Removal Hydrogen Sulfide (H_2S) from Crude Oil

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DOI:10.37648/ijiest.v12i01.005

[1]*Received: 04 January 2026; Accepted: 28 January 2026; Published: 10 February 2026*

ABSTRACT

Elimination of hydrogen sulfide gas H 2 S is the main aim of crude oil processing. This is done to decrease the amount of hydrogen sulfide that is present in large quantities in crude oil and reacts with water molecules to form sulfuric acid (H_2SO_4). It is a compound that leads to extreme and quick corrosion of metals particularly iron. It is important to perform the treatment process in order to prevent damage to the equipment since transportation of oil produced depends on equipment that is made of metal and the majority of the infrastructures required in the processing unit, including pipelines and pumps, is made of iron. Experiments carried out in the laboratory using crude oil of the Kirkuk oil field showed that the desulfurization process was effective in reducing the levels of hydrogen sulfide making the oil quality and safety improved. This study has highlighted the importance of additional developments in desulfurization processes in order to comply with strict environmental standards at the lowest possible operation cost. Research in the future must be aimed at enhancing the scalability and commercial feasibility of alternative desulfurization methods in areas with high sulfur content of the crude oil.

Keywords: *Crude Oil; Hydrogen Sulfide (H_2S); Hydro desulfurization (HDS); Biological Sweetening (BDS); Thermal desulfurization; Environmental Pollution.*

1. Introduction

Crude oil is a liquid fossil fuel that is naturally found and is formed mainly out of hydrocarbons (alkanes, cycloalkanes, and aromatic hydrocarbons) with some trace concentrations of sulfur, nitrogen, oxygen and trace metals [1]. Of these substances, sulfur especially in the form of sulfuric acid (H_2S) is very problematic during the extraction, transportation, and refining process. H_2S is commonly referred to as the silent killer because of its high toxicity and corrosive nature [2].

H_2S in crude oil causes massive corrosion of processing and transportation systems, especially pipelines, pumps, and tanks which are mostly made of iron and other prone metals. This type of corrosion will hasten the maintenance expenses and decrease the efficiency of operation [3]. Moreover, when using petroleum products that contain sulfur, a significant source of air pollution, and acid rain (SO_2), the burning process also contributes to the deterioration of the environment and increases the threat to the human population. [4].

Since the implication of H 2S is so serious, it is necessary to adopt efficient removal technologies when treating crude

[1] How to cite the article: Awad N.A., Dawood M.A, Ali O.M., Awad E.A.; February 2026; Removal Hydrogen Sulfide (H_2S) from Crude Oil; *International Journal of Inventions in Engineering and Science Technology;* Vol 12 Issue 1, 34-39, DOI: http://doi.org/10.37648/ijiest.v12i01.005

oil. Conventional methods such as Amine Gas Treating [5] and Hydrodesulphurization (HDS) [2,6] are the most popular methods, however, other techniques like Bio desulfurization (BDS) [7] and Oxidative Treatment [3,8] have been considered because they are less harmful to the environment and less costly. There are also modern advancements in terms of combining ultrasound-assisted procedures with activated carbon and hydrogen peroxide to increase the speed of sulphur removal [4].

This study investigates and compares different desulfurization technologies both chemical and physical in order to determine their suitability for removing H_2S from Iraqi crude oil specifically that extracted from the Kirkuk fields. Laboratory analysis is also conducted to measure the effectiveness of H_2S removal and its impact on crude oil quality.

2. Methodology

2.1 Experiment work

Used lubricating oils were collected from automotive workshops and subjected to preliminary dehydration to remove water and light hydrocarbons.

Determining the percentage of hydrogen sulfide (H_2S) in crude oil

Used tools

Funnel

- 50 ml
- 500 ml
- 250 ml

Chemicals used

- $Na_2B_4O_7$ Sodium borate (borax) at a concentration of 3%
- HgCl2 Mercury (II) Chloride [0.01 N]
- H2S04 Sulfuric acid at a concentration of 1.5%
- CCl4 Carbon Tetra Chloride (CTC)
- C13H12N4S Dithizone
- H2O Distilled water
- Demulsifies is a substance to separate an emulation into its component.

The method used is the Russian method, which is as follows

- Using a Separating Funnel, add 150ml of a 3% borax solution and 100ml of crude oil, then Close the valve.
- Shake the funnel to aid in the mixing process, then open the bottom valve tap once every (3 ~ 4) min to release gas. Place the funnel on a stand to allow for the separation of oil and borax solution, adding 3-4 drops of emulsification breaker to aid in the separation.
- After the oil is separated, measure out 10ml of the borax solution and place it into a conical flask, adding 5ml of diluted sulfuric acid (H2S04) to the flask. (The sulfuric acid volume should always be half the amount of Borax used in the previous step 3).

