H₂S Scavenging Capacity and Rheological Properties of Water-Based Drilling Muds

Sagheer A. Onaizi,* Monaf Abdalmajid Gawish, Mobeen Murtaza, Ibrahim Gomaa, Zeeshan Tariq, and Mohamed Mahmoud

1. INTRODUCTION

Drilling muds are an essential part of any drilling process, and they serve many important functions including cooling and lubrication of the rotating bit and downhole equipment, transport of drill cuttings to the well surface, and exerting pressure on the surrounding formation to prevent an undesirable influx of fluids or caving in of the borehole.1−5 To achieve such objectives, drilling muds must possess special rheological properties, which are frequently achieved through the use of different mud additives.6−12 For instance, for effective transport of drill cuttings, the drilling mud must display a shear thinning behavior.13,14 Additionally, when circulation is stopped, the fluid should possess a sufficient viscosity to attain a gel-like structure that maintains the solids suspended and prevents their return to the bit area.4,15 This unique rheological behavior can be obtained by a proper mud formulation using different additives; each one serves a certain purpose.16−19

A common scenario often encountered while drilling subterranean formations is the infiltration of drilling muds by pockets of hydrogen sulfide (H₂S). H₂S is a toxic, flammable,
and colorless acidic gas with a rotten egg smell at low concentrations.\textsuperscript{20} It is a heavy gas with a specific gravity of 1.18 compared to air. This makes it sink to the lowest possible level and escape to the confined spaces.\textsuperscript{21−23} H$_2$S can form explosive mixtures with air in a wide concentration range of 4.3−45% with an ignition temperature of 260 °C.\textsuperscript{24} It has been reported that the number of sour wells is increasing worldwide, especially for old oil fields, where the existence of H$_2$S was not previously witnessed.\textsuperscript{25} H$_2$S is considered to be one of the major health and safety issues in the oil and gas industry, not only for being dangerous to the working personnel but also for damaging metallic structures. It is a very lethal gas and extremely toxic to the working crew at the rig site. If not timely controlled, it can result in injuries, fatalities, fire, and explosion. It causes corrosion problems to all the upstream, midstream, and downstream steel structures. Pitting corrosion, hydrogen embrittlement, and sulfide stress cracking are all potential failure causes for drilling assembly, pipelines, processing units, and storage tanks when the handled streams contain H$_2$S. For example, cracking failure of high-strength steels can occur within minutes in the presence of only 50 ppm H$_2$S.\textsuperscript{26,27} Moreover, the presence of as low as 0.1 ppm H$_2$S in the handled streams can significantly reduce the equipment lifetime.\textsuperscript{28} Accordingly, the presence of H$_2$S carries significant safety, health, and economic penalties, requiring the effective removal of this lethal gas during drilling operations. This objective might be achieved through the addition of appropriate H$_2$S scavengers to drilling muds.

H$_2$S scavengers can be either in a solid or liquid form. The solid form can be soluble or insoluble in aqueous solutions (i.e., water-based drilling muds). Different types of H$_2$S scavengers exist in the gas and oil industry nowadays. These scavengers are mostly based on triazines, ethers, aldehydes, amines, and metal-based compounds.\textsuperscript{29−33} Among these H$_2$S scavengers, metal-based compounds are very attractive because of their affordable cost, effectiveness, and safety factors. Metal-based scavengers react with the dissolved H$_2$S in the drilling mud, forming insoluble metal sulfides. The metal sulfides are thermally stable and will not regenerate H$_2$S under drilling operating conditions, thus providing a safe way for sequestering H$_2$S.\textsuperscript{2,28,34−37} Most of the commonly used metal-based H$_2$S scavengers in the oil and gas industry are based on copper-, zinc-, or iron-containing compounds. Copper compounds such as copper carbonate (CuCO$_3$)\textsuperscript{38−40} and basic copper carbonate (Cu$_2$(OH)$_2$CO$_3$)\textsuperscript{30,36} were among the earliest metallic scavengers to be successfully applied in drilling processes. Reactions of copper compounds with H$_2$S are typically fast and efficient and lead to the formation of solid CuS or Cu$_2$S, both of which are highly stable and insoluble in acidic or basic media.\textsuperscript{36,41} However, copper compounds suffer from one inherent drawback, that is, their tendency to accelerate equipment corrosion by spontaneous copper plating.\textsuperscript{2,29,30,32,38−40} This type of corrosion occurs because copper, being a more noble metal than iron, tends to deposit on steel surfaces and creates a local corrosion cell that promotes the corrosion of iron on the surface. Consequently, copper-based scavengers are no longer used in the industry and have been largely replaced by scavengers based on zinc or iron compounds, which do not suffer from corrosion tendencies.

