Sulphide Scavengers in Oil and Gas Industry – A Review

M.K. Amosa, I.A. Mohammed, and S.A. Yaro

PROFESSIONAL PAPER

The application of sulphide scavengers is a widely adopted practice in production and processing operations in the Oil and Gas Industry. Particularly challenging is the search and development of new chemistries, which is aimed at safeguarding the health of personnel and maintaining good protection of materials under a variety of conditions whilst being environmentally acceptable. This paper includes an up to date history of the efforts which have been put forth so far in the industry to minimize or eliminate the various problems caused by hydrogen sulphide during Oil and Gas drilling operations by the use of some chemicals. The advantages and disadvantages of using the various chemicals for scavenging hydrogen sulphide drilling fluids and produced fluids are compared.

Key words: sulphide, sulphide scavenger, environmentally acceptable, drilling fluids, produced fluids

1. Introduction

We are fortunate to live in a world where awareness of the detrimental effects of pollution is on the increase. Such awareness will help ensure protection of the biosphere and safeguard the future generations of man and animals especially the aquatic creatures. One of the major industries responsible for all these pollutions is the Oil and Gas industry and also, among the major pollutants caused by this industry during oil and gas production and processing is hydrogen sulphide gas.

2. Description of Hydrogen Sulphide Gas

Hydrogen sulphide is a colourless gas, with an offensive odour and a sweetish taste. It is soluble in water, alcohol, oils, and many other solvents. It has a specific gravity of 1.1895 with reference to air. It is considered a weak acid, it is toxic to humans and corrosive to metals. Hydrogen sulphide can be dangerous to personnel on the surface as it is extremely toxic to human and even animal life, and is extremely corrosive to most metals as it can cause cracking of drill pipe and tubular goods, and destruction of testing tools and wire lines.

The hydrogen sulphide content of fluids in the permeable formations of oil wells has an important impact on the economic value of the produced hydrocarbons and production operations. Typically, the sulphur content of crude oils is in the range 0.3-0.8 weight percent and the hydrogen sulphide content of natural gas is in the range 0.01-0.4 weight percent, although concentrations of hydrogen sulphide in natural gas of up to 30 weight percent have been reported. Several recent reports have claimed a systematic increase in the sulphur content of crude oils over the past 10-20 years and anticipate further significant increases in the concentration of hydrogen sulphide in both oil and natural gas. The correlation between the hydrogen sulphide concentration of produced hydrocarbons from the Norwegian continental shelf and the reservoir temperature; above about 110 °C indicates that the hydrogen sulphide content of produced hydrocarbons increases exponentially with temperature, while below this temperature the hydrogen sulphide concentration is negligible.¹⁴

When hydrogen sulphide enters the borehole during drilling, completion, or testing for hydrocarbons, it creates several very detrimental problems. These problems are encountered regardless of the source of the hydrogen sulphide. Hydrogen sulphide has created unsolved problems in the oil field.

3. Origin of Hydrogen Sulphide

During oil and gas operations, hydrogen sulphide can be found as a component of formation gases, dissolved in water, hydrocarbons, or even liquid sulphur.¹⁵ Thermal degradation of organic materials and sulphate reducing bacteria (SRB) can create hydrogen sulphide along with other gases.

4. Problems Caused By Hydrogen Sulphide Gas

4.1. Health and Safety of the Personnel

One of the main problems hydrogen sulphide causes is in respect to the health and safety and safety of the personnel.

A maximum of eight hours exposure to concentrations greater than 100 ppm H_2S will cause hemorrhage and death.¹³ Concentrations above 600 ppm can be fatal in three to five minutes. Highly stressed, high strength steel can fail in a matter of minutes in the presence of 50 ppm H_2S . At high pressure, as little as 0.1 ppm H_2S can greatly reduce the time to failure of highly stressed, high strength steel.¹³

Relying solely on its odour is not a good idea because at concentrations above 100 ppm it deadens a person's sense of smell within a few minutes. The pure gas is heavier than air and can collect in low areas such as pit rooms and accommodation.¹⁶ Table 1 shows the poten-

SULPHIDE SCAVENGERS IN OIL AND GAS INDUSTRY ...

