Investigation of Using Various Quantities of Steelmaking Waste for Scavenging Hydrogen Sulfide in Drilling Fluids

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1. Introduction

The presence of hydrogen sulfide (H₂S) gas is a frequent problem encountered when drilling subsurface hydrocarbon formations. This gas is naturally found in oil and gas reservoirs and is formed either by geological or microbiological processes [1–4]. H₂S invades the drilling system through either invading formations containing H₂S-contaminated fluids, the metabolism of sulfate-reducing bacteria that survive in anaerobic conditions, or the thermal degradation of sulfur-containing drilling fluid additives [5–8]. H₂S gas is the most reduced form of sulfur, having a rotten-egg-like odor that can be recognized by smell at low concentration levels as 0.5 ppm; however, at high H₂S concentrations, the human ability to smell this lethal gas is lost. H₂S is denser than air with a specific gravity of 1.2 and is extremely corrosive, toxic, flammable, and reactive [9].

The transfer of this toxic gas to the surface poses a serious threat to personnel health and safety, with varying consequences depending on the duration and intensity of exposure.
The agencies, such as the National Institute for Occupational Safety and Health (NIOSH), define standard regulations and guidelines for H₂S exposure limits, which are updated on a regular basis. NIOSH, for instance, specifies a 10-minute exposure limit of 10 ppm, and a concentration of 100 ppm is considered an emergency life-threatening level. [8–12]

The interaction of H₂S gas with metallic components of equipment during drilling operations may cause brittle failure, sour, or pitting corrosion. Metal brittle failure is caused by hydrogen embrittlement and stress cracking, occurring from H₂S reaction with steel in equipment [8, 13–15]. Increasing the acidity of the contained fluids and generating corrosive iron sulfide result in the sour corrosion of equipment [3, 14, 16–21]. The iron sulfide scale that sticks to steel surfaces causes pitting corrosion, which reduces equipment life [22, 23]. When H₂S is introduced into the drilling fluid, it changes the viscosity, fluid loss, and density of the mud, causing a well kick problem as well as a drop in pH that makes the mud more corrosive to metallic equipment [3, 19, 24, 25]. Also, during an H₂S-containing kick, the H₂S remains in liquid form (because H₂S can liquefy at pressures as low as 350–400 psi) until it reaches the surface, where it changes to gaseous form with a rapid and massive volume increase, posing a difficult well control situation [8].

As mentioned above, H₂S is encountered during the drilling operations in significant amounts, posing serious safety challenges and equipment damage. As a result, the safe and immediate tackling of any released H₂S during the drilling operations is essential [26, 27]. A range of specialized additives have been used to selectively react with H₂S and effectively scavenge it without forming any undesired byproducts or deteriorating the drilling fluid properties. Since H₂S reacts with strong oxidizers and metals, oxidizers such as hydrogen peroxide and potassium permanganate were used as H₂S scavengers. Hydrogen peroxide is a nonselective reactant that causes an uncontrollable scavenging process, making it inappropriate for use in drilling fluid [3, 19, 28, 29]. Potassium permanganate has a better mud rheological effect, but it is ineffective with heavy mud weight [30–34].

Metal-based compounds are particularly appealing among other H₂S scavengers due to their low cost, efficacy, and safety. These compounds react with H₂S to produce insoluble metal sulfides, which are thermally stable and do not reproduce H₂S during drilling conditions, making them safe H₂S scavengers. Copper, zinc, and iron-containing compounds make up the majority of metal-based H₂S scavengers utilized in drilling operations [19, 24, 29, 35–37]. Table 1 describes the common metal-based scavengers used so far in drilling operations.

Although various scavengers have been used in the petroleum industry, each has its limitations, including reaction kinetics, scavenging methods, conditions, cost, environmental concerns, and effects on mud properties. As a result, research is still ongoing in order to obtain an optimal and feasible scavenger that can remove H₂S completely and quickly without forming any deleterious byproducts.

