Simulation for estimation of hydrogen sulfide scavenger injection dose rate for treatment of crude oil

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Abstract  The presence of hydrogen sulfide in the hydrocarbon fluids is a well known problem in many oil and gas fields. Hydrogen sulfide is an undesirable contaminant which presents many environmental and safety hazards. It is corrosive, malodorous, and toxic. Accordingly, a need has been long left in the industry to develop a process which can successfully remove hydrogen sulfide from the hydrocarbons or at least reduce its level during the production, storage or processing to a level that satisfies safety and product specification requirements. The common method used to remove or reduce the concentration of hydrogen sulfide in the hydrocarbon production fluids is to inject the hydrogen sulfide scavenger into the hydrocarbon stream. One of the chemicals produced by the Egyptian Petroleum Research Institute (EPRI) is EPRI H2S scavenger. It is used in some of the Egyptian petroleum producing companies. The injection dose rate of H2S scavenger is usually determined by experimental lab tests and field trials. In this work, this injection dose rate is mathematically estimated by modeling and simulation of an oil producing field belonging to Petrobel Company in Egypt which uses EPRI H2S scavenger. Comparison between the calculated and practical values of injection dose rate emphasizes the real ability of the proposed equation.

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1. Introduction

Hydrogen sulfide is a naturally occurring component of crude oil and natural gas. It often results from the bacterial breakdown or organic matter in the absence of oxygen. It is also formed in the refining process by the degradation of sulfur-containing compounds in crude at high temperatures [1,2]. Hydrogen sulfide is the chemical compound with the formula H2S. It is a colorless, very poisonous, flammable gas with the characteristic foul odor of rotten eggs at concentrations up to 100 part per million (ppm). It is known as di-hydrogen mono sulfide, hydrosulfuric acid, sewer gas, and sulfur hydride. Hydrogen sulfide is a toxic gas and it is recognized to be a potent inhibitor of cytochromeic oxide. Human health effects of exposure to hydrogen sulfide, an irritant and an asphyxiant, depend on the concentration of the gas and the length of exposure [3–5].
Hydrogen sulfide corrosion is often encountered where gas with a high \( \text{H}_2\text{S} \) content is produced. \( \text{H}_2\text{S} \) is a gas soluble in water where it behaves as a weak acid. It reacts with iron to form a very insoluble iron sulfide corrosion product and usually adheres to the steel surface as scale. It is an excellent electrical conductor and is cathodic to the underlying steel resulting in accelerated corrosion and defects in the scale layer. The \( \text{FeS} \) can also lead to well plugging when precipitating in resulting in accelerated corrosion and defects in the scale layer.

The concentration of \( \text{H}_2\text{S} \) is typically measured in parts per million by volume (ppmv) in the gas phase relative to a partition from oil and an aqueous phase with a pH equal to or less than 5 at standard temperature and pressure (STP), of 20 °C and 1 atm absolute pressure. When the concentration of \( \text{H}_2\text{S} \) exceeds 10 ppmv in the gas phase, the oil well is deemed to be sour, and precautions are necessary in design and operation of production, transport, and storage equipment due to \( \text{H}_2\text{S} \) toxicity, corrosion, plugging of reservoir formations, and increased sulfur content of produced oil [8–10].

Hydrogen sulfide (\( \text{H}_2\text{S} \)) scavengers have been used extensively in different field operations, such as drilling and acid stimulation treatments. Typically, \( \text{H}_2\text{S} \) scavengers are preliminarily designed to react effectively at different in-situ conditions. For example, triazine-based scavengers are designed for neutral-high pH conditions [11,12], while aldehyde based scavengers are intended for low pH conditions; however, reaction products of these scavengers with \( \text{H}_2\text{S} \) could lead to potential formation damage. Therefore, removal of \( \text{H}_2\text{S} \) content from formation or flow back fluids had become a necessity. There are many techniques to remove \( \text{H}_2\text{S} \), and one of these techniques is using \( \text{H}_2\text{S} \) scavengers [13].