Currently, zinc compounds are by far the most widely used scavengers. They emerged in the 1970s as a substitute to the problematic copper-based scavengers that offered a similar degree of protection against sulfide species without the additional corrosion damage.\textsuperscript{10,41,42} Zinc compounds are amphoteric; that is, they can act as acids or bases depending on the surrounding conditions. Consequently, many solid zinc-based scavengers would dissolve at highly basic conditions (water-based drilling muds are basic) to yield free zinc ions capable of scavenging H$_2$S.\textsuperscript{29,31,39,43} However, at pH greater than ~ 11, zincate ion Zn(OH)$_4^{2−}$ could form. While the zincate ion might still be effective in scavenging H$_2$S, excess amounts of Zn(OH)$_2^{−}$ could negatively interfere with the mud rheological properties, which might be detrimental to the drilling mud performance.\textsuperscript{32,33,44,45}

An alternative option to copper and zinc compounds are iron compounds. However, unlike zinc and copper, where metal sulfides form through a simple precipitation reaction, the interaction between iron compounds and H$_2$S is complex and might involve multiple steps and reaction products.\textsuperscript{41,46} Generally, six iron sulfide minerals could potentially form as a result of the scavenging reactions (see ref 47, for example); the reaction rate and type of product(s) formed are largely dependent on the ambient conditions including the oxidation state of iron in the parent oxide (Fe$^{2+}$ or Fe$^{3+}$), temperature, pH, and reaction time, among others.\textsuperscript{41} Currently, the only commercially available iron-based scavenger is the specially prepared, porous magnetite (Fe$_3$O$_4$), which is marketed under the trade name “Ironite Sponge.”\textsuperscript{30,31,39,48} This is highly insoluble iron oxide that reacts with H$_2$S to form the very stable pyrite.\textsuperscript{27,40,49,50} However, being an insoluble solid, the reaction between magnetite and H$_2$S is mostly limited to the external particle surface, which quickly becomes coated by a layer of reaction products that inhibit further reaction inside the particle, leading to an incomplete conversion (i.e., utilization) of magnetite.\textsuperscript{2} Additionally, because magnetite reacts primarily with H$_2$S, which is only dominant under acidic conditions (HS$^−$ and S$^{2−}$ species are dominant under alkaline conditions),\textsuperscript{41} the alkaline conditions encountered in drilling muds would result in a negative effect on the reaction kinetics.\textsuperscript{35,37,46}

Another approach for removing H$_2$S (or its dissociated forms) from drilling muds is through the use of oxidizing agents. Such chemicals, when applied in appropriate dosages, can oxidize H$_2$S to harmless sulfur compounds such as elemental sulfur S$^0$ or sulfate ions SO$_4^{2−}$.\textsuperscript{2,28,51} Examples of oxidizing agents include potassium permanganate (KMnO$_4$), hydrogen peroxide (H$_2$O$_2$), potassium thiosulfate (K$_2$S$_2$O$_3$), and calcium hypochlorite Ca(ClO)$_2$.\textsuperscript{28,29,38,51} Oxidizing agents typically react quickly and irreversibly with soluble sulfides and, owing to their high solubility, are easily dispersed in the drilling mud formulations.\textsuperscript{28,29}

In this paper, we aim to study the H$_2$S scavenging using water-based drilling mud formulations containing ZnO, copper nitrate, and KMnO$_4$. In addition to revealing and comparing the H$_2$S scavenging performances of these scavengers, their effects on the rheological and fluid loss properties of the base drilling mud will also be investigated. To the best of our knowledge, most of the published studies in this regard either tackled the rheological properties of drilling muds or the removal of H$_2$S using solid-phase adsorbents. Thus, this study is a novel contribution to the knowledge in this field, filling some of the missing gaps by studying the H$_2$S scavenging performance of commercially available materials and their impacts on the rheological properties of the base drilling mud. The only comparable studies, to the best of our knowledge, are
those recently published by Elkatatny and co-workers\textsuperscript{44,52} and Ghayedi and Khosravi.\textsuperscript{1} However, Elkatatny et al.\textsuperscript{44,52} focused only on the copper nitrate-containing drilling mud, while Ghayedi and Khosravi\textsuperscript{1} utilized ZnO–graphene oxide composites to scavenge a small amount of H$_2$S (\textasciitilde 800 ppm H$_2$S) generated locally using sodium sulfide as the H$_2$S precursor, unlike the case where H$_2$S is supplied from an inexhaustible source as we implemented in this study.

### 2. MATERIALS AND METHODS

The methodology adopted in conducting this study is depicted in Figure 1.