Massive amounts of waste are produced during the steelmaking process, with waste production projected to reach 2–4 tons per ton of steel generated [59–62]. The produced wastes were previously used in drill cutting disposal [63, 64], asphalt concrete binder [65–67], cement production [68–71], and heavy metal adsorption [72–74]. Steelmaking waste has recently been introduced as a viscosifier additive in drilling fluids by combining it in various ratios with bentonite [61]. Steelmaking waste is abundant and available as a byproduct from many steel factories. Waste management, on the other hand, poses significant economic and environmental challenges.

The purpose of this study is to incorporate steelmaking waste into water-based drilling fluids and investigate the effect of the steelmaking waste level in the drilling mud on H₂S scavenging capabilities and mud properties. The novelty of this study stems from utilizing the steelmaking waste as an H₂S scavenger for efficient and safe drilling operations, converting waste from a cost and environmental burden to a beneficial product.

2. Materials and Experiments

2.1. Materials. Water-based drilling fluid samples were prepared in laboratory using an actual field mud formula. Using fresh water as the base fluid, 350 cm³ of drilling fluid samples were prepared. The prepared mud formulations were presented in Table 2. A small amount of antifoam agent was added. To acquire the desired mud viscosity, xanthan polymer was used, while the starch was employed primarily to limit fluid losses and to aid in viscosity build-up. To prevent the formation shale from swelling, the sodium chloride was utilized. Caustic soda was used to maintain the desired alkaline pH value. Then, fine and medium calcium carbonate particles were used as bridging agents and densifiers. The prepared drilling fluid samples had a density of 9.8 ppg. The drilling fluid with the aforementioned compositions served as the base mud for this study. Drilling fluid services companies provided commercialized H₂S scavengers (i.e., triazine- and iron gluconate-based scavengers), which were utilized as benchmarks for comparison. To investigate the effect of incorporating steelmaking waste, different amounts (1, 2, and 3 g) were added to the base mud. The names of the drilling fluid samples used in this study were abbreviated as follows:

BASE: base mud without scavenger; TRZM: triazine-based mud; IGM: iron gluconate-based mud; SWM1: 1 g-steelmaking waste-containing mud; SWM2: 2 g-steelmaking waste-containing mud; and SWM3: 3 g-steelmaking waste-containing mud.

The triazine-base scavenger is obtained as a liquid, has a density of 1.073 g/cm³, a pH of 10.5, and an average concentration of 60 vol.%. The iron gluconate-base scavenger is a water-soluble powder with a density of 0.7 g/cm³, a pH of 4.5, and an average concentration of 60 vol.%. The mineralogy, chemical composition, and particle size distribution of steelmaking waste were determined using the X-ray Diffraction (XRD), X-ray fluorescence (XRF), and particle size distribution analyzer. Steelmaking waste characterization revealed that it contains 26.5% zincite, 14.3% orthopyroxene, 8.8% lawrencite, 3% siderite, and other minerals. The key metal oxides content was identified as 43.3% ZnO, 33.8% Na₂O, and 2.9% Fe₂O₃. The average particle size distribution (D₅₀) of the waste was found to be 11.77 μm.
2.2. Experiments. The effect of incorporating different quantities of the steelmaking waste on H₂S scavenging capacity, rheology, alkalinity, and filtering characteristics of the mud was studied and compared to those of the base mud and commercialized scavengers. The H₂S scavenging experiments were carried out at ambient conditions. In each experiment, a volume of 10 cm³ from each mud sample was placed in a burette with a gas intake from a cylinder containing 100 ppm of H₂S, while the burette outlet was attached to a MultiRAE gas detector having a minimum detection limit of 0.1 ppm. At the gas entry, a flowmeter with a flow controller was employed to control the gas flowrate at 150 cm³/min. The H₂S concentration in the outlet gas was continually recorded until it reached saturation (i.e., 100 ppm, which is equal to the inlet gas concentration). The test setup is depicted in Figure 1.