\( \text{H}_2\text{S} \) scavengers are chemicals that favorably react with \( \text{H}_2\text{S} \) gas to eliminate it and produce environmentally friendly products. These products depend on the type and composition of the scavenger and the conditions at which the reaction takes place. Certain scavengers produce solids, such as metal based scavengers, while others produce soluble products, such as triazines. Therefore, for a certain recipe, choosing the proper scavenger is as imperative as its function [14,15]. In well stimulation treatments, the products of the reaction between \( \text{H}_2\text{S} \) and a scavenger should not damage the formation by creating precipitation or hindering functions of another additive. Mainly, triazine based scavengers have been extensively used in stimulation treatments to remove \( \text{H}_2\text{S} \) from flowed back fluids [16,17].

During stimulation treatments, the efficiency of triazine based \( \text{H}_2\text{S} \) scavengers is susceptible to conditions, such as pH, temperature and exposure time [9–11]. Additionally, other factors, such as \( \text{H}_2\text{S} \)/scavenger stoichiometry, can affect the reaction of triazine based \( \text{H}_2\text{S} \) scavengers with \( \text{H}_2\text{S} \). For example, increasing the pH from 0 to 7 has amplified the scavenging capacity by an average of 176%. This is a result of the hydrolysis rate, which increases with acidity [18].

For any of the types of scavenger to be employed in the production operations, it has to meet some stringent requirements because the safety of both personnel and equipment depends on it. An ideal scavenger must have the following characteristics [19,20]:

1. Its reaction with sulfide should be complete, rapid, and predictable. The reaction product(s) formed should remain inert under all mud conditions.
2. Scavenging should occur in a wide range of the system’s chemical and physical environments. This includes a wide range of pH, temperature, pressure, competitive reactions, shear conditions all in the presence of an array of active chemicals and solids found in muds.
3. General system performance, e.g. mud archeology, filtration and cake quality should not be impaired by the application of excess scavenging in the system, even at high temperatures.
4. The true amount of scavenger available for reacting in a mud should have the capacity to be measured quickly and easily at the rig-site.
5. The scavenger, as well as its reaction products, should be non-corrosive to metals and materials contacted by the mud.
6. Using a scavenger should not risk the safety and health of personnel or pollute the environment. On the contrary, the scavenger should make drilling in \( \text{H}_2\text{S} \) zones or sweetening processes safer.
7. The scavenger should be widely available and economical for industry acceptance by having a low unit.

Alsabagh and Khalil developed a new amine base version of \( \text{H}_2\text{S} \) scavenger for scavenging \( \text{H}_2\text{S} \) gas from crude oil and got a patent for the invention [21]. The same investigators have been granted from the ministry state for scientific research in Egypt, another patent for the invention entitled “Preparation of new Olygemer Surfactants from Triazinan Tri Ethanol to Scaven- ger Hydrogen Sulfide Accompanied by Crude Oil and Natural Gas” [22]. The two versions of \( \text{H}_2\text{S} \) scavenger are successfully used in the Egyptian petroleum production companies. \( \text{H}_2\text{S} \) management in petroleum facilities is handled comprehensive studies on the scavenging process is the main object of the production problem companies during all petroleum processes [23].

The purpose of this study is to investigate the modeling and simulation for the rate estimation of H\(_2\)S scavenger injection dose to remove the \( \text{H}_2\text{S} \) from petroleum fields.

2. \( \text{H}_2\text{S} \) scavenger system and reaction rates of \( \text{H}_2\text{S} \) scavenger

The chemical system used for scavenging \( \text{H}_2\text{S} \) is illustrated elsewhere [10]. The equilibrium constant of hydrogen sulfide between oil and water phases (K \( \text{oil/water} \)) as a function of temperature, pressure, and gas-oil ratio is estimated using Figs. 1–3 in [10,24].

