Comparative analysis of the efficacies of ferrous gluconate and synthetic magnetite as sulphide scavengers in oil and gas drilling operations


1. Introduction

Many of the oil production fields experience increasing concentrations of hydrogen sulphide in the production stream. Carter et al. observed that sour gas has been reported in old fields where the presence of hydrogen sulphide had not been previously reported. The presence of H₂S presents problems associated with personnel safety, increased corrosion, hydrogen sulphide stress cracking, and the increased emission of sulphur dioxide during the burning of produced gas as fuel, which must be addressed by the field operator.

Being fully aware of the fact that the presence of free hydrogen sulphide in a formation can represent Health, Safety and Environment (HSE) problems during and after drilling, continuous research is performed for finding more reliable ways to solve the problems. The mud being circulated in the drill strings brings the toxic gas back to the surface where it is released creating severe hazards to rig personnel and the environment.

Hydrogen sulphide gas, H₂S, is naturally occurring gas, often found below the earth’s surface, in zones below which the oxidation of minerals does not occur. As a constituent of some oil and gas reservoirs, it is generally found in small percentages of the total fluid, though in some reservoirs H₂S may be found in concentrations as high as 30%. Sulphate reducing bacteria (SRB) also contribute to the production of hydrogen sulphide. The increasing levels of H₂S in produced fluids have been observed since water flooding began. The biogenic production of H₂S is certainly a cause of this problem in many of these reservoirs. But SRB is not really known to attack drilling fluids, however it has deleterious effects on packer fluids. The problems associated with sour gas production are well known: toxicity, corrosion, excess solids (indicating excessively high values of yield point, plastic viscosity, and gel strengths), filtration loss, emulsion and surface equipment problems, and the necessity to remove H₂S prior to sale. Millions of dollars are spent every year on detection and mitigation of weight loss and other kinds of corrosion in oil and gas industry equipment.

It is a standard in the Oil and Gas industry to run the drilling mud at high pH and including sulphide scavenger later. The sulphide scavenger then turns the sulphide into a safe, mild and non-reversible form.

Many industrial chemicals used for drilling operations, some of which are used in well construction, completion, work over and abandonment in Oil and Gas industry, are toxic and some may not biodegrade at acceptable rates. With the increasing awareness of the potential environmental impact of chemical additives, particularly in the marine environment, there is a continuous need to develop more efficient, less toxic alternatives.

2. Theory

2.1 A Brief Overview of the H₂S Scavengers Used in Drilling Fluids

Many well-known mechanisms have been employed for the immobilization of H₂S from drilling fluid:

- Copper carbonates
- Hydrogen peroxide
• Iron oxide: especially magnetite
• Chlorine containing compounds (e.g. chlorine dioxide and sodium hypochlorite)
• Organic compounds (e.g. acrolein and formaldehyde), methanol, glyoxal, amines, triazines, naphthenates, chelates of ethylenediaminetetraacetic acid – EDTA, hydroxyethylendiaminetriacetic acid – HEDTA, nitritotriacetic acid – NTA among others, etc.

An abundance of literature is available describing various methods in the abatement of hydrogen sulphide in gas and drilling fluid systems. Though few of the chemicals/methods suggested so far have efficient H2S removal, most of these methods appear impractical because of their cost and compatibility. For instance, copper compounds set up corrosion cell on ferretic materials and hydrogen peroxide is too reactive with other chemicals in the mud. Despite the fact that zinc carbonate is environmentally safe compared to zinc but there are outstanding questions concerning its scavenging efficiency and reaction rates. Majority of the organic compounds is more suitable for sweetening processes rather than the fixation of sulphides. Some of these compounds are harmful, corrosive or have explosive by-products, may be unstable or potentially explosive and may require special handling technique.

Eric disclosed in a US patent published in 2004 that ferrous gluconate could efficiently remove sulphide from drilling fluids. Eric therefore performed some tests to investigate the desulphurization effects of the ferrous complex. Major tests were performed to acquire the knowledge on the effects of the ferrous gluconate on the rheology of the drilling fluid and the conclusion was it had no adverse effect on it after the tests.

2.2 Characteristics of Ferrous Gluconate
The scavenger is a commercially available reactive iron complex. The gluconate is composed of iron, bound to two molecules of gluconic acid, which is the acid form of glucose (Anonymous, 2007). It has a molecular formula of C12H22FeO14·2H2O and a molecular weight of 482.17 g/mol. It is a non-toxic, non-corrosive soluble powder. The compound being a complex has no formal bonding, as opposed to a chelate and thus, has the advantage of the iron being easily released during the reaction with sulphides. This indicates that the complex is easily biodegradable considering disposal of cuttings after drilling operations. It is generally stable, especially when pH and temperature are considered. It has pH stability even with solution having as high as pH of 12 and above.

