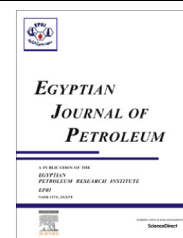




Egyptian Petroleum Research Institute
Egyptian Journal of Petroleum

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FULL LENGTH ARTICLE

Modeling of hydrogen sulfide removal from Petroleum production facilities using H₂S scavenger



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Received 12 December 2013; accepted 9 March 2014

Available online 27 June 2015

KEYWORDS

Hydrogen sulfide removal;
Sour oil production;
H₂S scavengers;
Multiphase flow;
Sour wells

Abstract The scavenging of hydrogen sulfide is the preferred method for minimizing the corrosion and operational risks in oil production facilities. Hydrogen sulfide removal from multiphase produced fluids prior to phase separation and processing by injection of EPRI H₂S scavenger solution (one of the chemical products of Egyptian Petroleum Research Institute) into the gas phase by using the considered chemical system corresponds to an existing oil well in Qarun Petroleum Company was modeled. Using a kinetic model the value of H₂S in the three phases was determined along the flow path from well to separator tanks. The effect of variable parameters such as, gas flow rates, chemical injection doses, pipe diameter and length on mass transfer coefficient $K_G a$, H₂S outlet concentration and H₂S scavenger efficiency has been studied. The modeling of the hydrogen sulfide concentration profiles for different conditions was performed. The results may be helpful in estimating injection rates of H₂S scavengers for similar fields and conditions.

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1. Introduction

In several Petroleum reservoirs, the concentration of hydrogen sulfide (H₂S) has been observed to increase unexpectedly in gaseous, oil, and aqueous phases of produced fluids. This concentration 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 H₂S 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 H₂S toxicity, corrosion, plugging of reservoir formations, and increasing sulfur content of the produced oil. Some oil fields in the North Sea and Campos Basin (Brazil) have turned sour after a few years of injection of seawater for improved recovery of oil [5]. Many studies have attributed this souring to the activity of sulfate-

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Peer review under responsibility of Egyptian Petroleum Research Institute.

<http://dx.doi.org/10.1016/j.ejpe.2015.05.003>

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reducing bacteria (SRB) and resultant production of biogenic H_2S , except in a few cases of very high pressure reservoirs where there is evidence for a geochemical mechanism as well [6]. Many production facilities were unfortunately previously designed and built without considering the effect of these organisms on their operation and maintenance.

The souring of Petroleum reservoirs is caused mainly by sulfate-reducing bacteria which can increase the concentration of hydrogen sulfide in the produced fluids. The H_2S is making it necessary to inject expensive chemical scavengers in production pipelines so that the corrosion and operational risks can be minimized. In-line scavenging of hydrogen sulfide is the preferred method for production of crude oil containing low hydrogen sulfide levels from wells. This may be occurring especially when the well is tied back via a flow line to a host facility at which there is no provision for H_2S scavenging and/or where a H_2S removal facility is too expensive and/or impractical to install [8]. As a result of this method, the hydrogen sulfide content of the crude oil that is delivered to the platform is reduced to safe and commercially acceptable levels and reaction by-product formation is manageable. The formation water provides a carrier phase for some of the reaction products and enhances the dispersion of some insoluble reaction products in the co produced aqueous phase. The H_2S injection models have been proposed for treating single-phase natural gas with liquid scavengers [7]. The main objective of this work is to model this chemical process using available field data so that the removal of hydrogen sulfide (H_2S) can be reduced by determining the rate of injection of H_2S scavengers in the production lines. Our attentions should be extended to study the removal model of hydrogen sulfide from multiphase streams.

2. Chemical system

The chemical system is a flow line connecting oil well to production facility. Fig. 1 is a schematic flow diagram of the scavenger metering and injection system existing in Qarun Petroleum Company, where the scavenger flow rate is measured periodically with a graduated cylinder installed on the

pump's suction line. The reservoir fluids, namely, formation water, crude oil, and its associated gas, flow into production lines and the oil phase is initially above the bubble point pressure. The used EPRI liquid H_2S scavenger is injected into the production line through a mandrel (oil, gas and water).