![Figure 1](image-url) Comparison between calculated and actual dose rate.
The kinetics of H$_2$S scavenger liquid reacting with gaseous hydrogen sulfide and buffered water solution was reported in [25]. In the scavenging reaction, the concentration variation of in contact with hydrogen sulfide gas was determined by isotopic nuclear magnetic resonance (NMR) studies and the rate was determined to be of first order in hydrogen sulfide concentration [10,25]:

$$\frac{dT}{dt} = -k_a[TH+] + [HS^-]$$  \hspace{1cm} \text{for \textsc{ph} > 10}  \tag{1}$$

with $k_a = 9.1 \times 10^7 \text{ Ka} \text{ [mol}^{-2} \text{s}]$ where $K_a$ is the acid constant of H$_2$S scavenger in solution.

The author has also concluded that the reaction will be of first order and fast for \textsc{ph} < 10. The reported kinetic constants may, however, have large errors, especially if extrapolated to low \textsc{ph} values. The H$_2$S scavenger is rapidly hydrolyzed on contact with water with reported kinetics as

$$\frac{dT}{dt} = -k_H[T][H]$$  \hspace{1cm} \text{for \textsc{ph} < 10}  \tag{2}$$

with $k_H = 1.42 \times 10^6 \text{ s}^{-1}$ at 22°C and 3.40 $\times 10^8 \text{ s}^{-1}$ at 60°C. The hydrolysis will be almost instantaneous for \textsc{ph} values of 5 or below.

In the model for natural gas treatment, the amount transferred is estimated using the rate equation [26]:

$$\frac{dy_{H_2S}}{dz} = \frac{K_g a P y_{H_2S}}{G_V}$$  \hspace{1cm} \text{(3)}$$

where $y_{H_2S}$ is the mole fraction of H$_2$S in the gas phase; $G_V$ is molar gas velocity, mol/m$^2$/s; $Z$ is tube length, ft; $K_g$ is overall ideal mass transfer coefficient, mol/m$^2$/s/bar; $a$ is interfacial area, m$^2$/m$^3$; and $P$ is pressure, bar. The pressure and molar gas velocity will vary along the path. The estimated of the rate constant ($K_g a$) using the field data of H$_2$S concentration injection of scavenger solution for the same rate of lift gas injection and flow rates in oil well is studied. The H$_2$S concentration at the entrance was obtained by mass balance at steady-state operation of the well without injecting H$_2$S scavenger. $K_g a$ was determined from the measured operational concentration of H$_2$S while injecting a known rate of H$_2$S scavenger solution with a known lift gas rate.

3. Estimation of injection dose rate

The average ideal mass transfer coefficient, expressed as $K_g a$ values, were calculated from the following simplified equation for estimating the absorption of H$_2$S from petroleum production:

$$\frac{K_g a D}{G_V}Z = \ln \frac{y_{in}}{y_{out}}$$  \hspace{1cm} \text{(4)}$$

where $K_g$ = overall ideal mass transfer coefficient, mol/m$^2$/s/bar, $a$ = interfacial area, m$^2$/m$^3$, $G_V$ = gas molar mass velocity, lb mol/(h ft$^3$), $P$ = pressure, atm, $Z$ = pipe length, ft, $y_{in}$ = inlet H$_2$S mole fraction, $y_{out}$ = outlet H$_2$S mole fraction.

This equation is derived based on an ideal model which assumes that the equilibrium vapor pressure of H$_2$S is zero, and that the $K_g a$ values remain constant along the length of the pipe. Test field data, however, show that the $K_g a$ value does in fact change (it decreases) along the length of pipe and the vapor pressure of H$_2$S does eventually rise as the stoichiometric limit of the scavenging agent is approached despite the limitations of the idealized model, Eq. (3) provides estimates of the average $K_g a$ value and can be used successfully to predict H$_2$S removal over the wide range of the studied flow conditions.