Table 1. Health effects from short-term exposure to hydrogen sulphide								
Concentration (ppm)	Health Effect							
0.01 – 0.3	Odour threshold							
1 – 20	Offensive odour, possible nausea, tearing of the eyes or headaches with prolonged exposure							
20 – 50	Nose, throat and long irritation; digestive upset and loss of appetite; sense of smell starts to become fatigued; acute conjunctivitis may occur (pain, tearing and light sensitivity)							
100 – 200	Severe nose, throat and long irritation; ability to smell odour completely disappears.							
250 – 500	Pulmonary edema (build up of fluid in the lungs)							
500	Severe lung irritation, excitement, headache, dizziness, staggering, sudden collapse (knockdown), unconscious- ness and death within a few hours, loss of memory for the period of exposure (results in permanent brain damage if not rescued immediately).							
500 – 1000	Respiratory paralysis, irregular heart beat, collapse and death without rescue.							
> 1000	Rapid collapse and death							

tial hazards hydrogen sulphide can cause to the personnel from short-term exposures. $^{\rm 16}$

To buttressize this, there are many historical cases to document the ill effects of hydrogen sulphide exposure. The documented cases reported in Table 2 indicate that hydrogen sulphide is very toxic and it takes only a matter of minutes to affect unprotected workers. There is a report that some 26 persons died from exposure to hydrogen sulphide in the high-sulphur fields of Wyoming and West Texas between October 1, 1974 and April 28, 1976.⁶

4.2. Effects of hydrogen sulphide on Metals

Hydrogen sulphide mainly cause corrosion problems to drill strings, transport pipes, storage tanks etc. Hydrogen sulphide causes sulphide stress cracking, hydrogen embrittlement and pitting corrosion in oil and gas operations.

The corrosion of iron in the presence of hydrogen sulphide and water is dependent upon the dissociation of the hydrogen-sulphide molecule. Iron is oxidized to the ferrous form at the anode and hydrogen sulphide undergoes a two-step -dissociation at the cathode. Tung et al²² propose the following equilibrium reactions below.

At the anode:

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$
 (1)

And at the cathode hydrogen is produced and either enters the steel or forms hydrogen gas and bubbles off:

If H₂S is present:

$$2H^{+} + 2e^{-} \rightarrow H^{\circ} + H^{\circ}$$
⁽²⁾

if H_2S is not Present:

$$H^{\circ} + H^{\circ} \rightarrow H_{2}$$
 (gas) (3)

Hydrogen enters the steel first by adsorption onto the water to steel interface and then by being absorbed into the steel as hydrogen. The amount of hydrogen entry depends on the corrosion rate of the steel surface and the concentration of anions such as HS⁻ that reduce the tendency to produce hydrogen gas (as shown in second equation above) and promotes the hydrogen (H^o) to enter the steel.²²

pH also has an influence on amount of corrosion damage. Basically, the term "sulphides" used in oil and gas operations includes all three water-soluble species, H_2S , HS° and S^2 , which coexist in a sulphide-water system. Shown in the ionization chart for hydrogen sulphide in figure 1, it can be observed that molecular H_2S predominates in the acidic range, where the pH is below 7. In the range of 7 to 12, monovalent HS⁻ predominates and above pH 12, divalent S²⁻ predominates.

The illustration in figure 1 indicates that the most important practice is that when H_2S enters in alkaline mud, it reacts to form an alkaline sulphide, most often sodium sulphide.¹⁷ While elevated pH is a good way to keep H_2S from causing problems under certain conditions, it does not remove it from the fluid and any drop in pH can create a significant hazard. This then brought about the advent of sulphide scavengers in the history of oil and gas operations.

	Table 2. Effects of Hydrogen Sulphide Inhalation on Humans											
	No of Subjects	Concentration (ppm)	Duration of Exposure	Effects								
	1	12 000	-	Death								
		2 000	Less than 20 minutes	Death								
1	I	4 000	-	-								
	10	1 000	Less than 1 minute	Death 1/10; unconsciousness, abnormal ECG.								
342	1 000	Loss than 20 minutes	Linearitelization of 200, doubt of 00 including 10 in beautiful residual newspaper system demons in 4									
	2 000	Less than 20 minutes	Hospitalization of 320, death of 22 including 13 in hospital, residual hervous system damage in 4.									
	5	1 000	Instant	Unconsciousness, death								
	4	290-540	-	Unconciousness								
	78	15-25	-	Burning eyes in 25, headache in 32, loss of appetite in 31, weight loss in 20, - dizziness in more than 19.								
	6 500	10-15	4 - 7 hours	Conjunctivitis								

Source: DHEN (NIOSH), 1977.

