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Removing all Forms of Soluble Sulphides From Drilling Fluid

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Abstract

The aim of this project is to remove or eliminate the effect of the highly toxic gas of H_2S on the health of personal, environment, drilling fluid reology, and drilling equipment materials by adding an economic mixture of sulphide scavengers to the contaminated drilling fluid. In this research mixture of 14.7 gm/l of iron oxide in the form of magnetite (Fe_3O_4) and 14.7 gm/l of ferrous oxalate $Fe(C_2O_4)$, which cost is 1.3 US$ per 1kg of mixture, was used to remove the all forms of soluble sulphides (H_2S, HS^-, S^{2-}) from water-base drilling fluid. The Fe_3O_4 reacts with dissolved H_2S and the reaction carry on fast at pH below 8, while $Fe(C_2O_4)$ reacts with HS^-, S^{2-} and this reaction proceed at high rate at pH above 8. Both reactions produce insoluble iron sulphides. The chemical analysis showed that the soluble species of sulphides in the drilling fluid, which its pH was 7.9, were present as dissolved H_2S gas and as bisulphide ions (HS^-). The analysis also explained that the total concentration of these sulphides in the drilling fluid was 3000 ppm.

The results of treatment of contaminated fluid showed that all forms of sulphides were removed from drilling fluid after adding the mixture of scavengers to the contaminated fluid. The results also explained that the drilling fluid reology recovered after removing the soluble sulphides, which were the main factors that effect on the drilling fluid reology, from the drilling fluid.

الخلاصة

الهدف من هذا البحث هو ازالة او التقليل من تأثير غاز كبريتيد الهيدروجين على كل من صحة الانسان والبيئة والخواص التيارية لسوائل الحفر والمادة المصنوعة منها معدات الحفر . وهذا يتم عن طريق اضافة مزيج من مادتي اوكزالات الحديدوز $(Fe(C_2O_4))$ وأوكسيد الحديد ثنائي التكافؤ او يسمى الحديد الاسفنجي (Fe_3O_4) الى سائل الحفر الملوث بغاز كبريتيد الهيدروجين (H_2S) لغرض أزالة جميع اشكال الكبريتيد الذائبة (H_2S, HS^-, S^{2-}) في سائل الحفر . أوكسيد الحديد يتفاعل مع كبريتيد الهيدروجين الذي يكون على شكل غاز ذائب ويكون هذا التفاعل سريعا عندما تكون الدالة الحامضية (pH) لسائل الحفر اقل من 8 في حين مادة اوكزالات الحديد تتفاعل مع كل من ايونات الكبريتيد السالبة (HS^-, S^{2-}) وتزداد سرعة هذا التفاعل عندما تكون الدالة الحامضية لسائل الحفر اعلى من 8. كبريتيد الحديد الغير ذائبة هو ناتج كلا التفاعلين . تركيز الكبريتيد الذائب والذي هوعلى شكل غاز كبر يتيد الهيدروجين وعلى شكل ايون ثاني كبريتيد السالب في التجربة الاولى كان 2980 ملغرام لكل لتر من نموذج سائل الحفر الذي دالته الحامضية 7.9 بينما تركيزهما في التجربة الثانية كان 3000 ملغرام لكل لتر من نموذج سائل الحفر الذي دالته الحامضية 6.7 هذا ما اظهره نتائج التحليل الكيمياوي لنموذجي سوائل الحفر المتلوث بغاز كبريتيد الهايدروجين. من خلال النتائج المختبرية لمعالجة النموذجين الملوثين بينت ان كل من غاز كبريتيد الهايدروجين (H_2S) و ايون ثاني كبريتيد السالب (HS^-) قد ازيلت تماما من سائل الحفر وتحولت الى مركب كبريتيد الحديد الغير ذائب والغير مؤثر على خصائص سائل الحفر.

Introduction

Oil and gas industries suffer from contamination of the drilling fluid by H_2S gas during drilling an oil /gas well. The principal function of drilling fluid is to bring the drilled cuttings from the bottom of the hole to surface. But there are several other purposes such as cool and clean the bit, lubricate the drill string, control formation pressures, and etc… [1, 2, 3].