Eq. (3) was used to calculate the average actual mass transfer coefficients for different pipe lengths, the inlet H$_2$S concentration, along with the H$_2$S measured for downstream at different pipe lengths of the injection point was used to calculate the average $K_g a$ values. The data were regressed using standard statistical method to find the best fitting coefficients for the following equation:

$$K_g a = C_1 G_V^{C_2} R_j^{C_3} D^{C_4}$$  \hspace{1cm} \text{(5)}$$

where $K_g a$ = mass transfer coefficient, lb mol/(h ft$^3$ bar), $D$ = pipe diameter, inches, $R_j$ = H$_2$S scavenger dose injection rate, gallons/MMscf, $G_V$ = gas molar mass velocity, lb mol/(h ft$^3$), $C_1$, $C_2$, $C_3$, $C_4$ = regression coefficients constant.

From Eqs. (4) and (5) then the finally empirical equation to calculate H$_2$S scavenger injection dose rate becomes:

$$R_j = \left[ \frac{\ln \frac{y_{in}}{y_{out}} G_V}{C_1 G_V^{C_2} R_j^{C_3} D^{C_4} Z} \right]^{1/C_4}$$  \hspace{1cm} \text{(6)}$$

4. System description

The flow diagram of the EPRI H$_2$S scavenger metering and injection system, where the scavenger flow rate is measured periodically with a graduated cylinder installed on the pump’s suction line is reported elsewhere [10]. The chemical system considered corresponds to an existing oil well in Petrobel Petroleum Company in Egypt. The reservoir fluids, namely, formation water, crude oil, and its flows into production lines and the oil phase is initially above the bubble point pressure. The used EPRI liquid H$_2$S scavenger is injected into the gas phase containing part of the H$_2$S is formed. The droplets of H$_2$S scavenger injected into the gas phase decompose H$_2$S.
by the substitution of sulfur into H₂S scavenger ring, and the droplets encountering water phase are rapidly hydrolyzed in a competing reaction. The reactions take place in the multiphase flow along the flow line.

The available wells' field data from an existing oil well in Petrobel Petroleum Company in Egypt for (Well Nos. 113–173, 113–188, 113–104, 113–142 and 113–124) are daily barrel flow production BFPD, barrel oil production per day BOPD, water cut BS & W %, associated gas mmmscf, gas oil ratio scf/bbl, temperature °C, well head pressure psi, EPRI H₂S scavenger dose rate liter/day, and H₂S blank readings ppmv. Retention time from well to 8–2 station, h, H₂S blank reading, ppm, H₂S Test separator reading, pipe diameter, inch and net oil production, bbl/d at Petrobel Petroleum Company well fields production Table 1.

5. Results and discussion

The H₂S scavenger injection dose rate as in the empirical Eq. (6) is a function of the factors; pipe length, pipe diameter, gas flow rate and pressure. The results of these effecting parameters on the H₂S scavenger injection dose rate are discussed in the following section.

5.1. Effect of pipe Length on H₂S scavenger injection dose rate

Table 2 shows the effect of pipe length (distance from the downstream of the injection point) on H₂S scavenger injection dose rate, at a given pipe diameter 4 inch, pressure 110 psi at H₂S inlet 6000 ppmv and H₂S outlet 10 ppmv, and gas flow rate 0.1 mmmscf. At pipe lengths equal 1100, 1600 and 2100 ft the H₂S scavenger injection dose rate is equal to 595, 390 and 287 liter per day, respectively. In general, the estimated results show that the effect of pipe length had a marked effect, increasing the pipe length caused a decrease the H₂S scavenger injection dose rate because of the time of reaction has been increased.

5.2. Effect of pipe diameter on H₂S scavenger injection dose rate

Table 2 shows the effect of pipe diameter (inch) at a given gas flow rate 0.1 mmmscf, distance 1600 ft from the downstream of the injection point at H₂S inlet 6000 ppmv provide and H₂S outlet 10 ppmv and pressure 110 psi. The results of different pipe diameters from 2, 4 and 6 inches respectively on H₂S scavenger injection dose rate liter/day are estimated. The output results of 2, 4, and 6 inch pipe diameters give the values of 54.6, 390 and 1230 l/day of H₂S scavenger injection dose rate respectively, consequently by increasing the diameter the H₂S scavenger injection dose rate will be increased due to reduction of gas velocity and turbulence and hence, absence of good mixing between the scavenger and the crude.