#### 2.1. Compositions of Drilling Muds

The water-based drilling mud (i.e., the base drilling mud) was prepared by adding various additives such as the defoamer, XC polymer, potassium hydroxide (KOH), starch, potassium chloride (KCl), and calcium carbonate (CaCO$_3$) to distilled water. The compositions (i.e., formulations) of the drilling muds (i.e., the base and the H$_2$S scavenger-containing drilling muds) used in this study are listed in Table 1. The drilling fluid additives were supplied by an oil field service company in Saudi Arabia. The concentration of additives was taken in weight percent (wt %). The ingredients of these drilling muds were thoroughly mixed in distilled water using a high-speed Hamilton beach mixer. The mixing sequence and time of mixing for each additive are given in Table 1. All the additives were mixed sequentially at a mixing rate of 21,000 rpm. First, the defoamer was added to water, followed by the XC polymer, KOH, starch, KCl, and CaCO$_3$. At the end, the H$_2$S scavenger (ZnO, Cu(NO$_3$)$_2$·3H$_2$O, or KMnO$_4$) was mixed in the base drilling mud for 10 min. Each additive was mixed at high shear for a particular time mentioned in Table 1. The pH of all drilling muds was maintained at 9–9.2 using KOH. The levels of the three utilized H$_2$S scavengers (ZnO, Cu(NO$_3$)$_2$·3H$_2$O, and KMnO$_4$) were kept the same (i.e., 0.1 wt %). ZnO (99.9%), Cu(NO$_3$)$_2$·3H$_2$O (99%), and KMnO$_4$ (\textgeq 99.0%) were purchased from Sigma-Aldrich. The average particle size of ZnO is 6.58 $\mu$m.

#### 2.2. H$_2$S Scavenging

In each H$_2$S scavenging experiment, 10 mL of one of the drilling muds is placed in a column. One end (gas inlet) of the column is connected to a gas cylinder containing 104 ppmv (parts per million by volume) H$_2$S, 1046 ppmv CO$_2$, and balanced N$_2$. The other end (gas outlet) of the column is connected to an H$_2$S detector with a minimum detection limit of 0.1 ppm. A demister is installed at the top of the column to capture moisture. A valve and a mass flowmeter are installed at the gas inlet (before the column) to control the gas flowrate. Additionally, a pressure gauge is installed at the gas inlet in order to measure the inlet pressure of the gas feed. At the beginning of each experiment, the valve is opened, and the gas flow rate is controlled at 100 mL/min. The sour gas is bubbled into the drilling mud in the column, and the H$_2$S concentration in the outlet gas stream is monitored and recorded continuously until saturation is established (i.e., H$_2$S...
concentration in the outlet gas stream reaches $\sim 104$ ppm). All \( \text{H}_2\text{S} \) scavenging experiments were conducted at room temperature ($\sim 25 \degree\text{C}$) and atmospheric pressure. The amount (in mg) of \( \text{H}_2\text{S} \) scavenged per gram of the utilized scavenger up to the breakthrough time is calculated using the following equation

\[
\text{H}_2\text{S} \text{ breakthrough capacity (mg/g)} = \frac{Q \cdot \rho_{\text{H}_2\text{S}} \int_0^{t_b} (C_{\text{in}} - C_{\text{out}}) \, dt}{m \cdot f}
\]  

(1)

Where \( Q \) is the inlet gas flow rate (mL/min), \( \rho_{\text{H}_2\text{S}} \) is \( \text{H}_2\text{S} \) density (equivalent to 1.391 mg/mL at room temperature and atmospheric pressure), \( t_b \) (in min) is the breakthrough time (i.e., when \( \text{H}_2\text{S} \) concentration in the outlet gas reaches 0.5 ppmv), \( m \) is the scavenger mass in the drilling mud (g), \( f \) is a conversion factor ($=10^6$), and \( C_{\text{in}} \) and \( C_{\text{out}} \) are the concentrations (ppmv) of \( \text{H}_2\text{S} \) in the inlet and outlet gas streams, respectively.

Similarly, the amount (in mg) of \( \text{H}_2\text{S} \) scavenged per gram of the scavenger at saturation conditions (i.e., scavenging capacity) is calculated using the following equation

\[
\text{H}_2\text{S} \text{ saturation capacity (mg/g)} = \frac{Q \cdot \rho_{\text{H}_2\text{S}} \int_0^{t_s} (C_{\text{in}} - C_{\text{out}}) \, dt}{m \cdot f}
\]  

(2)

where \( t_s \) (in min) is the saturation time (when \( \text{H}_2\text{S} \) concentration in the outlet gas reaches $\sim 104$ ppmv).

### 2.3. Rheological Measurements

The rheological properties of the base and the scavenger-containing drilling muds were conducted according to the standard procedures of the American Petroleum Institute (API). Each drilling mud formulation listed in Table 1 above was agitated (using a Grace viscometer, model no. M3600) at various shear rates starting from 3 up to 600 rpm; the shear stress value at each applied shear rate was recorded. Plastic viscosity (PV), yield point (YP), and apparent viscosity (AV) were calculated using the Bingham plastic model by applying the following equations

\[
\text{PV (cP)} = \Phi_{600\text{rpm}} - \Phi_{300\text{rpm}}
\]  

(3)

\[
\frac{\text{YP (lb/100 ft}^2\text{)}}{100} = \Phi_{300\text{rpm}} - \text{PV (cP)}
\]  

(4)

\[
\text{AV (cP)} = \frac{\Phi_{600\text{rpm}}}{2}
\]  

(5)

In the above equations, \( \Phi_{600\text{rpm}} \) and \( \Phi_{300\text{rpm}} \) are the dial readings at 600 and 300 rpm, respectively.