The scavenger droplets disperse through the produced fluid substantially homogeneously because of the natural turbulence of the fluid flow. As the pressure drops below the bubble point, a gas phase containing part of the H_2S is formed. The droplets of H_2S scavenger injected into the gas phase decompose H_2S by the substitution of sulfur into H_2S scavenger ring, and the droplets encountering the water phase are rapidly hydrolyzed in a competing reaction. The reactions take place in the multiphase flow along the flow line. The reaction products disperse in the liquid phase.

3. Modeling of the chemical system

The chemical system considered corresponds to an existing oil well in Qarun Petroleum Company in Egypt. The available data for south west Qarun field (SWQ-11 flow line) are: daily barrel flow production BFPD, barrel oil production per day BOPD, water cut BS & W %, associated gas mmscf, gas oil ratio scf/bbl, temperature °F, well head pressure psi, EPRI H_2S scavenger dose rate G/D, and H_2S blank readings ppmv (Table 1). The system is modeled using these available data along with several physical properties measured for the purpose of this study. The simulation is done for estimating the phase distribution of hydrogen sulfide from total amount or from gas phase concentration, and estimating scavenging reaction rates and gas phase concentration of hydrogen sulfide along the flow path.

4. Estimation of phase distribution of H_2S

From the available literature data [5] we developed a correlation to estimate the equilibrium constant of hydrogen sulfide between oil and water phases ($K_{oil/water}$) from temperature, pressure, and gas-oil ratio. The equilibrium Henry's constant

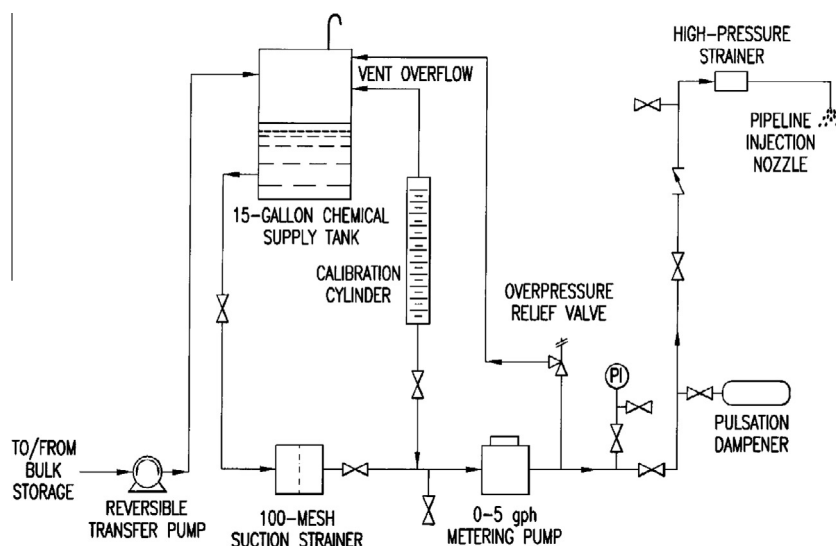


Figure 1 Flow diagram of EPRI H_2S scavenger metering and injection system.

Table 1 Daily flow production of SWQ-11 Qarun Petroleum Company.