Kulgawczuk et al. also determined that the complex is stable at high temperatures up to about 401 °F (205 °C) after which the decomposition can be observed.

Figure 1 shows the structural formula for ferrous Gluconate.

The proposed/probable reaction of ferrous gluconate with sulphides is as follows:

\[
\text{Fe} \left(\text{C}_6\text{H}_7\text{O}_7\right)_2 + \text{S}^2- \rightarrow \text{FeS} + 2 \left[\text{C}_6\text{H}_7\text{O}_7\right]^2-
\]

(1)

Ferrous gluconate + Sulphide → Ferrous sulphide + gluconate

3. Experimental

3.1 Materials and Instruments
Commercially available ferrous gluconate and magnetite were used as scavengers. The used water based mud is saturated brine mud (mud’s composition shown in Table 1). Analar grade reagents of potassium hydroxide, HCl, sodium sulphide pellets were used. Instruments such as pH meter (model OMEGA PHH-3X), Agitator (model INBS 3000), Chemetrics Vacuettes Kit (Vacuettes K-9510B), Filter paper (Whatman No. 50), Fann Viscometer (Fann 35A Model) and the API Filter Press were used during the experiments.

3.2 Desulphurization Tests
Typically, laboratory tests of sulphide scavengers have used easily handled sodium sulphide crystals instead of highly toxic H2S gas due to its difficulties and hazards. In this way, the sulphide would already be in ionic form. In this experiment, 700 mg/l of sodium sulphide were dissolved in the saturated brine mud to simulate the effect of absorbing H2S in mud at a high pH value. 700 mg/l of the scavenger under test were added, and the decrease in sulphide concentration over time was monitored. The ratio of the sulphide to scavenger was 1:1 (i.e. 700 mg/l each of the scavengers were used to scavenge the same concentration).

### Table 1. Composition of the Saturated Brine Mud

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride</td>
<td>80 lb/bbl</td>
</tr>
<tr>
<td>Caustic potash (KOH)</td>
<td>1.5 lb/bbl to pH of 12</td>
</tr>
<tr>
<td>Soda ash (sodium carbonate)</td>
<td>0.11 lb/bbl</td>
</tr>
<tr>
<td>API Bentonite</td>
<td>20 lb/bbl</td>
</tr>
<tr>
<td>Polyanionic cellulose</td>
<td>1.7 lb/bbl</td>
</tr>
<tr>
<td>Pregelatinized corn starch</td>
<td>2.0 lb/bbl</td>
</tr>
<tr>
<td>Chrome lignosulphonate</td>
<td>4.0 lb/bbl</td>
</tr>
<tr>
<td>Alcohol-based defoamer</td>
<td>2.0 lb/bbl</td>
</tr>
<tr>
<td>Sodium bisulphate</td>
<td>1.2 lb/bbl</td>
</tr>
<tr>
<td>API bante – barium sulphate of SG 4.2</td>
<td>15 lb/bbl</td>
</tr>
<tr>
<td>Xanthan gum</td>
<td>0.85 lb/bbl</td>
</tr>
</tbody>
</table>

**lb = 0.453 kg; bbl = 0.159 m³**
quantity of sulphide). This was carried out at the temperatures of 25 °C, 35 °C, 45 °C and 55 °C. In each case, the container was agitated at 60 rpm automatically using an agitator for an overall time of 140 minutes and the sulphide content was measured at intervals of 20 minute agitation. The sulphide content in the mixture was measured at intervals of mixing. This is in accordance with the method used by Garrett et al. 10 The solution was allowed to settle down and then filtered using filter paper; the sulphide content in the filtrate was then measured using the Chemetrics chemistry of methylene blue solution. Figure 2 is a depiction of the desulphurization process.

3.3 Rheology Tests
A Fann VG meter (model 35A), which is a 6 speed viscometer was used to carry out the rheological tests. The speeds attributed to this viscometer were 3, 6, 100, 200, 300 and 600 rpm.

Four different mud formulations were made and each was tested rheologically. The first sample contained neither sulphide nor any of the scavengers. This was done to serve as a control. The second sample contained sodium sulphide alone so as to measure the effect of the presence of sulphide on the mud’s rheology. Ferrous gluconate alone was added to the third sample, to confirm if the addition of the complex would have any adverse effect on the mud’s rheology. And lastly the fourth sample contained both sulphide and gluconate.