The gel strengths at 10 s and 10 min of each drilling mud were measured by first shearing the mud at 3 rpm and then leaving it under static conditions for 10 s and 10 min before taking the measurements of the maximum deflection obtained at this low shear rate.

### 2.4. Fluid Loss Tests

Fluid loss tests were conducted in order to evaluate the fluid loss control potential of the base and the scavenger-containing drilling muds using the API standard procedure (API-13B). API recommends conducting the fluid loss test at 100 psi pressure and room temperature conditions for 30 min. A FANN Series 300 API filter press was used to perform the tests. In each test, 350 mL of the drilling mud was placed in the cup of the filtration cell that was loaded with Whatman filter paper no. 50 at the bottom of the cup. The cup was placed in the frame of the apparatus, and the cap was tightly closed. With the necessary connections in place, 100 psi pressure was applied using compressed air. The filtrate was collected in a graduated cylinder for 30 min at different time intervals.

### 3. RESULTS AND DISCUSSION

#### 3.1. \( \text{H}_2\text{S} \) Scavenging Using the Base Drilling Mud

The performance of the formulated drilling muds in scavenging \( \text{H}_2\text{S} \) was investigated by bubbling a sour gas containing 104 ppmv \( \text{H}_2\text{S} \) into each mud. Figure 2 shows the changes in the \( \text{H}_2\text{S} \) concentration in the outlet gas stream as a function of time (i.e., breakthrough curves). The base drilling mud formulation (without \( \text{H}_2\text{S} \) scavenger) showed a quite low scavenging capacity. The breakthrough time is less than 1 min, corresponding to less than 1.5 \( \mu \text{g} \) \( \text{H}_2\text{S} \) scavenged per mL drilling mud at breakthrough. The total amount of \( \text{H}_2\text{S} \)
scavenged at saturation (when H₂S concentration in the outlet gas stream reaches ∼104 ppmv) is estimated using eq 2 to be around 24.2 μg/mL of the base drilling mud. This very low scavenging capacity of the base drilling mud is not surprising, given that it is merely based on H₂S solubility in the drilling mud formulation. It must be noted that the base drilling mud, and also, all scavenger-containing muds, have no affinity for CO₂, as judged from the unchanged inlet—outlet CO₂ concentrations throughout the scavenging process.

3.2. H₂S Scavenging Using ZnO-Containing Drilling Mud. Figure 2 also shows the H₂S scavenging performance of the commonly used H₂S scavenger (i.e., ZnO). Because all muds used in this study have pH values in the range of 9—9.2, more than 98% of the dissolved H₂S in the muds is expected to be in the HS⁻ form. However, the reaction between ZnO (and also other scavengers) and H₂S might also take place at the gas bubble—liquid interface. Regardless of whether the scavenger reacts with H₂S or with HS⁻, the stoichiometric ratio of the hydrogen sulfide/scavenger will remain the same. Consequently, all reaction equations will be written using H₂S. Thus, ZnO will scavenge H₂S according to the following reaction equation:

$$\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O} \quad (6)$$

According to the above stoichiometric equation, each gram of ZnO should scavenge about 419 mg H₂S when ZnO is fully utilized. As shown in Figure 2, the H₂S breakthrough time in the presence of 0.1 wt % ZnO in the base drilling mud is around 3.5 min, corresponding to an H₂S scavenging capacity at the breakthrough of around 5.5 mg H₂S/g ZnO, which suggests that only 1.3% ZnO is utilized up to the breakthrough time. The scavenged H₂S amount at saturation (t = 95 min) reached around 35.1 mg H₂S/g ZnO, which despite being around 6.4 times higher than the breakthrough capacity, is still quite low with only 8.8% ZnO utilization. Nonetheless, Dhage et al. reported a lower H₂S scavenging capacity (19 mg/g) using unsupported ZnO (from BASF). Another unsupported ZnO sample (from SudChemie) showed a H₂S scavenging capacity of 32 mg/g, which is slightly lower than the obtained value in this study. Li et al. reported an H₂S scavenging capacity (at breakthrough) in the range from 3.4 to 37.6 mg/g (corresponding to ZnO utilization in the range from 2.17 to 31.9%), depending on the ZnO loading and the support type, upon which ZnO was impregnated. A scavenging capacity of 8.9 mg/g (at breakthrough) has been obtained by Song et al. using unsupported ZnO. It must be noted that the H₂S scavenging performance of ZnO could be significantly improved through mixing it with other metals or dispersing it on an appropriate support with high surface area and porosity, as shown by a number of studies (see, e.g., ref 56–59 and the relevant references cited therein). However, such scavengers are not still commercially available, and their production costs are expected to be several folds higher than the commercially available (unsupported) ZnO. Thus, H₂S scavenging using supported ZnO was not pursued in this study.