Well name	BFPD	BOPD	BS & W %	Gas mmscf	GOR scf/bbl	Temp °F	WH psi	Dose G/D	Average H ₂ S blank in gas phase
SWQ-11	8120	81	99	0.118	443	149	200	200	11,000

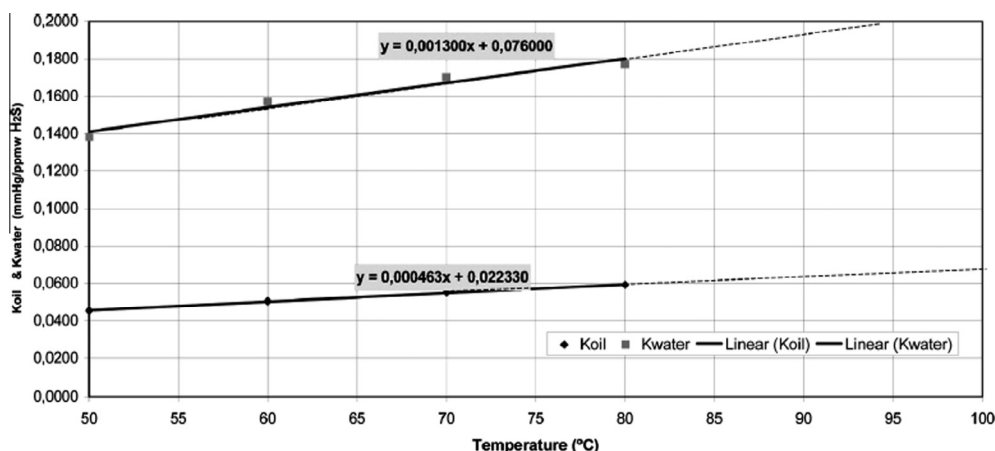
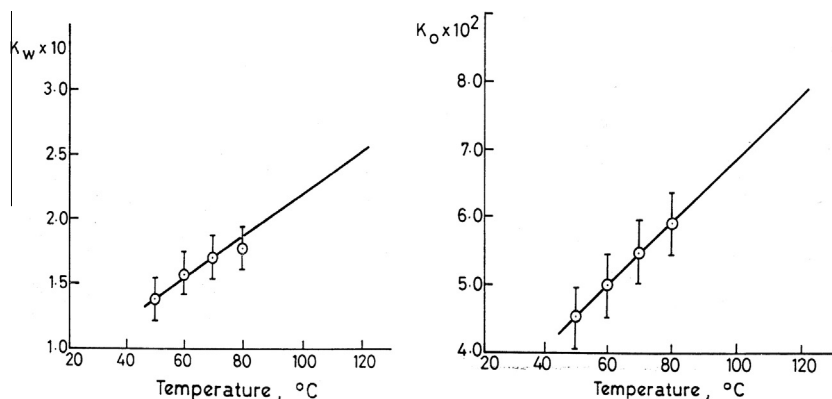
K_{H_2S} for the gas/oil phases and for gas/water phases was correlated with temperature at low pressures. The correlation is shown in Fig. 2. In this condition, the equilibrium constants are independent of composition and pressure and the distribution coefficient K oil/water is calculated at each temperature (Fig. 3). The salt concentration of the particular case under study was similar to that in the literature data used. If the compositions of the phases are very different from the literature case, it is advisable to determine the equilibrium constant by experiment. Wilson's API-Sour Model for handling sour water systems can be applied to sour water processes containing hydrocarbons, acid gases, and H₂O. The method uses Wilson's model to account for the ionization of the H₂S, CO₂, and NH₃ in the aqueous water phase. The fugacity of the vapor and liquid hydrocarbon phases as well as the enthalpy for all three phases were calculated using this equation of state. The K -values for the aqueous phase were calculated using Wilson's API-Sour method [1].

5. Estimation of reaction rates

Buhaug [3] reported the kinetics of H₂S scavenger liquid reacting with gaseous hydrogen sulfide and buffered water solution. In the scavenging reaction, the concentration variation of H₂S scavenger in contact with hydrogen sulfide gas was determined by isotopic nuclear magnetic resonance (NMR) studies and the rate was determined to be first order in hydrogen sulfide concentration:

$$\frac{dT}{dt} = -k_a[TH^+][HS^-] \quad \text{for } pH > 10 \quad (1)$$

with $K_a = 9.1 \times 10^7 \text{ Ka} [\text{mol}^{-2} \cdot \text{s}]$ where K_a is the acid constant of H₂S scavenger in solution. Beggs and Brill [2] have also concluded that the reaction will be first order and fast for $pH < 10$. The reported kinetic constants may, however, have large errors, especially if extrapolated to low pH values.

