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Oxidative Removal Of Hydrogen Sulfide From Kurdistan Region - Iraq Crude Oil

Qasim Y. Mohammed Ali

Oil Technology Department, Koya Technical Institute, Kurdistan Region – **IRAQ**

Email: qyahya@yahoo.com

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ABSTRACT

Hydrogen sulfide is a very dangerous, toxic and corrosive gas. Hydrogen sulfide should be removed from the crude oil to reduce the environmental pollution, protect the health of drilling workers and prevent corrosion of pipelines and equipments.Removal of hydrogen sulfide (H_2S) has been achieved from different types of crude oil from Shiwashouk and Kormalah fields Kurdistan region- Iraq, by using of (H_2O_2/NH_4OH and $FeCl_3/EDTA$) mixtures. The results revealed that there is tremendous decrease in sulfide concentration when used ($FeCl_3/EDTA$) mixture. Also, the effect of time on H_2S removal attempted using different percentages of $CuCO_3$ (1 and 2) %.

Keywords: Hydrogen sulfide, oxidation.

INTRODUCTION

Crude oil generally contains a definite amount of sulfur compounds, and the crude that contains especially hydrogen sulfide (H_2S) in excess of 5.1×10^{-3} kg/m^3 is called a sour one. The main focus is aimed at removal of hydrogen sulfide, because other sulfur compounds are far less toxic and not so aggressively corrosive. The presence of brine exacerbates the equipment corrosion as does CO_2 [1].
Personnel safety and equipment protection require that H_2S and other sulfur compounds be removed as far as possible.

The most important source of H_2S production in oil reservoirs is propped up by the activity of sulfate reduction bacteria (Desulfovibrio, Desolfotomaculum, Desolfococcus, Desolfonema and Desolfosarcina) at injected water contact zone with existing water in formation [2]. Regardless of the source, the remaining H_2S content in crude should be decreased to 2.1×10^{-5} kg/m^3 to protect personnel, mitigate corrosion and meet sales specification. Crude oil can be sweetened by many of the same chemicals used to remove acid gases from sour natural gas. Amines, caustic, zinc salts and other bases and/or oxidizing agents have been considered but because crude oil usually contains far more contaminants, the liquid/liquid chemical processes are seldom used [3]. H_2S exists in the biogeochemical cycle as the product of anaerobic oxidation by sulfur-reducing bacteria. Anaerobic bacteria use sulfate as the electron acceptor in the respiration process, resulting in the production of H_2S. They exist at a wide range of pH, pressure, temperature, and salinity conditions and are widely distributed in habitats[4]. In anaerobic organic rich soils, H_2S is commonly present due to the reducing nature of the sediments and the precursor SO_4^{2-} is the second most common anion in seawater [3]. Bacteria break down organic matter produce H_2S. These microorganisms favor low-oxygen environments, such as in swamps and sewage. Small amounts of H_2S exist in crude petroleum while up to 90% in natural gas. About 10% of total global emissions of H_2S are due to human activity including petroleum refineries, coke ovens, paper mills (using the sulfate method), and tanneries. Normal concentration of H_2S in clean air is about 100-200 ppb [4]. Burstyn et al. [5] conducted a survey of average concentrations of SO_2 and H_2S at rural locations in western Canada and determined that the average concentration is 0.1-0.2 ppb for H_2S, and 0.3-1.3 ppb for SO_2. The concentrations vary at different locations and are affected by seasons. Measured concentrations were affected by the wells.

More rapid and non-biological technologies are also being developed. For example, mesoporous materials can be generally used as adsorbents to remove impurities from gases. Melo et al. studied the use of Zeolite 13X and Zinox 380 to remove H_2S at 25 °C. X-ray fluorescence and atomic absorption, X-ray diffraction, particle size distribution analyses and FTIR spectroscopy were employed to characterize these sorbents. The results show that both materials have promising future in the removal of H_2S from natural gas [6].

MATERIALS AND METHODS

Materials: The samples were collected from Taq Taq field, Kormalh field and Kirkuk at Kurdistan region-Iraq, and the experiments were conducted at Koya technical institute – oil technology department laboratories.

Ferric Chloride (Scharlau) 98%, Ethylenediamine tetraacetic acid disodium salt(EDTA) (Thomas baker) 99.8%, Hydrogen peroxide (Thomas baker) 50% w/w, Ammonium hydroxide (Scharlau)32% w/w and Copper carbonate (Merck) 98% reagents were obtained in the highest purity available and were used without further purification.

Experimental procedure:

1.10 g of a crude oil sample is weighed to a conical flask, then the desired amount of oxidation mixture added as follows: $FeCl_3$/EDTA (2:1) and H_2O_2/NH_4OH (1:1). The flask is tightly closed and manually shaken then placed in the magnetic stirrer (the stirring ball is placed inside the flask). The mixing is done gradually; starting at low speed and increasing towards full speed. The mixing time is 15 minutes for each type of mixtures at room temperature. After mixing, extraction and volumetric determination using dithizone indicator was employed.