3.3. H₂S Scavenging Using Copper Nitrate-Containing Drilling Mud. Figure 2 also shows H₂S scavenging using a drilling mud containing 0.1 wt % Cu(NO₃)₂·3H₂O. The copper nitrate was dissolved in the drilling mud formulation without being calcined or supported on any support. The H₂S breakthrough time and the H₂S scavenged capacity at the breakthrough time in the presence of 0.1 wt % copper nitrate in the drilling mud are around 11 min and 15.8 mg/g, respectively. The H₂S scavenged capacity increased to around 146.8 mg/g at saturation (t = 418 min), which is more than fourfold higher than the scavenging capacity of ZnO. The application of copper nitrate-containing drilling mud for H₂S scavenging was studied by Elkatatny and co-workers. They noted that copper nitrate was effective in eliminating H₂S from a sour gas stream with a scavenging capacity that is almost three times higher than that of a commercial triazine-based scavenger. Elkatatny et al. proposed the following reaction equation between copper nitrate and H₂S:

$$\text{Cu(NO}_3\text{)}_2 + \text{H}_2\text{S} \rightarrow \text{CuS} + 2\text{HNO}_3 \quad (7)$$

According to the above equimolar reaction equation, 1 g of Cu(NO₃)₂ would scavenge 181.8 mg H₂S upon the full utilization of copper. However, when Cu(NO₃)₂·3H₂O is used instead of Cu(NO₃)₂ (as it is the case in this study), 1 g of the scavenger would scavenge around 141.1 mg of H₂S when copper is fully utilized. Accordingly, the scavenging capacity of 146.8 mg/g obtained in this study is slightly above the theoretical full utilization capacity of copper. The excess amount of H₂S scavenged (5.7 mg/g) might stem from the reaction of H₂S with the generated nitric acid.

Boutillara et al. prepared activated carbon using CuCl₂, which was carbonized at 800 °C in the presence of N₂ or CO₂. The sample that was carbonized in the presence of N₂ possessed the highest Cu loading of 25.43 wt %. This material showed a H₂S scavenging capacity of 28.6 mg/g, corresponding to around 21% copper utilization. Huang et al. impregnated activated carbon with solutions having different copper nitrate concentrations (0.05, 0.1, 0.15, and 0.2 M) and at different pH values (1, 2, and 3). After drying at 105 °C, the sample impregnated with 0.2 M copper nitrate at pH 3 provided the highest H₂S scavenging capacity of 42.2 mg/g (excluding the contribution from the H₂S adsorption on the activated carbon, which was 4.3 mg/g). Miccoli et al. modified zeolite with copper and zinc using ion exchange and impregnation methods. The highest H₂S scavenging capacity (∼40 mg/g) was obtained for the sample modified with copper using the ion exchange method. For either method, copper samples showed as high as five times H₂S scavenging capacity than zinc samples, in line with our observation herein. Wang et al. prepared a series of 3D ordered mesoporous structures containing CuO and used them to scavenge H₂S. The highest copper utilization was found to be 73.5% despite that an H₂S scavenging capacity (147 mg/g) similar to the one obtained in this study was reported. However, the 147 mg/g reported by Wang et al. also comprises the contribution from H₂S adsorption on the CuO support. Accordingly, the H₂S scavenging capacity of the mud formulation of 0.1 wt % copper nitrate reported in this work is higher than the previously reported values with the exception of Wang et al. However, the material utilized by Wang et al. is more expensive and not commercially available, unlike Cu(NO₃)₂·3H₂O.

3.4. H₂S Scavenging Using KMnO₄-Containing Drilling Mud. In addition to studying H₂S scavenging using drilling mud formulations containing ZnO and copper nitrate, the scavenging performance of a drilling mud formulation comprising 0.1 wt % potassium permanganate was also investigated, and the result is shown in Figure 2. As displayed in Figure 2, the use of this drilling mud formulation delayed the H₂S breakthrough time to more than 90 min. This is much longer than the breakthrough times observed using other
drilling mud formulations (see Table 2), suggesting a fast and efficient reaction of KMnO₄ with H₂S. Besides the fast reaction between KMnO₄ and H₂S, this scavenger is also capable of scavenging a larger amount of H₂S relative to ZnO and copper nitrate (see Table 2). The amount of H₂S scavenged (125.3 mg/g) up to the breakthrough time using the KMnO₄-containing drilling mud is around 23 and 8 times higher than the corresponding values obtained using ZnO-containing and copper nitrate-containing drilling muds, respectively.