**Figure 2** Linear correlations for equilibrium constants of oil and formation water.**Figure 3** Equilibrium constant K oil/water for hydrogen sulfide (unassociated hydrogen sulfide and formation water with $pH = 5$).

The H₂S scavenger is rapidly hydrolyzed on contact with water with reported kinetics of

$$\frac{dT}{dt} = -k_H[T][H] \quad \text{for } \text{pH} < 10 \quad (2)$$

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 pH values of 5 or below.

We model the kinetics of hydrogen sulfide removal by H₂S scavenger injection with the following considerations. The H₂S scavenger solution is injected into gas stream in nearly uniform droplets. The highly reactive H₂S scavenger in the droplets will be destroyed almost instantly on contact with the water phase flowing near the wall. The rate of removal of hydrogen sulfide is limited by the rate of mass transfer of H₂S from the gas phase to scavenger solution droplets. The oil, water, and gas phases are in thermodynamic equilibrium along the flow path. The rate of removal of H₂S is estimated using a model that combines mass transfer resistance and reaction.

Fisher et al. [7] have used this model for natural gas treatment. The amount transferred is estimated using the rate equation:

$$\frac{dy_{H_2S}}{dz} = \frac{K_G a P y_{H_2S}}{G} \quad (3)$$

where y_{H_2S} is mole fraction of H₂S in the gas phase; G is molar gas velocity, mol/m²s; Z is tube length, m; K_G is overall mass transfer coefficient, mol/m² s bar; a is interfacial area, m²/m³; and P is pressure, bar. The pressure and molar gas velocity will vary along the path. We have estimated the rate constant ($K_G a$) using the field data of H₂S concentration injection of scavenger solution for same rate of lift gas injection and flow rates in the offshore oil well under study. The H₂S concentration at the entrance was obtained by mass balance at steady-state operation of the well without injecting H₂S scavenger. $K_G a$ was determined from the measured operational concentration of H₂S while injecting a known rate of H₂S scavenger solution with known lift gas rate.

6. Results and discussion

The majority of the effecting parametric variables over a wide range of piping length, chemical injection rates, gas flow rates and piping diameter to determine the effect of these variables on mass transfer coefficient $K_G a$, H₂S outlet concentration and H₂S scavenger efficiency, are discussed below.

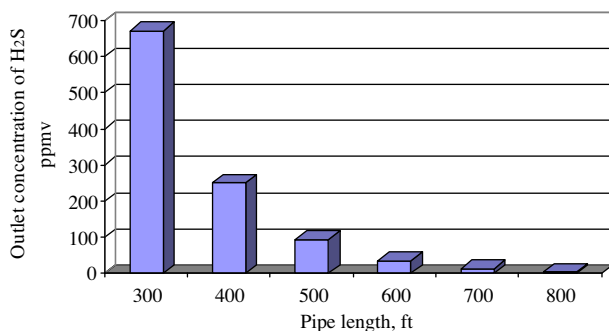


Figure 4 Effect of pipe length on outlet H₂S concentration at 12,800 ppmv.

6.1. Effect of pipe length, ft

Figs. 4 and 5 and Table 2 show the concentration of H₂S in the fluid as a function of distance down the pipe. The results have been estimated at different distances from 300 to 800 ft downstream of the injection point. From Fig. 3 the calculated values of H₂S concentration dissolved in the oil phase and water were 1266 and 534 ppmv, respectively. The concentration of H₂S in the mixture was 12,800 ppmv. It can be noticed that, the pipe length has no effect on mass transfer coefficient $K_G a$ as shown in Table 2. At pipe length equal to 300, 500 and 800 ft the outlet H₂S was equal to 671, 94.1 and 4.95 ppmv respectively, while the removal of H₂S percentage efficiency has been increased from 94.7% at pipe length 300 ft to 100% at pipe length 800 ft as shown in Fig. 5. In general, the estimated results show that the effect of pipe length had a pronounced effect on H₂S outlet concentration and H₂S removal efficiency. This is attributed to the increase of contact time between the scavenger and the H₂S gas. Hence the reaction had enough time to be completed.