The presence of free H_2S in drilling fluid can create a severe hazard to rig (drilling equipment materials), drilling fluid rheology, health of personnel and environment if the highly toxic, flammable gas reaches the surface.

As soon as the H_2S gas dissolves in the drilling fluid, the pH of the drilling fluid decreases and it becomes corrosive solution. Consequence, the drill strings, pipes; storage tanks of drilling fluid are corroded. In the presence of H_2S gas, equipments and unit operations of the oil and gas industries are susceptible to the corrosion in the forms of sulphide stress cracking, hydrogen embrittlement and pitting corrosion. The corrosion rate of steel in the presence of H_2S and water is controlled by the dissociation of the H_2S molecule [4]. Dissociation of the H_2S into soluble sulphide ions depends on the pH of the water as shown in the figure (1). As can be seen from the figure the dissociation of the H_2S consists of two steps. In the first step, H_2S dissociates into bisulphide anion (HS^-) and hydrogen proton (H^+) at pH above 4. The second step involves dissociation of HS^- into sulphide anion (S^{2-}) and H^+ at pH above 12 according the following equations [4, 5]:

$$\mathbf{H_2S + e^- \rightarrow HS^- + H^o} \qquad \mathbf{(1)}$$

And

$$\mathbf{HS^- + e^- \rightarrow S^{2-} + H^o} \qquad \mathbf{(2)}$$

The first attempt to eliminate the effect of H_2S gas on the rheology of the drilling fluid and on the material of the well drilling machine is by modification the pH of drilling fluid to become alkaline solution. This is achieved by adding a certain amount of sodium hydroxide (NaOH) to the drilling fluid. The NaOH acts as neutralized agent and it reacts with H_2S gas, which is present in the drilling fluid as dissolved gas, producing sodium sulphide [4]. Hence, H_2S is detered from causing problems under certain conditions.

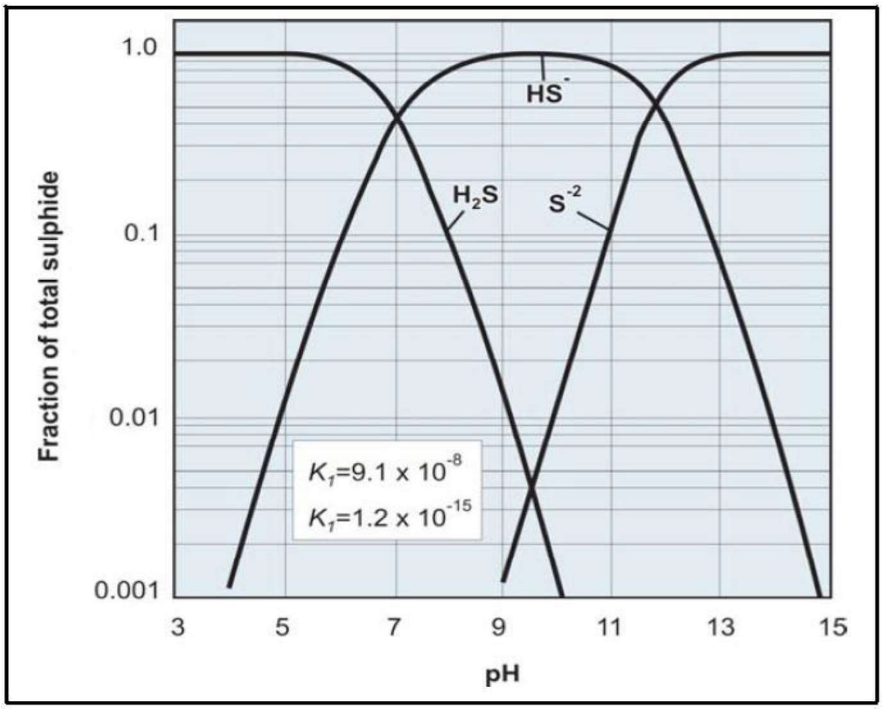

Fig. (1) Shows the effect of pH of mud on the concentration of sulfides species [4,13]

On the other hand, this treatment does not remove H_2S from the fluid and any drop in pH can create a significant hazard. The only safe method for the total removal of hydrogen sulphide or soluble sulphides is with a sulphide scavenger [4].