5.3. Effect of gas flow rates on H₂S scavenger injection dose rate

Table 2 shows the effect of gas flow rates, mmmscf at a given pipe diameter, 4 inch, distance 1600 ft from the downstream of the injection point at H₂S inlet 6000 ppmv provide and H₂S outlet 10–20 ppmv, and pressure 110 psi. The effect of gas flow rates at 0.05, 0.1 and 0.15 mmmscf on H₂S scavenger injection dose rate was calculated. When gas flow rates equal to 0.05, 0.1 and 0.15 mmmscf the H₂S scavenger injection dose rate is equal to 370, 390 and 402 l/day, respectively. By increasing the gas flow rates the H₂S scavenger injection dose rate will be increased. The estimated results show that the effect of gas flow rates had a weak effect.

5.4. Effect of pressure on H₂S scavenger injection dose rate

The effect of pressure, psi at a given pipe diameter, 4 inch, the distance from the inlet concentration at 1600 ft down hole of the injection point to separator at H₂S inlet 6000 ppmv provide and H₂S outlet 10 ppmv, and gas flow rate 0.1 mmmscf is shown in Table 2. The effect of different pressures on H₂S scavenger injection dose rate using the estimated empirical equation was done. When the pressures are 90, 110, 130 psi the H₂S scavenger injection dose rate is 464, 390 and 287 l/day respectively. By increasing the pressure the H₂S scavenger injection dose rate will be decreased according to the estimated empirical equation.

5.5. Effect of temperature on H₂S scavenger injection dose rate

The effect of different temperature on H₂S scavenger injection dose rate, when the temperatures are 45, 65, 75, 85 and 120 °C the H₂S scavenger injection dose rate are 455, 390, 395 and 389 l/day respectively. From these results, it is clear that no improvement in H₂S scavenger injection dose rate at a higher temperature (120 °C) is seen while at a low temperature (45 °C) the H₂S scavenger injection dose rate has been.

| Table 1 Wells conditions of Petrobel Petroleum Company fields. |
|----------------------|------------------|------------------|------------------|------------------|------------------|
| Net Prod., bbl/d     | 1295             | 1687             | 136.35           | 605              | 85.2             |
| BS & W, %            | 41               | 13.7             | 77.7             | 79               | 85.3             |
|GOR, scf/bbl         | 16               | 0                | 26               | 18               | 21               |
|Pressure, psi        | 110              | 150              | 400              | 180              | 120              |
|H₂S Blank, ppmv      | 6000             | 12,000           | 1700             | 1600             | 200              |
|Pipe diameter, in     | 4                | 4                | 4                | 4                | 2                |
|Retention time, h     | 2.5              | 3                | 3                | 3                | 2                |

| Table 2 Results of effect of different pipe diameters, pipe lengths, gas flow rate, pressure and temperature on injection dose rate liter/day. |
|----------------------|------------------|------------------|------------------|------------------|------------------|
| Pipe length, ft      | 1100             | 1600             | 2100             |
|Dose rate, liter/day  | 595              | 390              | 287              |
|Diameter, inch        | 2                | 4                | 6                |
|Dose rate, liter/day  | 54.6             | 390              | 1230             |
|Gas flow rate, mmmscf | 0.05             | 0.1              | 0.15             |
|Dose rate, liter/day  | 370              | 390              | 402              |
|Pressure, psi         | 90               | 110              | 130              |
|Dose rate, liter/day  | 464              | 390              | 335              |
|Temperature, °C       | 45               | 75               | 120              |
|Dose rate, liter/day  | 455              | 390              | 389              |
increased to reach 455 liter/day as in Table 2. The temperatures are preferably in the range from 60 to 75 °C where at this range of temperatures it is enough to release H₂S solved in oil and water to gas phase. The values of outlet total concentration of H₂S in oil, water and gas mmscfd, cross sectional area of pipe line, ft², mol mass velocity, (mol/ft²/h), mass transfer coefficient, lb mol/(h atm ft²) and scavenger dose rate, liter/day are calculated using the modeling for removal of hydrogen sulfide from petroleum production using H₂S scavenger are shown in Table 3.