Additionally, the amount of H₂S scavenged reached around 307.5 mg/g at the saturation condition. This value is more than 2- and 8.7-fold higher than the corresponding values obtained using copper nitrate-containing and ZnO-containing drilling muds, respectively, demonstrating the superiority of KMnO₄-containing drilling mud. Under alkaline conditions (as it is the case in this study), KMnO₄ reacts with H₂S according to the following reaction equation:

$$\text{8KMnO}_4 + 3\text{H}_2\text{S} \rightarrow 3\text{K}_2\text{SO}_4 + 8\text{MnO}_2 + 2\text{KOH} + 2\text{H}_2\text{O} \quad (8)$$

According to the above reaction equation, 3 mol of H₂S will fully consume 8 mol of KMnO₄ if the above reaction proceeds to completion. In other words, under 100% utilization of KMnO₄, 80.9 mg of H₂S would be scavenged per gram of KMnO₄. This value is much lower than the 307.5 mg/g mentioned above. However, the above reaction produces MnO₂; we have observed that manganese oxides are good H₂S scavengers (results not shown). Manganese oxides (MnOₓ) react with H₂S according to the following reaction equation:

$$\text{MnO}_x + x\text{H}_2\text{S} \rightarrow \text{MnS}_x + x\text{H}_2\text{O} \quad (9)$$

Other researchers have also reported H₂S scavenging using manganese oxides. For example, Li et al. reported that manganese oxides supported on alumina can scavenge around 120 mg/g (H₂S scavenging was performed at a reaction temperature of 500 °C and above). Additionally, Huang et al. showed that manganese oxides (generated via the calcination of manganese nitrate, supported on MCM-48, at 550 °C under air environment) are more effective than iron oxides and zinc oxide in scavenging H₂S. Furthermore, Wang et al. reported that composites of manganese/aluminum oxides are able to scavenge H₂S with as high as 96% manganese utilization. Accordingly, the high H₂S scavenging capacity of the KMnO₄-containing drilling mud likely stems from the contribution of both KMnO₄ and the in situ generated manganese oxides upon the reaction of KMnO₄ with H₂S. Considering the superiority of KMnO₄, it might have a potential to be added to water-based drilling mud formulations when drilling wells in hydrocarbon-bearing subterranean formations, where H₂S is present. It must be noted that despite being a strong oxidizing agent, a corrosion rate of metal casing in the presence of KMnO₄ was much lower than that in the presence of copper nitrate (results not shown).

3.5. Rheological Studies. As shown in Figure 2 and Table 2, KMnO₄ is an excellent H₂S scavenger, followed by copper nitrate, and then ZnO. However, in order for an H₂S scavenger to be included in drilling mud formulations, it should not compromise the drilling mud rheological properties. Therefore, we have performed a number of rheological tests of the drilling muds in the presence of ZnO, copper nitrate, and KMnO₄ and compared the obtained results with those of the base drilling mud. One of the performed rheological tests is the shear stress–shear rate up to a shear rate of 1000 s⁻¹. Figure 3 shows the shear stress–shear rate curves for the various drilling muds used in this study. As displayed in Figure 3, all drilling muds show pseudoplastic (shear thinning) behavior, which is a key requirement for effective transport of the drill cuttings. Furthermore, the addition of ZnO and copper nitrate did not significantly alter the shearing properties of the base mud. However, the addition of KMnO₄ resulted in a significant increase in shear stress, particularly at higher shear rates. This higher shear stress is associated with higher viscosity as will be discussed subsequently. Thus, pumping energy of the KMnO₄-containing drilling mud would be higher than those of the other three drilling mud formulations. Nonetheless, such high shear stress of the KMnO₄-containing drilling mud will improve the ability of the drilling mud in cleaning the well from the drill cuttings.

A rheological property that can be extracted from the shear stress–shear rate curve is the AV. More precisely, the AV is the ratio of the shear stress to shear rate. Figure 4 displays the AV values of the base and the scavenger-containing drilling muds. The base drilling mud has an AV of 14.9 cP, which remained almost the same (15.0 cP) upon the addition of 0.1 wt % ZnO or copper nitrate. On the other hand, the addition of 0.1 wt % KMnO₄ increased the AV of the base drilling mud to 17.9 cP (about 20% increase). According to Fink, an AV of ≥15 cP is required in order to achieve an API fluid loss of less than 50 mL/30 min. Accordingly, all scavenger-containing drilling
muds satisfy this requirement. However, unlike the borderline AV values of the ZnO-containing and copper nitrate-containing drilling muds, the AV value of the KMnO4-containing drilling mud is around 20% higher than the minimum AV value required. Nonetheless, Perween et al.71 stated that the recommended AV range for water-based drilling muds is 20−35 cP. Accordingly, the AV value of the KMnO4-containing drilling mud is the closest to the recommended range. A slight increase in the concentration of KMnO4 or the XC polymer (i.e., the viscosifier used in preparing the drilling muds in this study) in the base drilling mud will bring the AV value of the KMnO4-containing drilling mud to the desired range, unlike the case of the other drilling muds, where relatively higher amounts of the XC polymer would be required.