6.2. Effect of scavenger dose rate, gallon/hr

Table 3 and Fig. 6 show the effect of scavenger dose rate on mass transfer coefficient lb mol/(hr atm.ft²), outlet H₂S concentration ppmv and H₂S removal efficiency. The chemical injection rate, expressed as L/G ratio (H₂S EPRI scavenger

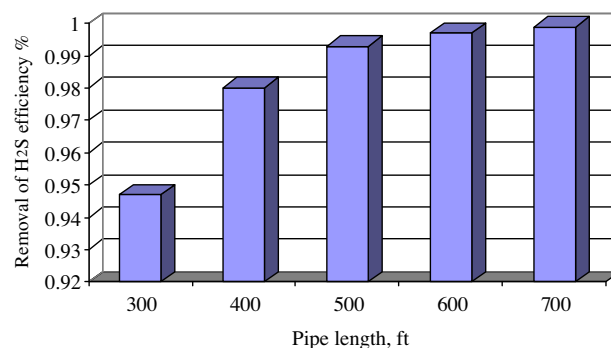


Figure 5 Effect of pipe length on H₂S removal efficiency at 12,800 ppmv.

Table 2 Effect of pipe length on mass transfer coefficient, outlet H₂S and removal of H₂S percentage efficiency with the given pipe diameter of 4 inch, gas flow rate of 0.118 mmcf/d, scavenger injection rate of 8.3 gallon per hr and the inlet concentration of H₂S in the mixture is 12,800 ppmv.

Pipe length, ft	$K_G a$, mass transfer coeff., lb mol/(hr atm.ft ²)	Outlet concn. of H ₂ S, ppmv	H ₂ S removal efficiency, %
300	2.38E-02	671	94.7
400	2.38E-02	251	98
500	2.38E-02	94.1	99.3
600	2.38E-02	35.3	99.7
700	2.38E-02	13.2	99.9
800	2.38E-02	4.95	100

Table 3 Effect of scavenger dose rate on K_{Ga} , mass transfer coefficient lb mol/(hr atm.ft²), outlet concentration of H₂S, ppmv and H₂S removal efficiency at given pipe diameter of 4 inch, gas flow rate of 0.118 mmcsfd and distance of 400 ft from the downstream of the injection point at H₂S inlet 12,800 ppmv.

Scavenger dose rate, gallon/hr	K_{Ga} , mass transfer coeff., lb mol/(hr atm.ft ²)	Outlet concn of H ₂ S, ppmv	H ₂ S removal efficiency, %
2	0.00908	2850	77.7
3.5	0.0133	1430	88.8
5	0.0169	785	93.8
6.5	0.0201	457	96.4
8.3	0.0238	251	98
9.5	0.0260	173	98.6
10.5	0.0279	128	99

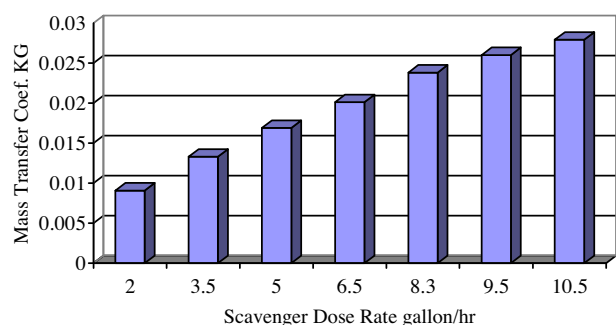


Figure 6 Effect of scavenger dose rate on mass transfer coefficient k_G at 12,800 ppmv.