2. Also, 20 ml of Copper carbonate ($CuCO_3$) in different percentages (1 and 2) % was added to 10 gm of crude oil sample. The mixing time varied from 5-20 minutes with 5 minutes intervals at a room temperature.

RESULTS AND DISCUSSION

The hydrogen sulphide content of fluids in the permeable formations of oil wells has an important impact on the economic value of the produced hydrocarbons and production operations. Typically, the sulfur content of crude oils is in the range 0.3-0.8 weight percent and the hydrogen sulphide content of natural gas is in the range 0.01-0.4 weight percent, although concentrations of hydrogen sulphide in natural gas of up to 30 weight percent. The correlation between the hydrogen sulphide concentrations of produced hydrocarbons at about 110 °C indicates that the hydrogen sulphide content of produced hydrocarbons increases exponentially with temperature, while below this temperature the hydrogen sulphide concentration is negligible [7] .When hydrogen sulphide enters the borehole during drilling, completion, or testing for hydrocarbons, it creates several very detrimental problems. These problems are encountered regardless of the source of the hydrogen sulphide. Hydrogen sulphide has created unsolved problems in the oil field.

Hydrogen sulphide mainly cause corrosion problems to drill strings, transport pipes, storage tanks etc. Hydrogen sulphide causes sulphide stress cracking, hydrogen embrittlement and pitting corrosion in oil and gas operations.
The corrosion of iron in the presence of hydrogen sulphide and water is dependent upon the dissociation of the hydrogen-sulphide molecule. Iron is oxidized to the ferrous form at the anode and hydrogen sulphide undergoes a two-step -dissociation at the cathode. Tung et al.[8] propose the following equilibrium reactions below.
At the anode:
$Fe \longrightarrow Fe^{2+} + 2e^-$
And at the cathode hydrogen is produced and either enters the steel or forms hydrogen gas and bubbles off.
If H_2S is present:
$2H^+ + 2e^- \longrightarrow H^o + H^o$
if H_2S is not Present:
$H^o + H^o \longrightarrow H_{2\,(gas)}$
Hydrogen enters the steel first by adsorption onto the water to steel interface and then by being absorbed into the steel as hydrogen. The amount of hydrogen entry depends on the corrosion rate of the steel surface and the concentration of anions such as HS^- that reduce the tendency to produce hydrogen gas (as shown in second equation above) and promotes the hydrogen (H^o) to enter the steel [9].
Hydrogen peroxide has also been suggested as an additive to mud at the flow line to convert hydrogen sulfide to free sulfur according to the reaction:
$H_2O_2 + H_2S \longrightarrow S^0 + H_2O$

The chemistry of the reaction is sound but the practical application is very limited as the hydrogen peroxide is too reactive with other components of the system [10]. Due to this, it will be impossible to have a satisfactory removal of hydrogen sulphide. Table 1 shows the results of crude oil treatment of H_2S removal using H_2O_2/NH_4OH mixture.

Table 1. Removal of H_2S by using of (H_2O_2/NH_4OH) mixture

Sample	Concentration of H2S (ppm)	
	Before treatment	After treatment
TT-04	22.523	9.170
TT-05	128.30	8.354
TT-06	19.52	4.673
TT-07	16.180	3.441
TT-08	30.420	18.645
TT-12	97.822	7.33
TT-13	32.56	7.492
TT-14	19.445	4.225
TT-15	154.873	5.776
Khormala	17.200	3.688
Kirkuk 1	275.881	19.742
Kirkuk 2	180.826	3.100
Kerosene	3.253	1.123

The absorption of H_2S into aqueous solutions of ferric chelates to ethylenediamine tetra acetic acid (EDTA) is related the oxidation of H_2S:
$H_2S_{(aq)} + 2Fe^{3+}L_n \rightarrow 2Fe^{2+}L_n + 2H^+ + S\downarrow$
Where L_n is an organic ligand, in this case ethylenediamine tetraacetic acid (EDTA, n = 4). Limtrakul et al. [39] used [Fe^{3+} EDTA] to remove H_2S. The removal reaction takes place and regeneration is performed.

Iron (II) ethylenediamine tetraacetic acid [Fe^{2+} EDTA] could be regenerated to [Fe^{3+} EDTA]. It was found that the conversion of H_2S decreased with increasing superficial gas velocity, which is due to the decrease in the liquid-phase circulation time. Desulfurization and regeneration can be carried out in the same vessel, which would reduce the capital costs, and the resulting density or pressure difference leads to a natural liquid circulation without any pump [11].

The ferric chelate ratio was taken as 1:2 and the initial concentration of ferric was taken 10000 ppm(1%). The results illustrated in table 2.