Another important rheological property of drilling muds is PV. This property is related to the resistance of drilling muds to flow. Higher PV is associated with higher resistance to flow and vice versa. Accordingly, drilling muds with low PV are preferred in terms of pumping cost. On the other hand, the density of the drilling muds should be high enough in order for the drilling muds to exert sufficient hydrostatic pressure. Drilling mud density is usually manipulated through the addition of solids (e.g., weighting agents). However, the addition of solids usually increases PV of the drilling muds and, consequently, the mud circulating (pumping) cost. Accordingly, there is an optimum PV range of the drilling muds that has to be maintained. Figure 5 shows the PV values of the base and the scavenger-containing drilling muds. As displayed in Figure 5, the PV of the base drilling mud is 7.3 cP. Upon the addition of copper nitrate to the base drilling mud, the PV remained unchanged. The addition of ZnO to the base drilling mud also did not significantly alter its PV (increased by only 2.7%). However, upon the addition of KMnO4 to the base drilling mud, its PV increased by around 33%, demonstrating the strong viscosifying characteristic of KMnO4. Perween et al.71 and Ismail et al.69 recommended that the PV value of water-based drilling muds should not exceed 25 cP. Accordingly, all drilling muds used in this study satisfy this requirement. However, considering the PV range (10 to 60 cP) for biodiesel-based drilling muds recommended by Li et al.,72 only the PV value of the KMnO4-containing drilling mud falls close (9.7 cP) to this range. Increasing the concentration of KMnO4 and/or the XC polymer in the base drilling mud will bring the PV of the KMnO4-containing drilling mud to the desired range.

YP is also one of the important properties of drilling muds. YP is defined as the minimum shear stress required to initiate fluid flow. It stems from the electrochemical attraction between the ingredients of drilling muds. YP is correlated to the drilling mud ability to lift the drill cuttings out of the wellbore; drilling muds with higher YP would have better lifting characteristics. However, higher YP values are associated with higher mud viscosities, increasing the circulation energy requirement. Thus, an optimum value that is high enough to ensure efficient lifting of the drill cuttings but at the same time is low enough to avoid excessive pump pressure is required. Such an optimum YP value for water-based drilling muds is below 50 lb/100 ft2.73 As shown in Figure 6, the addition of ZnO and copper nitrate resulted in negligible changes in the YP of the base drilling mud. However, the addition of KMnO4 increased the YP of the base drilling mud from 15.07 to 16.44 lb/100 ft2 (about 10% increase). Such an increase in the YP of the base drilling mud upon the addition of KMnO4 suggests that some electrochemical forces have developed in the presence of KMnO4. The improvement in the YP (which is still significantly below the maximum limit) of the base drilling mud upon the addition of KMnO4 would improve the mud ability of lifting and cleaning the drill cuttings from the downhole. Consequently, the sticking tendency of the drill string and its torque would decrease,74 resulting in a more efficient drilling process.

The carrying capacity (i.e., YP/PV) is another important rheological property of drilling muds. It is related to the ability of the drilling mud to suspend the drill cuttings and, consequently, its capacity to remove them from the wellbore.75 Figure 7 shows the carrying capacity (YP/PV) values of the
base drilling mud and the scavenger-containing drilling muds. It has been reported in the literature that a YP/PV value of \( \geq 0.75 \) is correlated with a good carrying capacity behavior of the drilling muds,\(^6\) which in turn results in an improved wellbore cleaning performance. Accordingly, all three scavenger-containing drilling muds (in addition to the base drilling mud) possess a good wellbore cleaning and drill-cutting suspension ability. However, KMnO\(_4\)-containing drilling mud displayed a YP/PV value that is around 20% lower than that of the base drilling, unlike the other two scavenger-containing drilling mud, which displayed comparable values to that of the base drilling mud. Although a threshold YP/PV value of 0.75 is required, higher YP/PV values will surge the annular frictional pressure loss and, thus, increase the equivalent circulating density in the wellbore, which may break the formation rock if the fracture pressure is exceeded. Accordingly, KMnO\(_4\)-containing drilling mud has a better carrying capacity with less load on the circulating pumps, which are key requirements in drilling operations.