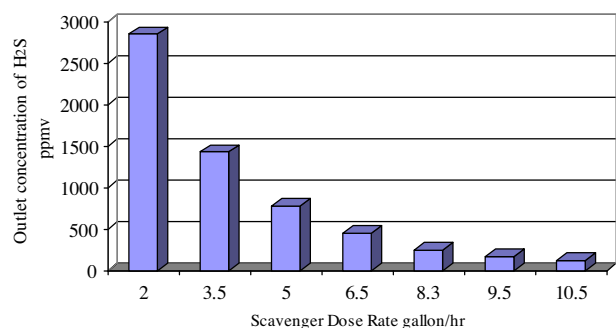


Figure 7 Effect of scavenger dose rate gallon/hr on outlet H₂S concentration at 12,800 ppmv.

injection rate/gas rate), produced a strong effect on the mass transfer coefficient, k_{Ga} for most conditions. From Table 3 and Fig. 6 we can notice that when scavenger dose rate increases the mass transfer coefficient increases. Besides, increasing the scavenger rate caused a dramatic decrease in outlet H₂S concentration and a significant improvement in H₂S removal efficiency, increasing from 77.7% at scavenger dose rate of 2 gallon/hr to 99% at scavenger dose rate of 10.5 gallon/hr as shown in Figs. 7 and 8. This may be attributed to the completion of reaction between the H₂S gas and the scavenger.

6.3. Effect of gas flow rate, mmcsfd

Table 4 and Figs. 9–11 show the effect of gas flow rate, mmcsfd on mass transfer coefficient lb mol/(hr atm.ft²), outlet H₂S concentration ppmv and removal efficiency of H₂S at the same previous conditions. It is shown that increasing the gas flow rate causes a noticeable decrease in outlet H₂S concentration. Consequently the gas flow rate affects H₂S removal efficiency, the value is increased from 96.9% at gas flow rate, 0.05 mmcsfd to 98.7% at gas flow rate of 0.25 mmcsfd. The mass transfer coefficient also increases. Increasing the gas flow rate at a constant pipe diameter increases the superficial velocity

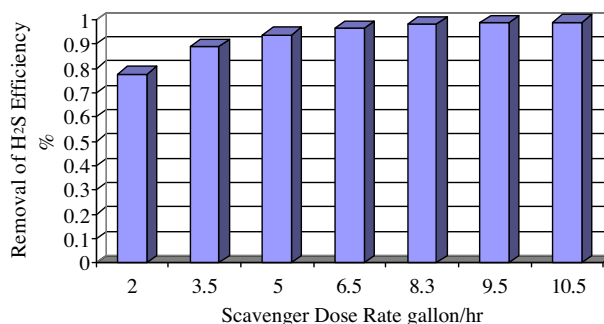


Figure 8 Effect of scavenger dose rate on H₂S removal efficiency at 12,800 ppmv.

Table 4 Effect of Gas flow rate on mass transfer coefficient, outlet H₂S concentration, and H₂S removal efficiency at given pipe diameter of 4 inch, dose rate of 8.3 gallon/hr and distance of 400 ft from the downstream of the injection point at H₂S inlet 12,800 ppmv.

Gas flow rate, mmcsfd	K_{Ga} , mass transfer coeff., lb mol/(hr atm.ft ²)	Outlet concentration of H ₂ S, ppmv	H ₂ S removal efficiency, %
0.05	0.0089	397	96.9
0.1	0.0197	276	97.8
0.118	0.0238	251	98
0.15	0.0313	219	98.3
0.2	0.0434	184	98.6
0.25	0.0561	160	98.7