Table 2. Removal of H_2S by using of (Fe^{+3}/EDTA) mixture

Sample	Concentration of H_2S (ppm)	
	Before treatment	After treatment
TT-04	22.523	6.435
TT-05	128.30	6.415
TT-06	19.52	3.122
TT-07	16.180	2.456
TT-08	30.420	15.734
TT-12	97.822	6.113
TT-13	32.56	6.513
TT-14	19.445	3.245
TT-15	154.873	3.226
Khormala	17.200	3.688
Kirkuk 1	275.881	17.235
Kirkuk 2	180.826	2.870
Kerosene	3.253	1.125

Copper compounds, especially copper carbonate [10] have been used in the drilling operations to remove H_2S. Actually if added to water-base muds, the H_2S will precipitate out as insoluble copper sulphide according the following equation:

$$CuCO_3 + H_2S \longrightarrow CuS\downarrow + H_2O + CO_2\uparrow$$

Even though, tests have shown that its reaction with sulphide is very fast and efficient, it is impractical to use it as a pre-treatment during drilling operations as copper will plate out on any ferretic material and set up a corrosion cell[5]. The ability of $CaCO_3$ solution to remove H_2S has been studied. AS shown, there is a remarkable difference between the two $CaCO_3$ percentages (1and 2) % as shown in table 3 and figure 1.

Table 3. The percentage of $CaCO_3$ solution used to remove H_2S versus time (min.)

Time (min.)	Concentration of H_2S (ppm) by using of 1% $CaCO_3$ solution	Concentration of H_2S (ppm) by using of 2% $CaCO_3$ solution
5	30.6	46.5
10	21.4	33.7
15	15.3	30.1
20	13.4	28.9

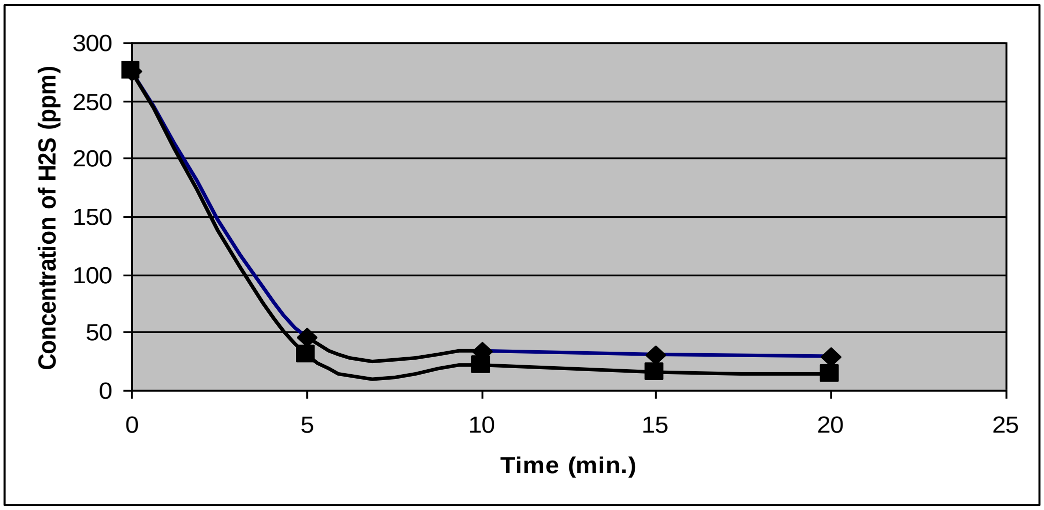

Figure 1: Effect of percentage of $CaCO_3$ on removing of H_2S from crude oil versus time
▪ 1% $CaCO_3$ ♦ 2% $CaCO_3$

Moreover, it can be concluded that copper compounds can be used to remove hydrogen sulphide where there will be no contact with any ferretic material, for instance if hydrogen sulphide is brought to the surface due to a large influx of the gas [4].

During the process of removing H_2S, there are two main kinetic steps. The first is controlled by oxidation/adsorption reaction while the second is controlled by the by-products which reduce the carbon site accessibility. In the first step, the amount of water introduced, sulfurization temperature, pressure of influent gas mixture, amount of catalysts used, and so forth can affect the H_2S removal efficiency. In terms of catalyst, the surface area, pore width, pore volume, and functional groups on catalysts have certain effect on H_2S adsorption/oxidation [12].

The selectivity for oxidation of H_2S to elemental sulfur is dependent on the textural, structural, and chemical characteristics of the carbon catalyst. Catalytically-active nitrogen species in the carbon postponed breakthrough time and increased capacity for H_2S uptake but inversely catalyzed the early formation of SO_2 and COS into the treated fuel gas stream. The significant micropore volume and narrow pore width of carbon aid the capture of elemental sulfur and SO_2 formed and the retaining of these oxidation products for a longer time. Furthermore, they found that activated carbon could convert COS to sulfur due to a large amount of highly reactive basic groups on the carbon surface [13].

APPLICATIONS

This work provides a simple method to eliminate the dangerous H_2S concentration in refineries, storages and fields.

CONCLUSIONS

The results show that the iron-chelated and copper carbonate with a percentage of 1% has high efficiency to remove H_2S from crude oil at room temperature.

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