- Add 5ml of CTC Indicator (increase in volume will also yield brighter green coloration).
- Slowly add the solution containing activated HgCl2 until the mixture becomes brown and precipitate. Use activation HgCl2 with a concentration of [0.01N].
- Record the amount of activated HgCl2 that was used to change the color of the CTC reagent from green to brown.
- The following equation is applied to find the percentage of H_2S gas in the model:

$$H_2S = \frac{170 * V_{Hgcl_2} * \left[\frac{150}{X}\right]}{SP.Gr * 100}$$

2.2 Reaction Mechanism

H2S gas dissolves in the borax solution and when shaken, the borax solution absorbs all the gas present in the crude oil according to the following equation:

$Na_2S + HgCl_2 \rightarrow 2NaCl + HgS \downarrow$

Then after adding dilute **H2SO4** acid, i.e. making the medium acidic" and titration with hyaluronic chloride, a brown, black or orange precipitate is formed from which we can deduce the end point of the reaction (**End Point**) as in the following equation: -

$Na_2B_4O_7 + H_2S \rightarrow H_2B_4O_7 + Na_2S$

It is worth mentioning that the evidence used in the reaction is (CTC 500ml and dissolves 0.05g of dithizone).

What happens in the above equation is that **HgCl2** reacts with **Na2S** and dithizone, but it reacts with **Na2S** stronger and faster than its reaction with dithizone, so after the Na2S is enough of lily chloride, the last drop of your lily chloride will react with dithizone, and then a precipitate will form and the color will change from green to brown and from it we infer the **End Point**.

The reaction of **HgCl2** with dithizone dye can only take place with an acidic medium.

3. Results and Discussion

Table 1. Daily tests for H2S content in Crude Oil

Sample (Crude oil)	Density of Crude Oil (g/ml) Before treatment	Density of Crude Oil (g/ml) After treatment	H2S Ratio (PPM) Before treatment	H2S Ratio (PPM) After treatment
Day1	0.8426	0.8362	91	30
Day2	0.8448	0.8431	121	30
Day3	0.8369	0.8358	91	27

Day4	0.8521	0.8495	86	30
Day5	0.8492	0.8418	105	32
Day6	0.8379	0.8288	84	29
Day7	0.8304	0.8198	92	34
Day8	0.8425	0.8399	98	36
Day9	0.8381	0.8324	79	22
Day10	0.8457	0.8402	117	39
Day11	0.8356	0.8319	87	28
Day12	0.841	0.8383	92	29
Day13	0.8482	0.8459	103	30
Day14	0.8392	0.8348	91	31
Day15	0.8425	0.8397	106	32

Figure 1. Density of Crude Oil

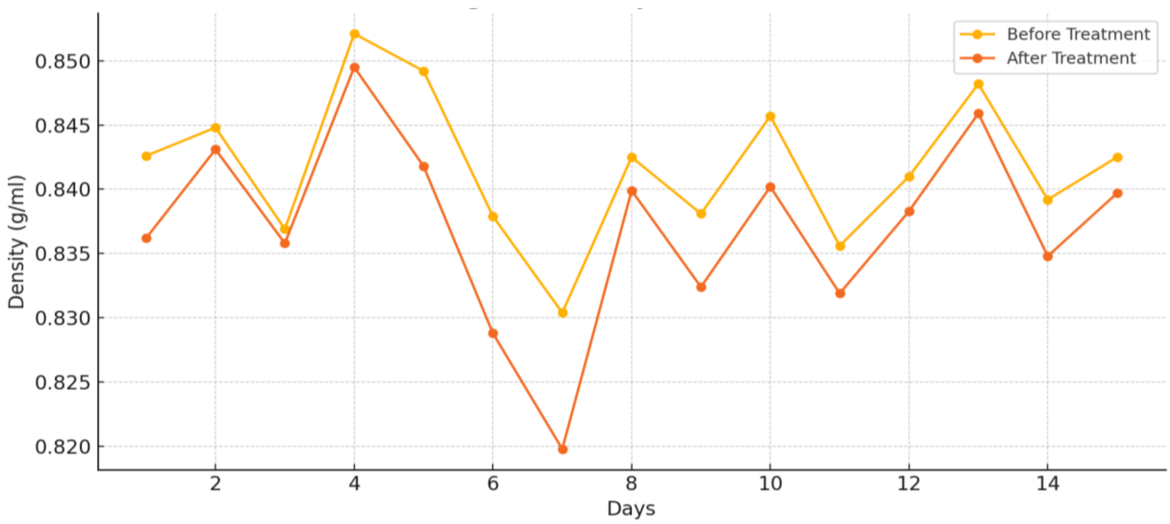
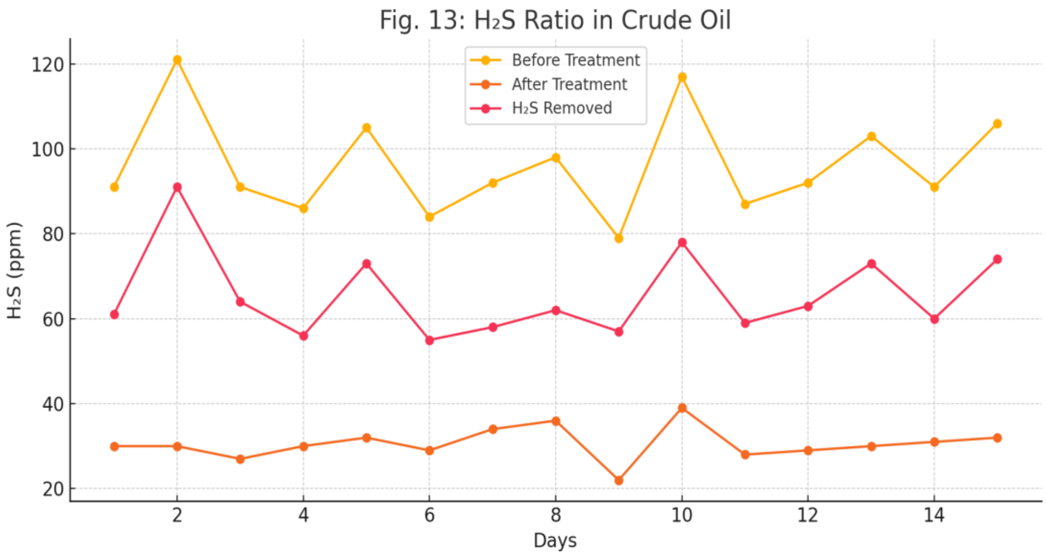