According to Garrett et al, “sulphide scavenger” can be defines as a chemical substance that reacts with either dissolved hydrogen sulphide gas (H_2S) or anions sulphide species (HS^- and S^{2-}) to produce insoluble and inert reaction products [6].

A common substance, which is used to remove H_2S from drilling fluid, is zinc based compounds such as zinc oxide (ZnO), zinc carbide ($ZnCO_3$), and ZnO nanoparticles. These compounds react with hydrogen sulphide to form insoluble zinc sulphide [7]. On the other hand, using zinc compounds to remove H_2S from drilling fluid is restricted. This is because of zinc considers as a toxic metal (i.e. unfriendly to the environment) [8].

U.S. Pat. No. 6,748,611 B2 to Eric discovers a hydrogen sulphide scavenger of ferrous gluconate that is friendly to the environment. It is used to remove sulphide from drilling fluid only at high pH. This means ferrous gluconate only reacts with anions sulphide (HS^- or S^{2-}), but it does not remove dissolved H_2S gas that is predominant at low pH [8].

U.S. Pat. No. 6,365,053 B1 to Egil et al. disclose insoluble substance of divalent iron oxide type magnetite (Fe_3O_4) used for removing sulphide at low pH (lower than 8). At this pH, most soluble sulphide, which exists in the drilling fluid, is in the form dissolved H_2S gas. This type of H_2S scavenger is not efficient at high pH [9].

EP Pat. No. 1,144,540 A1 to Egil et al. invents an environmentally friendly H_2S scavenger of divalent ferrous oxalate (FeC_2O_4). This type of H_2S scavenger is slightly soluble in the drilling fluid and it able to remove all anion sulphides of HS^- or S^{2-} with high efficiency. This means FeC_2O_4 is prefer to use at alkaline condition of drilling fluid (i.e. at high pH) and it does not used to remove dissolved H_2S gas [10].

The aim of the present work is used mixture of two types of scavenger in order to remove all forms of dissolved sulfides that lead to contaminate the drilling fluid. The mixture of scavengers consists of equal amount of iron oxide in form of magnetite (Fe_3O_4) and iron (II) oxalate or called ferrous oxalate (FeC_2O_4). Fe_3O_4 is insoluble in both water and drilling fluid and the magnetite only used to remove sulfide in form dissolved H_2S gas that is predominate at low pH. Whereas, Ferrous oxalate

Fe (C_2O_4) is an organic substance, which has low solubility in the drilling fluid, is used to remove soluble sulfide anions in the form HS^- and S^{2-} that are predominate in the drilling fluid at high pH.

Experimental Work

The experiments are divided into two parts, the first part involved treatment a contaminated drilling fluid (i.e. it was contaminated by H_2S gas). The second part included pre-treatment a drilling fluid before exposure to the H_2S gas. Solutions of drilling fluid, which were used in both parts, were water-based drilling fluid. The drilling fluid was prepared by dissolution of 1.4 gm NaOH, 90 gm bentonite, and 4 gm FCl in 1.2-1.4 L distilled water. The composition of the prepared drilling fluid as same as the composition of the drilling fluid that is used in the mining operation of a real well.

Figure (2) shows the system used in all tests for both experimental parts. The system comprises of two glass vessels that are connected to the glass beaker (1.5 L volume) through 4 mm diameter of plastic tubes.

Fig. (2) Shows the experimental glass unit (system)

The first part of the experiments included filling the glass beaker with 1-1.2 L of the drilling fluid that its rheology was known. Then, the drilling fluid was exposed to hydrogen sulphide gas for 24 hours. The H_2S was prepared in the small glass vessel which is located at the left side of the glass beaker as shown in figure (1).