When the scavenger is entirely consumed (i.e., saturation is reached), the following equation [30] can be used to estimate the scavenging capacity (in mg H₂S/l mud) of each mud sample.

\[
\text{Saturation capacity \( \frac{\text{mg}}{\text{l}} \) } = \frac{Q \times \rho \times 10^{-6}}{V} \times \int_{0}^{t_s} (C_{\text{in}} - C_{\text{out}}) \, dt,
\]

where \( Q \) is the inlet gas flowrate (150 cm³/min), \( \rho \) is the H₂S density (1.391 mg/cm³), \( t_s \) represents the saturation time in

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**Table 1: Various metal-based scavengers used in drilling operations.**

<table>
<thead>
<tr>
<th>Chemical compound</th>
<th>Chemical reaction</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper carbonate</td>
<td>( \text{CuCO}_3 + \text{H}_2\text{S} \rightarrow \text{CuS}↓ + \text{H}_2\text{O} + \text{CO}_2↑ )</td>
<td>It has a quick and efficient reaction, but the copper electrodeposition causes corrosion on the metal surface [28, 29, 38–40].</td>
</tr>
<tr>
<td>Copper nitrate</td>
<td>( \text{Cu(NO}_3\text{)}_2 + \text{H}_2\text{S} \rightarrow \text{CuS}↓ + 2\text{HNO}_3 )</td>
<td>It improves the mud rheology and filtration performance with a lower corrosion affinity [27, 41].</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>( \text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS}↓ + \text{H}_2\text{O} )</td>
<td>They are amphoteric in nature, with predictable reactivity but larger concentrations may deteriorate mud rheology and produce flocculation and fluid loss, particularly at high pH levels [6, 37, 38, 40, 42–48].</td>
</tr>
<tr>
<td>Iron oxide</td>
<td>( \text{Fe}_3\text{O}_4 + 6\text{H}_2\text{S} \rightarrow 3\text{FeS}_2↓ + 4\text{H}_2\text{O} + \text{H}_2 )</td>
<td>They work better at low pH levels and help to densify the drilling fluid [24, 40, 49–55].</td>
</tr>
<tr>
<td>Iron gluconate</td>
<td>( \text{Fe(C}<em>6\text{H}</em>{12}\text{O}_7\text{)}_2 + \text{H}_2\text{S} \rightarrow \text{FeS}↓ + 2\text{C}<em>6\text{H}</em>{12}\text{O}_7 + \text{H}_2\text{O} )</td>
<td>It is an ecofriendly compound with a quick reaction; however, it significantly lowers the pH and is ineffective with heavy mud weight [56–58].</td>
</tr>
</tbody>
</table>

**Table 2: The prepared drilling fluid formulation.**

<table>
<thead>
<tr>
<th>Additive</th>
<th>BASE</th>
<th>TRZM</th>
<th>IGM</th>
<th>SWM1</th>
<th>SWM2</th>
<th>SWM3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh water</td>
<td>316 cm³</td>
<td>316 cm³</td>
<td>316 cm³</td>
<td>316 cm³</td>
<td>316 cm³</td>
<td>316 cm³</td>
</tr>
<tr>
<td>Defoamer</td>
<td>0.08 cm³</td>
<td>0.08 cm³</td>
<td>0.08 cm³</td>
<td>0.08 cm³</td>
<td>0.08 cm³</td>
<td>0.08 cm³</td>
</tr>
<tr>
<td>Xanthan</td>
<td>1 g</td>
<td>1 g</td>
<td>1 g</td>
<td>1 g</td>
<td>1 g</td>
<td>1 g</td>
</tr>
<tr>
<td>Starch</td>
<td>6 g</td>
<td>6 g</td>
<td>6 g</td>
<td>6 g</td>
<td>6 g</td>
<td>6 g</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>34 g</td>
<td>34 g</td>
<td>34 g</td>
<td>34 g</td>
<td>34 g</td>
<td>34 g</td>
</tr>
<tr>
<td>Caustic soda</td>
<td>0.25 g</td>
<td>0.25 g</td>
<td>0.25 g</td>
<td>0.25 g</td>
<td>0.25 g</td>
<td>0.25 g</td>
</tr>
<tr>
<td>Calcium carbonate (fine)</td>
<td>24 g</td>
<td>24 g</td>
<td>24 g</td>
<td>24 g</td>
<td>24 g</td>
<td>24 g</td>
</tr>
<tr>
<td>Calcium carbonate (medium)</td>
<td>36 g</td>
<td>36 g</td>
<td>36 g</td>
<td>36 g</td>
<td>36 g</td>
<td>36 g</td>
</tr>
<tr>
<td>Triazine-based scavenger</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Iron gluconate-based scavenger</td>
<td>—</td>
<td>—</td>
<td>1 g</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Steelmaking waste</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1 g</td>
<td>2 g</td>
<td>3 g</td>
</tr>
</tbody>
</table>