We have also evaluated the effect of the scavenger addition on the gel strength of the drilling mud. The gel strength represents the ability of a drilling mud to keep the drill cuttings and the solid ingredients (e.g., weighting agent) of the drilling mud suspended when mud circulation is ceased. It originates from the particle interactions between the mud ingredients under static conditions. The gel strengths of the base and the scavenger-containing drilling muds measured at 10 s and 10 min are shown in Figure 8. The 10 min gel strength for all drilling muds is much higher than the 10 s gel strength, demonstrating the time effect on the gel strength of these muds. Figure 8 also shows that the addition of all scavengers did not significantly alter the 10 s gel strength of the base mud. Furthermore, the addition of 0.1 wt % ZnO and copper nitrate had almost no effect on the 10 min gel strength of the base mud. However, the gel strength of the KMnO\(_4\)-containing drilling mud increased by more than 3.5-fold upon keeping this mud under static conditions for 10 min instead of 10 s, demonstrating the superior gelling and suspension capacity of the KMnO\(_4\)-containing drilling mud. Nonetheless, although high gel strength is required for efficient suspension of the drill cuttings under static conditions in order to avoid their settling and accumulation in the wellbore, causing drill string sticking; excessively high gel strength might lead to fluid loss, fracturing of the formation, and ineffective solid control.\(^7\) High gel strength might also require a high torque when mud circulation is resumed. Accordingly, the gel strength should not be excessively high or low in order to avoid the above problems.\(^7\)

According to Katende et al.,\(^8\) the gel strengths at 10 s and 10 min of water-based drilling muds should not exceed 15 and 35 lb/100 ft\(^2\), respectively. Therefore, all drilling muds studied herein satisfy this requirement. However, drilling muds with higher gelling characteristics (below the maximum limits mentioned above) are more appropriate.\(^7\) Thus, KMnO\(_4\)-containing drilling mud seems more attractive. Nonetheless, further studies to explore any undesirable interactions of KMnO\(_4\) with the drilling mud ingredients are required.

### 3.6. Fluid Loss

Fluid loss tests were conducted in order to get insights into the fluid loss-controlling characteristics of the base drilling mud and how the addition of the H\(_2\)S scavengers affects its characteristics. As displayed in Figure 9, the 30 min fluid loss from the base drilling mud is around 9.1 mL. The fluid loss from the ZnO-containing drilling mud is almost identical to that of the base mud, indicating its negligible effect on the fluid loss-controlling characteristics of the base mud. Unlike ZnO, the addition of the other two scavengers (i.e., copper nitrate and KMnO\(_4\)) increased the 30 min fluid loss to around 11 and 13 mL, respectively. It is recommended that the fluid loss from a water-based drilling mud should not exceed 15 mL/30 min under the standard API test conditions.\(^8\) Accordingly, despite that the addition of copper nitrate and KMnO\(_4\) increases the fluid loss of the base
drilling mud, the 30 min fluid loss extents are still below the capped limit.

4. CONCLUSIONS
K\text{MnO}_4-containing drilling mud possesses an excellent H\text{2}S scavenging performance. This drilling mud has also more favorable rheological properties compared to copper nitrate-containing and ZnO-containing drilling muds. The latter two drilling muds did not significantly alter the rheology of the base drilling mud. In terms of fluid loss characteristics, despite the increase in the fluid loss upon the addition of copper nitrate and K\text{MnO}_4, the extents of the encountered fluid loss are still within the recommended range for all the tested scavengers. The H\text{2}S scavenging performance of copper nitrate-containing drilling mud, despite being more than twofold lower than that of the K\text{MnO}_4-containing drilling mud, is still satisfactory (it is more than four times higher than the H\text{2}S scavenging capacity of ZnO-containing drilling mud). The superior H\text{2}S scavenging capacity of the K\text{MnO}_4-containing drilling mud and its favorable rheological properties suggest that K\text{MnO}_4 addition to water-based drilling mud formulations would be beneficial. However, further studies are required to elucidate the compatibility of K\text{MnO}_4 with other drilling mud additives, particularly under high-temperature and high-pressure conditions.

■ AUTHOR INFORMATION

Corresponding Author
Sagheer A. Onaizi — Department of Chemical Engineering and Center of Excellence in Nanotechnology, King Fahd University of Petroleum and Minerals, Dhahran 31216, Saudi Arabia; orcid.org/0000-0002-6674-4542; Phone: +966-13-860-3882; Email: onaizi@kfupm.edu.sa; Fax: +966-13-860-4234

Authors
Monaf Abdalmajid Gawish — Department of Chemical Engineering, King Fahd University of Petroleum and Minerals, Dhahran 31216, Saudi Arabia
Mobeen Murtaza — Department of Petroleum Engineering, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia; orcid.org/0000-0003-4279-4665
Ibrahim Gomaa — Department of Petroleum Engineering, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia
Zeeshan Tariq — Department of Petroleum Engineering, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia
Mohamed Mahmoud — Department of Petroleum Engineering, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia; orcid.org/0000-0002-4395-9567

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04953

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