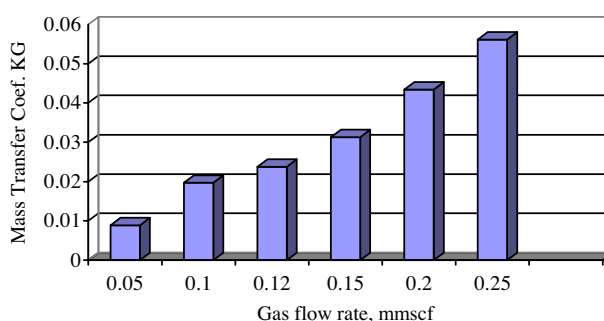


Figure 9 Effect of gas flow rate on mass transfer coefficient k_G at 12,800 ppmv.

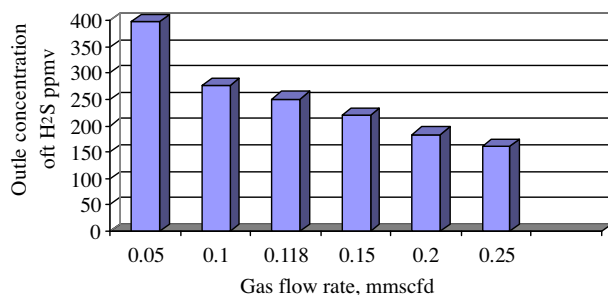


Figure 10 Effect of gas flow rate mmscfd on outlet H₂S concentration at 12,800 ppmv.

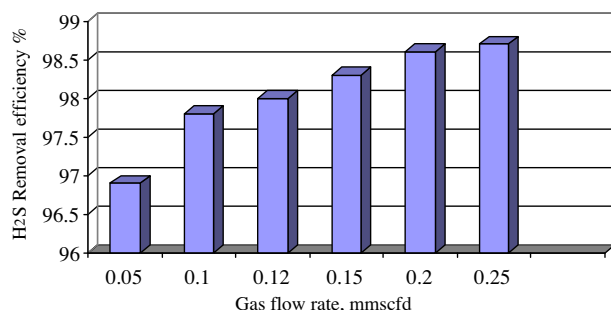


Figure 11 Effect of gas flow rate mmscfd on H₂S removal efficiency concentration at 12,800 ppmv.

Table 5 Effect of pipe diameter on $K_G a$, mass transfer coefficient, outlet concentration of H₂S, and H₂S removal efficiency at a given scavenger dose rate of 8.3 gallon/hr, pipe diameter of 4 inch, gas flow rate of 0.118 mmscfd and distance of 400 ft from the downstream of the injection point at H₂S inlet 12,800 ppmv.

Pipe diam., inch	$K_G a$, mass transfer coeff., lb mol/(hr atm.ft ²)	Outlet concn. of H ₂ S, ppmv	H ₂ S removal efficiency, %
2	0.47	0.0000125	100
3	0.0751	7.32	99.9
4	0.0238	251	98
6	0.00323	3480	72.8

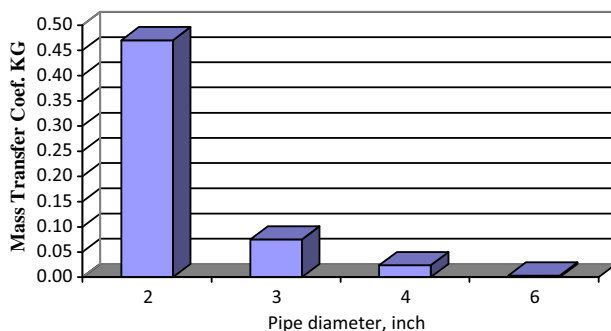


Figure 12 Effect of pipe diameter on mass transfer coefficient k_G at 12,800 ppmv.