The viscometer was rotated at all the available speeds. Each sample was stirred at 600 rpm while being heated to 120 °F (49 °C). It was ensured that the dial reading had stabilized at this speed before noting the result and proceeding to the 300, 200, 100, 6 and 3 rpm speeds. The dial readings for the various speeds were used for the measurement of the rheological properties of the samples.

The following simple calculations were used to get the plastic viscosity (PV) and the yield point (YP) values:

PV (cP) = 600 rpm reading – 300 rpm reading
YP (lb/100 ft²) = 300 rpm reading – PV

Each sample was then stirred at 600 rpm for approximately 15 seconds and was left undisturbed for 10 seconds before taking the 10-second gel strength at 3 rpm.

Each sample was also re-stirred at 600 rpm for approximately 15 seconds and left undisturbed for 10 minutes. Then the 10-minute gel strength reading at 3 rpm was taken. 13

For the fluid loss tests, the API filter press was used for API fluid loss test while an HTHP fluid loss cell was used for the determination of HTHP fluid loss. A dry graduated cylinder, with a Whatman No. 50 filter paper, was placed under the drain tube to receive the filtrate. For the API fluid loss, the relief valve was closed and the regulator was adjusted to a pressure of 100 psi (6.89 bar) for 30 seconds. In the case of the HTHP fluid loss test, the temperature was set to 260 °F (126.6 °C) of temperature and 500 psi (34.5 bar) of pressure. The volume of the filtrate, in the two tests, was then measured at the end of 30 minutes of the test. The fluid loss was measured in ml/30min. 13

4. Results and Discussion
4.1 Desulphurization Tests
Figure 3 shows the results obtained for the comparative desulphurization efficiency of magnetite and ferrous gluconate.

4.1.1 Relationship Between Desulphurization Efficiency and the Surface Area.
Magnetite is an insoluble solid while ferrous gluconate is soluble. The soluble ferrous gluconate has a larger surface area than the insoluble magnetite and dissolves rapidly. As can be seen from the results, this indicates that the larger the surface area, the higher the desulphurization efficiency. This can be clearly seen if the desulphurization effects of both the magnetite and ferrous gluconate in Figure 3 are compared. The ratio of the sulphide to scavenger was 1:1 (i.e. 700 mg/l each of the scavengers were used to scavenge the same quantity of sulphide). The results shown in Figure 3 are exactly what would be expected when comparing the action of a soluble scavenger with that of an insoluble solid. The soluble iron (ferrous gluconate) is available for instant and complete reaction; the reaction is almost certainly of the extremely rapid ionic type. Although the solid (magnetite) has an initial fairly fast reaction, the rate reduces rapidly as the reaction proceeds. Usually in the case of magnetite, the reaction rate reduces as the pores available in it get occupied. 2 Figure 1 indicates that diffusion into the interior of the solid magnetite is very slow and for practical purposes can be considered negligible.

It is clear that using a soluble scavenger results in high speed of reaction. For instance in Figure 3, the soluble scavenger (ferrous gluconate) achieved maximum removal after the first 20 minutes whereas the insoluble
magnetite required more than 60 minutes to achieve its maximum as can be observed in Figure 3. For instance, tests performed at 25 °C show that after 20 minutes the mud was observed to contain only 30 mg/l sulphide in the case of the ferrous gluconate. It achieved maximum removal when the mud was tested with zero sulphide content after 40 minutes. But in the case of magnetite, tests after 20 minutes show that 690 mg/l sulphide was still remaining in the mud. The magnetite achieved its maximum while the mud still contains 600 mg/l of sulphide after the duration of 60 minutes. This kind of relationship is always expected in the case of any soluble and insoluble scavenger.

4.1.2 Effect of Temperature on the rate of Desulphurization

According to Chen and Huang (1986), higher temperature brings about higher sulphide capturing effect. It can as well be seen from Figure 3 that the sulphide capturing effect increases as the temperature increases. There was a rapid response to temperature change in the action of scavengers. This benefited the insoluble scavenger to some extent as the reaction was fast initially. However, due to the limited surface area it possessed, the diffusion rate decreased gradually thereby lowering the capturing effect.

When the temperature was increased, the diffusion coefficient and the solubility of the ferrous gluconate (soluble scavenger) became larger. Meanwhile, the chemical reaction of the scavenger was speeded up. The desulphurization reaction tends to be completed in the case of ferrous gluconate when the temperature was 131 °F (55 °C) within the first 20 minutes. In the case of magnetite (insoluble scavenger), the sulphide content remaining in the mud was 600 mg/l (maximum removal) at 77 °F (25 °C) in 60 minutes. At 95 °F (35 °C), the maximum removal was in 80 minutes when the sulphide content remaining in the mud was 560 mg/l. The same trend continues up to 131 °F (55 °C) showing that the temperature increase assisted in the capturing effect of the two scavengers.