In all experiments, H_2S gas was produced from the dissolution of iron sulfide (FeS) in 10% acidic solution according to the following reaction [11]:

$$\mathbf{FeS + 2H^+ \rightarrow Fe^{2+} + H_2S_{(g)}} \qquad \mathbf{(3)}$$

2 M of sodium hydroxide solution (NaOH) was used to absorb the excess H_2S gas that left the system from a vent that was present at the top of the glass beaker as shown in figure (2). After contamination the drilling fluid by H_2S gas, the drilling fluid rheology and concentration of the total soluble sulphide in the drilling fluid were tested. Then, the contaminated drilling fluid was mixing in order to homogenate the gas of H_2S throughout the drilling fluid. After that, the contaminated drilling fluid was treated by adding mixture of sulphide scavengers. The mixture consisted of 14.7 gm of iron oxide in form magnetite (Fe_3O_4) and 14.7 gm of ferrous oxalate (FeC_2O_4). Finally, the drilling fluid rheology and concentration of the total soluble sulphide in the drilling fluid were tested after treating.

The second part of the experiments, which included pr-treatment the drilling fluid before exposure to the H_2S gas, involved adding the mixture of sulphide scavengers (Fe_3O_4 and FeC_2O_4) into the drilling fluid then, the pr-treated drilling fluid was exposed to hydrogen sulphide gas for 24 hours after its rheology were examined. After contamination the pre-treated drilling fluid, its rheology and concentration of the total soluble sulphide in the drilling fluid were tested.

Results and Discussion

The discussion can be divided into two parts. The first part involves discussion the results of the treatment of the drilling fluid after contamination by H_2S gas. Results of the pre-treatment drilling fluid are discussed in the second part of this discussion.

In the first part of this discussion, the drilling fluid samples, which had pH of 9.74, was exposed to the H_2S gas for 24 hours followed by mixing the H_2S gas-containing drilling fluid. The Rheology of the solution of drilling fluid samples were studied before and after contamination by H_2S gas as shown in Table1. As can be seen from the table (1), the H_2S gas effected on the rheology of the fluid and made it as corrosive solution. Except its pH, all the drilling fluid rheology increased as the concentration of the dissolved hydrogen sulfide in the solution increased.

Table (1) Results the Rheology of drilling fluid before and after contamination

الخواص التيارية لنماذج سائل الحفر	Before contamination	After Contamination by gas of H_2S
pH	9.7	7.9
R600(600 rpm)	26	41
R300(300 rpm)	17	27
Gel 10 sec.	4	10
A.V.(centipoises)	13	20.5
P.V.(centipoises)	9	14
Y.P.(Lb/100ft^2)	8	13
Filtrate(ml/30min)	11	11

Result of the chemical analysis of the water-base drilling fluid explained that the total amount of the sulphide species was 3000 ppm. Using figure (1) and according to the pH of the contaminated fluid (pH = 7.9) it can be concluded that the fluid consisted of only two types of dissolved sulfides that were dissolved H_2S gas and HS^-. As can be seen from figure (1), at pH of 7.9 the amount of HS^- is eight times of that of dissolved H_2S gas.

Mechanism of Dissociation

The H_2S gas dissolved in water, which was the main component of the drilling fluid sample according to the following equation:

$$H_2S_{(g)} + H_2O_{(L)} \rightarrow H_2S_{(aq)} + H_2O_{(L)} \qquad (4)$$

Solubility of H_2S gas in water at 25 °C and atmospheric pressure is 0.1mol/L [12]. Then, the dissolved gas of H_2S dissociated to produce (HS^- and S^{2-}) and (H^+) Therefore, concentration of H^+ in the drilling fluid increased. Consequence, pH of the drilling fluid reduced from 9.7 to 7.9 as shown in table (1). Dissociation of H_2S in drilling fluid occurs through two steps.

The first step involves decomposition of H_2S into HS^-, and H^+ followed by dissociation of HS^- into S^{2-} and H^+ in the second step according to the following equilibrium equations [4, 13]:

$$H_2S_{(aq)} + H_2O \rightarrow H_3O^+ + HS^- \quad (5) \qquad K1 = 9.1x10^{-8}$$

$$HS^- + H_2O \rightarrow H_3O^+ + S^{2-} \quad (6) \qquad K2 = 1x10^{-13} - 1.2x10^{-15}$$

Concentration of the reactants and products of the above reactions were controlled by the pH of the drilling fluid as explained in the figure (1) [4, 13].