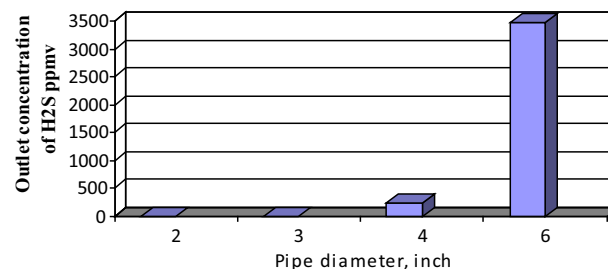


Figure 13 Effect of pipe diameter on H₂S outlet concentration at 12,800 ppmv.

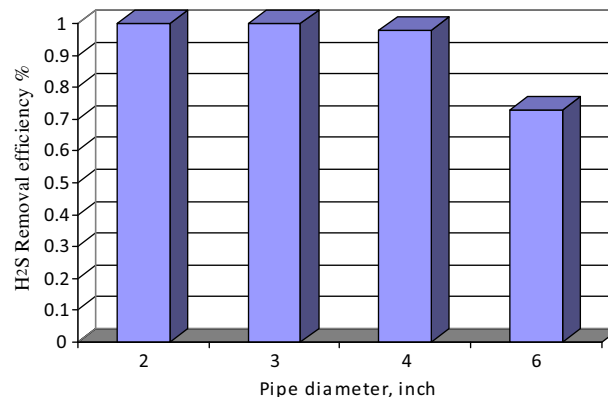


Figure 14 Effect of pipe diameter on H₂S removal efficiency at 12,800 ppmv.

and the turbulence of the mixture. This ensures better mixing of the reactants.

6.4. Effect of pipe diameter

Table 5 and Figs. 12–14 show the effect of pipe diameter on $k_G a$, mass transfer coefficient, outlet concentration of H₂S, and H₂S removal efficiency. From the Table and Figures, it was cleared that the difference in the results between the six-inch pipe and the two-inch pipe. For a given gas flow and injection rate, the mass transfer coefficient and the H₂S removal efficiency, were significantly higher for the two-inch pipe. The increased removal in the two-inch pipe may result from the availability of a large wetted surface area for mass transfer per unit volume of pipe.

7. Conclusion

The scavenging process of hydrogen sulfide from the multi-phase fluid produced in one of the Egyptian Petroleum Companies was modeled. The initial concentration of H₂S in the crude mixture is 12,800 ppmv and it is desired to reduce it to a minimum value below 10 ppmv before shipping. This is achieved by injecting H₂S scavenger chemical produced by the Egyptian Petroleum Research Institute EPRI. The scavenging process does not depend only on the scavenger efficiency, but also on other parameters such as pipe diameter, pipe length, gas flow rate and scavenger injection rate. The effect of these parameters on mass transfer coefficient, H₂S

outlet concentration, H₂S removal efficiency was studied. It was found that – within the investigated range of parameters – the following findings can be concluded:

- The pipe length has a noticeable effect on the scavenging process. As pipe length increases, the outlet H₂S concentration decreases because the contact time increases (Table 2). Therefore, it is preferable to increase the pipe length as possible to give the scavenger enough time to react with H₂S contained in the crude. If the field area is limited, sometimes loops are used to increase the pipe length.
- The opposite argument can be said on pipe diameter. As H₂S outlet concentration dramatically increases and both the mass transfer coefficient and removal efficiency significantly drop due to the reduction of gas velocity and turbulence and hence, absence of good mixing between the scavenger and the crude (Table 5).
- The scavenger dose rate has a considerable effect on H₂S outlet concentration and removal efficiency. However it can be said that is not the dominant factor. From Table 3 it can be seen that although the scavenger dose has increased almost five times (from 2 to 10.5 gallon/hr), the target H₂S outlet concentration (10 ppmv) has not been achieved (at 4 inch pipe diameter and 400 ft pipe length).
- Increasing the gas flow rate at a constant pipe diameter increases the superficial velocity and the turbulence of the mixture. This ensures better mixing of the reactants. Hence, the outlet H₂S decreases and removal efficiency increases.
- The obtained results may be helpful in estimating the scavenger injection dose for similar fields and condition.

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