figure 7). For measuring the corrosion rate corrosion coupons must be regularly recovered, cleaned, and weight. Determination of the corrosion rate is usually done while the plant is running by using of specialized retrieval equipment. However, because of the risk of H<sub>2</sub>S emission, retrieval is usually delayed until shutdown so that the tube part can be isolated, depressurized, cleaned, and aerated. The unit for calculation is MPY which is miles per year. Corrosion rate (CR) can be calculated by the following equation:

#### C.R=534 WD/A.T

Where; W is weight loss measured in mg, D is the density of alloy in g/cm<sup>3</sup>, A is the surface area of the specimen exposed to the solution in  $cm^2$ , and T is the total exposure time in an hour.<sup>[47]</sup>

However, if the result is over 1MPY that means a high corrosion rate, as well operation team, have must be done an investigation; of corrosion inhibitors, salinity, H<sub>2</sub>Ssolubility, pH, and SRB bacteria count.



Figure (7): corrosion coupon

#### 8.2 Probes detecting corrosion.

There are many probes instruments such as ERP (Electrical Resistance (ER) probe) and Linear Polarisation Resistance (LPR) probes which are instruments mechanism due to electrical conduction (Figure 8), however, it has a disadvantage because the corrosion products, such as iron sulfide deposited on the walls, are electrically conductive and can generate misleading data. These Probes will not measure the corrosion that occurs to such pipe walls; instead, they will merely monitor how corrosive the process fluid is. These devices will break out rapidly as a result of the severe  $H_2S$  corrosion as they will be required to be changed and shut down oil constructions.<sup>[46]</sup>



Figure (8): shows A is ERP and B is LPR instrument.

#### 8.3 Wave-guided systems

The method employs acoustic waves that propagate along an elongated structure while guided by its boundaries (Figure 9). Despite in fact that these tools make it possible to verify pipe sections by locating corroded spots. They offer little insight into the possible severity of corrosion damage that can occur, and the data gathered need further manual assessment using conventional methods.<sup>[46, 48]</sup>



Figure (9): wave guided system.

#### 8.4 Field analysis

Field analysis is usually done for scale corrosion such as CaCO<sub>3</sub>, CaSO<sub>4</sub>, and BaSO<sub>4</sub>, otherwise, field analysis can be done for other types of corrosion to predict whether corrosion is likely or unlikely and if instruments are not available. The type of field analysis that can be done for non-scale corrosion is; water salinity, H2S solubility, H2S count, pH, CO<sub>2</sub> solubility, salt in crude oil, and SRB bacteria count. The advantages of field analysis include; simple methods, it can expect corrosion is likely or unlikely as well as some methods do not need instruments for analysis, finally field analysis can expect which type of chemical will be used in the system. However, there are disadvantages likewise first field analysis relies on parameters such as temperature, the second needed skills and experiments of the operator as well as field analysis is a high risk to the safety person and field analysis must be done frequently.

#### 9. Future work

The consequences of  $H_2S$  corrosion are contamination, loss of product, and shutdown which leading loss of millions of dollars per year as well as encouraging many scientists related to corrosion science using nanotechnology to try manufacturing plants alloys more resistant than carbon steel and stainless steel such as using three different layers made from three types of metals. Based on this, they are working hard to fabricate transparent plants that could be more non-corrosive and likewise easy to monitor.

#### **10. Summary**

Hydrogen sulfide ( $H_2S$ ) is often present in oil and gas production fluids. Even with low concentration, the gas is poisonous, corrosive to mild steel, and induces localized sulfide corrosion cracking (SCC) in materials with susceptible metallurgical properties. The density of H<sub>2</sub>S is heavier than air and other gases, which is make H<sub>2</sub>S found in low places, however for safety person, must stay in high places. The pH will increase with the presence of hydrogen sulphide as hydrogen sulphide can be dissolved in water and becomes acidic. The Chlorine, humidity, temperature, pressure, and time can enhance H<sub>2</sub>S to attack the metals. The highly corrosive acid sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) is chemically created when H<sub>2</sub>S reacts with water. Sour corrosion is the name given to corrosion caused by H<sub>2</sub>SO4. Stock tanks that are submerged in water may sustain severe damage because hydrogen sulfide and water combine rapidly. Moreover, when hydrogen sulfide dissolves in water, it produces a weak acid. As a result, it is a source of hydrogen ions. It has the potential to serve as a catalyst for the adsorption of atomic hydrogen in steel, promoting sulfide stress cracking (SSC) in high-strength steel. Production of liquids and gases containing H2S can cause severe corrosion because of H<sub>2</sub>S stress cracking, especially on equipment that has not been fabricated and designed to deal with sour conditions In addition, when hydrogen sulfide interacts with elemental sulfur, polysulfides may result. Treatment with H<sub>2</sub>S scavengers can enable the use of less-expensive low-alloy carbon steel materials. The H<sub>2</sub>S scavenger type must be non-nitrogen-containing, as H<sub>2</sub>S scavengers containing nitrogen can make corrosion problems because the amines will react with sulphides/ H<sub>2</sub>S to form acid/ base salts in a fully reversible reaction. The oil and gas sector typically uses triazine, the most popular H<sub>2</sub>S scavenger, to remove hazardous and corrosive hydrogen sulfide from natural gas, refinery streams, and olefins cracker products. Based on the Claus process, this system is outstanding at converting H<sub>2</sub>S to sulfur and has numerous industrial applications. Moreover, Claus's method is exceptional for lowering sulfur compound emissions into the atmosphere. The drawbacks of H<sub>2</sub>S scavenger use, however, are low efficiency, corrosively, scalability, and emulsification. Corrosion coupons are remarkable tools for monitoring corrosion rates. They can give accurate corrosion rates in vessels, tanks, and pipes, but they needed the skills of the operator. Moreover, to minimize corrosion rate engineering must be considering as following; the type of metals used to fabricate the plant, chose the suitable area for constructing the plant, the corrosion allowance, and the processing system.

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