As be mentioned in the introduction that the first attempt to protect the drilling fluid rheology and the well drilling machine from the hazard of the H_2S gas was by modification the pH of drilling fluid samples to become alkaline solution. This was achieved by adding 1 gm of sodium hydroxide (NaOH), which was used as neutralized agent, per liter of sample. Then, the alkaline solution of drilling fluid sample exposed to the H_2S gas. When H_2S entered in alkaline solution, it reacted with NaOH to form sodium sulphide (Na_2S) according to the following equations [14]:

$$H2S + NaOH \rightarrow NaHS + H2O \qquad (7)$$

$$NaHS + NaOH \rightarrow Na2S + H2O \qquad (8)$$

Hence, the effect of the dissolved H_2S gas on the either properties of the drilling fluid or on the material of the well drilling machine reduced. Therefore, all drilling fluid samples, which were utilized in the experimental works for this research, were prepared with high pH value above 9.

On the other hand, complete removing of (H_2S) gas from the fluid cannot achieve by increasing the pH of the drilling fluid because of any drop in pH can create a significant hazard. This is because of the above reactions are reversible and when the pH of drilling fluid decreases, the sodium sulfide (Na_2S) decomposes into H_2S and NaOH (Eq.8). As it mentioned previously the only safe method for the total removal of hydrogen sulphide or soluble sulphides is with a sulphide scavenger [4, 13].

In this research, mixture of two types of scavengers was used in order to remove all types of dissolved sulfides that led to contaminate the drilling fluid. The mixture of scavenger consisted of 14.7 gm/L of iron oxide (Fe_3O_4) and 14.7 gm/L of ferrous oxalate. (Fe_3O_4) is insoluble in both water and drilling fluid and it only was used to remove sulfide in form dissolved (H_2S) gas according to the following reaction [4, 9].

$$Fe_3O_4 + 6H_2S \rightarrow 3FeS_2 \downarrow + 4H_2O + 2H_2\uparrow \qquad (9)$$

The above reaction proceeds faster at low pH (below pH of 8).

Ferrous oxalate Fe (C_2O_4) is an organic substance and has low solubility in the drilling fluid/water. Fe (C_2O_4) was used at high pH in order to remove soluble sulfide anions in the form HS^- and S^{2-}, which existed in the drilling fluid, and it not used to remove dissolved (H_2S) gas. The ferrous oxalate reacted with either HS^- or S^{2-} producing insoluble compound of iron sulfide according to the following reactions [10]:

$$Fe\,(C_2O_4) + HS- \rightarrow FeS + HC_2O_4 \qquad (10)$$

$$Fe\,(C_2O_4) + S^{2-} \rightarrow FeS + C_2O_4 \qquad (11)$$

At high pH, the ferrous oxalate is able to scavenge the sulphide at 100% efficiency and the above reaction reaches to the maximum rate [10]. Treatment the contaminated drilling fluid by using this mixture led to improve and recover the rheology of the drilling fluid sample as can be seen in the table(2). The chemical analysis for the test explained both forms of soluble sulfides (H_2S gas and HS^-) completely removed, and it showed there were no any amounts of soluble sulfides species in the drilling fluid.

Table (2) Results the Rheology of drilling fluid sample before and after contamination and after treatment

Rheology of the drilling fluid	Before contamination	After Contamination by gas of H_2S	After Treatment by Fe_3O_4 & $Fe(C_2O_4)$
pH	9.7	7.9	7.5
R600(600 rpm)	26	41	28
R300(300 rpm)	17	27	19
Gel l0 sec.	4	10	6
A.V.(centipoises)	13	20.5	14
P.V.(centipoises)	9	14	9
Y.P.(Lb/100ft^2)	8	13	10
Filtrate(ml/30min)	11	11	11

On the other hand, Fe (C_2O_4) led to decrease the pH of the drilling fluid sample that was used in the first experiment as shown in the table (2). This because of the reaction of Fe (C_2O_4) with sulfide anions produce iron sulfide and oxalic acid. Consequence, pH of the fluid decreased. Therefore, in addition to the ferrous oxalate iron oxide (Fe_3O_4) was used in order to remove dissolved (H_2S) gas, which its concentration may be increased in the drilling fluid due to decrease its pH.