Figure 2. H2S Ratio in Crude Oil



The effectiveness of the chemical treatment of crude oil with the view to eliminate H 2 S is clearly shown in the results of the experiment. The figures 1 and 2 show the considerable changes in the oil density and the concentration of hydrogen sulfide in the form of the result of the treatment.

Figure 1 indicates that the crude oil density declined in each of the samples after treatment. This density difference is explained by the elution of light volatile gases especially H 2S and other dissolved gases hence a more stabilized and refined product. The treated crude exhibited densities ranging from 0.8288 to 0.8431 g/ml, compared to pre-treatment values that ranged between 0.8304 and 0.8521 g/ml.

Figure 2 shows that there was a significant decrease in the concentration of hydrogen sulfide gas (H_2S). The initial levels of H 2 S were 79 to 121 ppm and the levels of H 2 S were constantly under 22 to 39 ppm after the treatment. The highest removal was 92 ppm, which proves that the method used can have a high removal. Such decreases in (H_2S) levels improve the quality of oil and its market price, and decrease corrosion risk, environmental pollution, and safety risks. Additionally, the elimination of (H_2S) enhances the conformity to international requirements of sweet crude oil. The experiment confirms that the desulfurization process taken is sound enough to be put into practice particularly where crude oil of high sulfur content like Kirkuk is involved. Nevertheless, issues like chemical and/or operational condition control and cost are to be taken into consideration in order to implement it at a commercial scale.

4. Conclusions

Having surveyed what was contained in this study, with the actual observations and field visits by experts in the processing units, we are left with the following conclusions:

- **Cold Desulfurization Processing**

According to the existing situation in the oil market, cold desulfurization processing is not a profitable process. This is attributed to the fact that it relies on sweet gas that is not only costly but is also limited. The small players are not able to supply the high demand in particular with the rising demand of sweet gas in the power plants. This pressure has increased tremendously with the current trend of the major industrialized countries abandoning the nuclear fuel stations which have mainly been caused by the environmental and social hazards that they cause as seen in the Chernobyl disaster that not only polluted extensive regions but also consumed a tremendous amount of resources to clean up.

This has brought an advantage to the gas producing countries. The moderate oil producers such as Qatar and Algeria have become leading market players in the international gas market second only to Russia. It is necessary to mention that cold desulfurization was first developed in the early 1970s, because of the existence of gas reservoirs that accompany crude oil Production.

- **Hot Processing**

Hot processing is not so sensitive concerning the availability of sweet gas since this unit can use sour gas produced in the very processing tower. Hence, it does not shut down as a result of the unavailability of fuel gas. Also, in colder nations, certain units do not have any electric motors and rely on steam turbines. These turbines use steam constantly produced by boilers that are important in the safety of equipment, suppression of fire, and gas leaks containment.

Since crude oil is very viscous and therefore sticks to surfaces, steam would be the best medium of cleaning and removal. Hot processing is the most salient and effective of crude oil treatment that assures that byproducts that were not regarded as wealthy in the past such as sweet and sour gas now have more economic value than oil itself.

Experimental studies at the laboratory level performed on the crude oil of the Kirkuk oil field showed that desulfurization process was effective in reducing the level of hydrogen sulfide that improves the quality and safety of oil. The study highlights the fact that more improvements in desulfurization processes are necessary to ensure that all the regulations are met concerning the environment without causing much on cost of operation. Future research must be directed on enhancing scalability and commercial feasibility of alternative desulfurization methods especially in areas that have large reserves of crude oil containing high levels of Sulphur.

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