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*Figure 1: Setup for the H₂S scavenging experiment.*
minutes (when the H$_2$S concentration in the outlet gas stream reaches 100 ppm), $V$ is the used volume of drilling fluid (10 cm$^3$), $C_{in}$ is the H$_2$S concentration in the burette’s inlet (100 ppm), and $C_{out}$ represents the time-dependent concentration in the outlet gas stream (ppm).

It is important for drilling fluids to have capable rheological performance, which was assessed by evaluating the apparent viscosity (AV), plastic viscosity (PV), yield point (YP), and gel strengths adhering to the American Petroleum Institute standard procedures at 120°F [75]. Additionally, the pH values of the prepared mud samples were determined at room temperature.

A filtration test was carried out at 250°F and a differential pressure up to 300 psi in order to assess the filtering performance and to analyze the obtained filter cake. The filtration media used in the test was a 40μm saturated porous ceramic disc. The filtrated liquid was collected for 30 minutes, and its volume was determined. The thickness of the filter-cake was then measured.

3. Results and Discussion

3.1. H$_2$S Scavenging Test. Table 3 summarizes the findings of the H$_2$S scavenging experiments, and Figure 2 shows the timely recorded concentrations of the stepped out H$_2$S gas after contacting the mud samples.

For BASE, H$_2$S began to breakthrough after 20 minutes and reached saturation concentration after 42 minutes, yielding a scavenging capacity of 84.3 mg H$_2$S/l of mud. Using TRZM, the H$_2$S breakthrough and saturation periods were pushed up to 42 and 146 minutes, respectively, with a 179% improved scavenging capacity of 235.5 mg/l. IGM, on the other hand, showed H$_2$S breakthrough and saturation times of 29.5 and 163 minutes, respectively, resulting in a 131% increase in H$_2$S scavenging capacity to 194.8 mg/l. Adding different amounts of steelmaking waste to the base drilling fluid improved the H$_2$S scavenging capacity and delayed the breakthrough and saturation periods to varying extents.

The addition of 1 g steelmaking waste (SWM1) raised the scavenging capacity to 172.8 mg/l, which is the double of that obtained using the base mud, with extended breakthrough and saturation periods of 61 and 116 minutes, respectively. When the waste content was increased, the scavenging performance was preferably improved, as in SWM2, the scavenging capability was tripled with 168- and 216-minute breakthrough and saturation durations, while it reached up to a 363-minute saturation period and 508.3 mg/l capacity with SWM3, showing a 503% improvement over the base mud.

Because both zinc and iron compounds are utilized as H$_2$S scavengers in drilling operations with proven efficacy, the extraordinary scavenging performance of the steelmaking waste might be attributed to the presence of zinc and iron components in the steelmaking waste as revealed by the XRD and XRF test analyses.

According to the findings of the H$_2$S scavenging experiments, increasing the steelmaking waste content in the water-based drilling fluid significantly boosted the mud ability to adsorb the associated H$_2$S by driving the scavenging capacity to substantially higher levels. The effects of adding 1, 2, and 3 g of steelmaking waste on essential mud characteristics (i.e., rheology, alkalinity, and filtration) were studied and discussed hereunder.