The Second part of this discussion includes pre-treatment the drilling fluid samples before exposure to the H_2S gas. This was achieved by adding equal amount (14 gm) of (Fe_3O_4) and Fe (C_2O_4) to the one liter of each sample and studied their rheologies as shown in the Table3. Then, the pre-treated fluids were subjected to the H_2S gas for 24 hours flowed by continuous mixing. The drilling fluid rheology was monitoring and it tested after 5 hours and after 24 hours during contamination by (H_2S) gas as shown in the table (3) shows the results of experiment.

Table (3) Results the Reology of drilling fluid sample for pre-treatment stage

Rheology of the drilling fluid	Before adding mixture of H_2S gas scavengers	After adding mixture of H_2S gas scavengers	After 5 hours of contamination by H_2S gas	After 24 hours of contamination by H_2S gas
pH	9	7.043	7.043	6.87
R600 (600 rpm)	21	28	28	42
R300 (300 rpm)	14	19	19	31
Gel losec.	4	5	5	12
A.V. (centipoises)	10.5	14	14	21
P.V. (centipoises)	7	9	9	11
Y.P. (Lb/100ft^2)	7	10	10	20
Filtrate (ml/30min)	10.9	10.9	10.9	10.8

As can be seen from above Tables, the rheology of the drilling fluid samples increased slightly after adding the mixture of the scavengers to drilling fluid before contamination by (H_2S). This because of (Fe_3O_4) is a solid material and is insoluble in the fluid, whereas Fe (C_2O_4) is slightly soluble and its solubility decreased with decreasing pH of the fluid. Hence, both of them led to increase the drilling rheology such as their viscosities.

On the other hand, pH of the fluids decreased after adding the mixture of the scavengers. As be mentioned before that ferrous oxalate led to decrease the pH of the fluid due to its organic acid base.

It also can be seen from table (3) that the pre-treated drilling fluid rheology did not change after 5 hours of continuous exposure to the H_2S. This because of iron oxide (Fe_3O_4) reacted with dissolved H_2S gas, whereas ferrous oxalate Fe (C_2O_4) reacted with sulfide anions of HS^- that were present in the fluid.

On the other hand, the pre-treated fluid rheology changed after 24 hours of continuous contamination by (H_2S) gas. This due to all the mixture of scavengers was consumed by the reaction with sulphide species and then the concentration of dissolved H_2S gas and HS^- in the drilling fluid samples started to increase.

Conclusion

From the experimental results can be concluded the following points:

1. Acidic gas of H_2S can be completely removed by using mixture of iron oxide Fe_3O_4 and ferrous oxalate Fe (C_2O_4) that added to the drilling fluid as either pre-treatment or treatment. This led to refresh the fluid rheology and its functions.
2. Fe (C_2O_4) only reacted with bisulfide (HS^-) and divalent sulfide anions (S^{2-}) and the maximum rate of reaction occurred at high pH. Fe (C_2O_4) led to decrease the pH of the drilling fluid.
3. Fe_3O_4 only reacted with dissolved (H_2S) gas and the maximum rate of reaction occurred at pH lower than 8.

Symbols

Rheology = Properties.

R600 = Viscosity obtained when cylinder of the Fann Viscometer is rotated at 600 rpm.

R300 = Viscosity obtained when cylinder of the Fann Viscometer is rotated at 300 rpm.

Gel 10 sec. = Gel loss.

A.V = Average viscosity (centipoises).

P.V = Plastic viscosity (centipoises).

Y.p =Yield point ($Lb/100ft^2$).

H_2S = Hydrogen sulphide gas.

HS^- = Bisulphide anion.

S^{2-} = Divalent sulphide anion.

Fe_3O_4 = Divalent iron oxide (magnetite).

FeC_2O_4 = Ferrous oxalate.

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