The simulation of the hydrogen sulfide concentration profiles for different field data with different conditions and the calculation of the injection rates of expensive chemical scavengers are estimated. The results of actual and calculated scavenger dose rate, liter/day are shown in Table 4, Fig. 1. The deviation between calculated and actual H₂S scavenger dose rate is ranged from 0.7% to 7.5%, while the average deviation for all the comparison results of field wells is 3.66%. The Deviation between actual and calculated results of H₂S scavenger efficiency ranged from 0.03% to 0.43% and the average deviation for all the comparison results of H₂S scavenger efficiency is 0.272%. From the previous results the computation model based on the estimated empirical equation is compatible with the actual H₂S scavenger injection dose rate and H₂S scavenger efficiency for all oil field wells as shown in Fig. 2, hence the model of the hydrogen sulfide removal from multiphase produced fluids can be successfully used by injection of H₂S scavenger solution into their gas phase.

6. Conclusion

The modeling and simulation of the scavenging process of hydrogen sulfide from the multiphase fluid produced in one of the Egyptian petroleum companies was studied. The initial concentration of H₂S in the crude mixture ranges from 200 to 12,000 ppmv and it is desired to reduce it to a minimum value below 10 ppmv before processing. This is achieved by injecting H₂S scavenger chemical produced by the Egyptian Petroleum Research Institute (EPRI). The scavenging injection dose rates depend on pipe diameter, pipe length, gas flow rate, pressure and temperature. The effect of these parameters on the H₂S scavenger injection dose rate was studied. It was found that within the investigated range of parameters- the following findings can be drawn:

1. Increasing of the pipe diameter has a negative effect on the scavenging process as a result of reduction of gas velocity and turbulence and hence, absence of good mixing between the scavenger and the flow.
2. The pipe length has a noticeable effect on the scavenging process. As pipe length increases, H₂S scavenger injection dose rate decreases because the contact time increases. Therefore, it is preferable to increase the pipe length as much as possible to give the scavenger enough time to react with H₂S contained in the crude.
3. By increasing the gas flow rate at a constant pipe diameter the H₂S scavenger injection dose rate increases. The gas flow rate has a weak effect on the H₂S scavenger injection dose rate.
4. By increasing the pressure the H₂S scavenger injection dose rate decreases. The pressure has a considerable effect.
5. The temperatures are preferably in the range of 60–75 °C where this range of temperature is enough to release the dissolved H₂S in oil and water to gas phase.
6. The modeling and simulation of the hydrogen sulfide concentration profiles for different field data with different conditions and the determining of the injection rates of the chemical scavengers were estimated.
7. The results of computation based on the empirical equation are compatible with the practical injection dose rate at the petroleum field.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Results of computation model based on data obtained from Petrobel Company well fields.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total H₂S in (O,W,G), ppmv</td>
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</tr>
<tr>
<td>Cross sec. area, ft²</td>
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<tr>
<td>Mol mass vel., mol/ft²/h</td>
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<td>Mass tran. coeff., lb mol/(h atm ft²)</td>
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<td>Calc. scavenger Dose rate, L/D</td>
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<td>Calc. scavenger efficiency, %</td>
<td>99.7</td>
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<table>
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<th>Table 4</th>
<th>Comparison between the actual and calculated scavenger dose rate and the efficiency of H₂S scavenger as a function of data obtained at Petrobel Company data field.</th>
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</thead>
<tbody>
<tr>
<td>Actual scavenger dose rate, L/D</td>
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<tr>
<td>Calc. scavenger dose rate, L/D</td>
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<tr>
<td>Deviation between calc. and act scavenger dose rate, %</td>
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<tr>
<td>Actual scavenger efficiency, %</td>
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<td>Calc. scavenger efficiency, %</td>
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<td>Deviation between calc. and act scavenger efficiency, %</td>
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References