3.2. Rheology Measurements. The rheological properties including the apparent viscosity (AV), plastic viscosity (PV), and yield point (YP) were calculated using the Bingham plastic rheology model. In which the AV is one-half of the dial reading at 600 rpm, while the PV, which refers to the internal resistance to flow when force is applied, was calculated from the difference between the dial readings at 600 and 300 rpm. The YP is a measurement under flowing conditions of the electrochemical forces in the drilling mud; it was calculated by subtracting the determined PV from the dial reading at 300 rpm.

The rheology measurements (Figure 3) revealed that the base mud had an AV value of 18.7 cP, a PV of 8.8 cP, and a

<table>
<thead>
<tr>
<th>Mud sample</th>
<th>Breakthrough time (min)</th>
<th>Saturation time (min)</th>
<th>Saturation capacity (mg H$_2$S/l mud)</th>
<th>Scavenging improvement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASE</td>
<td>20</td>
<td>46.5</td>
<td>84.3</td>
<td>—</td>
</tr>
<tr>
<td>TRZM</td>
<td>42</td>
<td>146</td>
<td>235.5</td>
<td>179</td>
</tr>
<tr>
<td>IGM</td>
<td>29.5</td>
<td>163</td>
<td>194.8</td>
<td>131</td>
</tr>
<tr>
<td>SWM1</td>
<td>61</td>
<td>116</td>
<td>172.8</td>
<td>105</td>
</tr>
<tr>
<td>SWM2</td>
<td>168</td>
<td>216</td>
<td>421</td>
<td>399</td>
</tr>
<tr>
<td>SWM3</td>
<td>213.5</td>
<td>363</td>
<td>508.3</td>
<td>503</td>
</tr>
</tbody>
</table>

FIGURE 2: The H$_2$S concentration in the outlet gas stream as a function of time.
YP of 14.4 lb/100 ft². The TRZM exhibited higher AV, PV, and YP values of 21 cP, 10 cP, and 17.9 lb/100 ft², respectively. While the IGM had comparable AV and PV values to the TRZM, it had a higher YP of 19.2 lb/100 ft². On the other hand, SWM1 raised the YP to 15.4 lb/100 ft² with a minor PV increase to 9 cP and no effect on AV. When the steelmaking waste content was doubled, the AV began to rise, as the SWM2 yielded 19.2 cP-AV with a PV of 9.4 cP and a higher YP value of 15.7 lb/100 ft². Additionally, the SWM3 increased the AV and PV to 19.7 and 9.8 cP, respectively, with the same YP value as the SWM2. As displayed in Figure 4, there were no significant variations in the 10-second/10-minute gel strengths for the examined mud samples. Nevertheless, the slight reduction in gel strength values caused by the addition of steelmaking waste could be contributed to reducing the equivalent circulation density.

The rheological properties of the water-based drilling fluids have practical prescribed ranges that are: the AV is recommended to be greater than 15 cP and, preferably, in the range of 20–35 cP for better fluid loss behavior [76, 77], and the PV is recommended not to exceed 25 cP [77, 78] to minimize friction and pressure losses, while high YP values, but not exceeding 50 lb/100 ft², are preferred [79] in order to improve the solids carrying capability. In light of the aforementioned ranges, both the TRZM and IGM muds meet the criteria. Also, increasing the steelmaking waste content aids in approaching the recommended AV value while increasing both the PV and YP. The PV increment is related to the increase in solids amount into the drilling mud [80–82]. The composition of steelmaking waste, which is similar to bentonite clay, justifies this elevation in rheological parameters [61].
YP/PV ratio that measures solids’ carrying capacity and hole cleaning performance [83], the BASE had a value of 1.64, which was improved to 1.72 by SWM1 and 1.66 by SWM2, but lowered by SWM3 to 1.64. All values, however, satisfy the requirement of being higher than 0.75 [12, 33, 61].