4.1.3 Effect of Agitation on Desulphurization Efficiency.

Agitation of the solution directly affects the thickness of the diffusion layer. In each case, the sample solution was agitated for about 140 minutes and the level of the sulphide content remaining in the drilling fluid was checked at 20 minute intervals. The efficiency of capturing sulphide was relatively high in the case of the ferrous gluconate. As could be seen from Figure 3, the ferrous gluconate had already removed high sulphide content within the first 20 minute agitation at all temperature conditions, and zero sulphide was tested after the second 40 minute agitation at all temperatures. In the case of the magnetite (insoluble scavenger), the efficiency of capturing sulphide was not as high as that of the ferrous gluconate. Figure 3 shows that even after 60 minutes of agitation, there was still high sulphide content in the drilling mud when the magnetite was used for the scavenging as it achieved its highest maximum so far at 131 °F (55 °C) and after 100 minutes when the sulphide content remaining in the mud was tested to be 410 mg/l.

4.2. Rheology Tests

Due to the fact that a normal mode of operation would include the ferrous gluconate scavenger in the mud as prophylactic component (in case H₂S might be encountered), it was relevant to investigate the potential effect of the scavenger on mud properties in the absence of sulphide. An example of this performance is given in Table 2, which compares mud properties after hot rolling at 120 °F (49 °C), with and without the scavenger. Clearly, the scavenger did not have any adverse effect on the fluid properties.

The next stage was to investigate the impact of including sulphide in untreated mud and in mud that had been treated with scavenger. The results of the tests were given in Table 2. Sample 1 column shows the rheology of the mud without any scavenger or sulphide, of sample 2 column shows the effect of the inclusion of sodium sulphide alone, sample 3 column shows the effect of the scavenger alone, while sample 4 column gives the results when both sulphide and the stoichiometrically equivalent quantity of the scavenger were included. The visible effect of including both sulphide and scavenger was that the mud instantly turned black because of the usual formation of iron sulphide as was observed in the previous tests.

According to Suhascaryo et al.20, the results obtained for the plastic
viscosity (PV) when the ferrous gluconate was added fall between the API recommended range (8 cP – 35 cP), (0.008 Pa·s – 0.035 Pa·s). The minimum recommended API value for the yield point (YP) is 5 lb/100 ft² (Baker Hughes, 1999), while the maximum YP can be observed that all the values obtained for the yield point also fall within the recommended values. The lower the PV and YP, as could be seen from samples 3 and 4 results, the better the performance of the mud.

The fluid losses obtained, especially when ferrous gluconate was added, also fall within the recommended range (3 ml – 15 ml) and were even much lower than the maximum as could be seen from samples 3 and 4 in Table 2.11

The recommended values for 10 seconds gel strength is between 2 lb/100 ft² and 5 lb/100 ft² (Max and Martin, 1996) so that the mud could be suspended barite, while the maximum value of 10 minute gel strength is 35 lb/100 ft².11

Inspection of the results in samples 3 and 4 shows that inclusion of the scavenger did not have any detrimental effect on the mud properties. The results even indicate that inclusion of the scavenger improved the ability of the mud to withstand being hot rolled at 120 °F (49 °C) without being destabilized or upset.

5. Conclusions and Recommendations

5.1 Conclusions

1. Ferrous gluconate can be used in a wide range of mud pH values. It provides efficient desulphurization as the mud was tested “zero-sulphide” content after the desulphurization tests. This indicates that it can protect operating personnel from the toxic H₂S. Magnetite was only able to remove about 30 % of the sulphide from the mud.

2. Ferrous gluconate generally has no adverse effect on mud properties, even at larger concentrations. It can even serve as a rheology modifier in mud. Magnetite in larger concentrations can cause unwanted weight additions to the mud.

3. Ferrous gluconate has the advantages of being more readily available and cheaper than synthetic magnetite.

5.2 Recommendations

1. This information needs to be translated into realistic rig-site hydrogen sulphide scavenging tests.

2. More research should be conducted on the existing organic products to identify their true scavenging capabilities under realistic wellbore drilling conditions.
3. Optimization of the scavenging processes of the ferrous gluconate should be looked into.

Acknowledgement

The authors wish to gratefully acknowledge the management and operations of MI SWACO, Port-Harcourt, Nigeria for their support by granting us access to their laboratory for this study and to the management of Chemical Engineering Department, Ahmadu Bello University, Zaria, Nigeria for their insightful comments.

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