3.3. pH Measurements. The pH tests yielded pH values of 11.0, 11.1, and 7.9 for BASE, TRZM, and IGM, respectively (Figure 5). These pH values reveal a significant drop in the mud pH in the presence of iron gluconate and a slight increase in the presence of triazine. On the other hand, the addition of 1, 2, and 3 g steelmaking waste to the base mud reduced its pH to 10.4, 9.8, and 8.5, respectively. In general, the acceptable pH range of water-based drilling fluids is in the range 9.0–11.0; yet, maintaining a pH value greater than 10 is required when drilling H2S-bearing formations [84]. As a result, the pH of SWM1 passes the pH criterion, SWM2 is near to the threshold limit of 10, and SWM3 is less than this limit. However, increasing the amount of caustic soda or any pH controller can restore the pH to the accepted level [85].

3.4. Filtration Test. According to the filtration experiment, steelmaking waste exhibited superior filtration efficacy in terms of fluid loss, as SWM1 reduced the filtrated liquid volume by 32%, to 3.2 cm³, compared to 4.7 cm³ for the BASE (Figure 6). The improvement of mud rheology and the characteristics of steelmaking waste particles led to a faster plugging process with less filtrated volume and solids invasion, and therefore less formation damage. Similarly, SWM2 showed a 19% decrease in filtrated volume. However, increasing the amount of waste to 3 g increased the filtrated volume to 5.7 cm³. Because the thickness of the generated filter-cake is proportional to the solids content, increasing the steelmaking waste content raised the thickness, as the resulting thickness with SWM1, SWM2, and SWM3 was 3.3, 4.0, and 4.8 mm, respectively, as compared to 2.9 mm for the BASE. The TRZM, on the other hand, slightly reduced the filtration volume to 4.5 cm³ and had a filter-cake thickness of 3.5 mm, while the IGM increased the filtrated liquid to 5.7 cm³ and the filter-cake thickness to 3.9 mm. Practically, the amount of filtrated liquid in water-based drilling fluids should not exceed 15 cm³ [86]; therefore, all prepared mud samples meet the standards.

The management of steelmaking waste, which is produced in abundant quantities by many steel manufacturers, presents substantial economic and environmental issues. By utilizing these wastes as an H2S scavenger for efficient and safe drilling operations, they are shifted from an economic and ecological burden to a valuable product. This study revealed that increasing the quantity of steelmaking waste improved the H2S scavenging capacity of the drilling fluid. Adding 2 g of waste improved mud performance in terms of alkalinity, rheological, and filtration properties. Nevertheless, the waste content can be increased to 3 g to realize the outmost scavenging capacity with practically acceptable mud performance; however, an extra alkalinity controller is necessary to supplement the associated pH drop. Moreover, preparatory testing is essential for practical implementations to account for any changes in mud composition and test parameters.

4. Conclusions

Various amounts of steelmaking waste (0–3 g) were employed in this study to improve the H2S scavenging ability of water-based drilling fluid. The scavenging capacity and impacts on mud characteristics were evaluated and compared to those of the base, triazine-containing, and iron gluconate-containing muds), yielding the following findings:

(i) Increasing the amount of steelmaking waste greatly boosted the H2S scavenging capacity of the drilling fluid by 105, 399, and up to 503% with SWM1, SWM2, and SWM3, respectively

(ii) The rheological characteristics, including AV, PV, and YP, increased to varied extents with increasing the steelmaking waste content in the mud, with 2 g providing the best carrying capacity

(iii) The addition of steelmaking waste reduced mud pH to 10.4, 9.8, and 8.5 with SWM1, SWM2, and SWM3, respectively, compared to 11.0 for the base mud, noting that a 10 pH is recommended for drilling in sour environments and amounts of alkalinity controller could be added to restore the mud pH

(iv) Using 1 and 2 g of steelmaking waste helped to lower the filtrated volume, unlike the SWM3 that resulted in slightly more filtrated liquid. The filter-cake thickness, on the other hand, increased as solid content increased

(v) When compared to commercial scavengers, higher quantities of inexpensive steelmaking waste could be employed instead, yielding significantly improved H2S scavenging capacity and efficient mud performance, while meeting the practical recommended properties

Data Availability

All the data are included in the submitted manuscript.
Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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