SULPHIDE SCAVENGERS IN OIL AND GAS INDUSTRY.



The only safe method for the total removal of hydrogen sulphide or soluble sulphides is with a sulphide scavenger.

5. Hydrogen Sulphide Scavenger Technology

According to Garrett *et al*¹¹, the term "sulphide scavenger" refers to any chemical (usually a commercial additive) that can react with one or more sulphide species and can convert them to a more inert form. Effective scavenging is based on attaining an *irreversible* and *complete* chemical reaction between the scavenger and one or more sulphide species. Because a mutual equilibrium exists between the three species in solution, irreversible end complete removal of one species serves to remove all three. Incomplete chemical reaction between a species and the scavenger cannot remove all soluble sulphides present.

Most H_2S scavengers function on a surface adsorption manner or through ionic precipitation. If the scavenger being used is based upon the surface adsorption technique, the mud must be in constant flow to assure that the additive and the sulphides actually collide with one another in order for the necessary reactions to take place. A turbulent flow type of situation would be ideal for this and would assure many random collisions of the two particles. When the scavenger is based on an ionic reaction, properties of the scavenger must be understood to assure that variables such as pH and salinity are conducive to the usage of the additive.

Before a particular scavenger may be selected, a determination of the form of sulphides that exist in a particular mud system must be made. Under most conditions, sulphides will exist in one of three different forms, depending upon the pH factor of the mud. Refer back to Figure 1. It is interesting to note that the HS⁻ and the S⁼ sulphide ions result from maintaining a high pH. Most government regulations require that a minimum pH level of 10 be maintained at all times in an H₂S environment.⁶

Popularly, only two types of scavengers are being marketed to the drilling industry currently: (1) zinc – containing chemicals; and (2) iron-oxide, Fe_3O_4 . Other commercial chemicals are also available for the job but the aforementioned two dominates in the sulphide scavenging of the oil and gas industry.

In the first premise, it is pertinent to note that several hydrogen sulphide scavengers are being employed in the oil and gas industry. The type of the scavenger needed for a specific field application depends.¹ Some scavengers work best in drilling fluids while some render themselves more readily to sweetening processes in the produced oil and gas. Therefore, the reliability of a sulphide scavenger is best evaluated in a medium where it fits most. In fact, recent studies on sulphide scavenging from drilling fluids particularly are scarce in comparison with simi-

lar studies in produced fluids or gas.

For any of the types of scavenger to be employed in the production operations, it has to meet some stringent requirements because the safety of both personnel and equipment depends on it. According to Garrett *et al*¹¹, an ideal scavenger must have the following characteristics:

- 1. Its reaction with sulphide should be complete, rapid, and predictable. The reaction product(s) formed should remain inert under all mud conditions.
- 2. Scavenging should occur in a wide range of the system's chemical and physical environments. This includes a wide range of pH, temperature, pressure, competitive reactions, shear conditions all in the presence of an array of active chemicals and solids found in muds.
- 3. General system performance, e.g. mud rheology, filtration and cake quality should not be impaired by the application of excess scavenging in the system, even at high temperatures.
- 4. The true amount of scavenger available for reacting in a mud should have the capacity to be measured quickly and easily at the rig-site.
- 5. The scavenger, as well as its reaction products, should be non-corrosive to metals and materials contacted by the mud.
- 6. Using a scavenger should not risk the safety and health of personnel or pollute the environment. On the contrary, the scavenger should make drilling in H_2S zones or sweetening processes safer.
- 7. The scavenger should be widely available and economical for industry acceptance by having a low unit

SULPHIDE SCAVENGERS IN OIL AND GAS INDUSTRY ...

cost plus high sulphide reaction efficiency under all conditions of use.

6. Hydrogen Sulphide Scavengers Used So Far in the Industry

The first generation of hydrogen sulphide scavengers developed as could be observed from literatures are those to be discussed first.

Copper compounds, especially copper carbonate⁵ have been used in the drilling operations to remove H_2S . Actually if added to water-base muds, the H_2S will precipitated out as insoluble copper sulphide according the following equation:

$$CuCO_3 + H_2S \rightarrow CuS \downarrow + H_2O + CO_2 \uparrow$$
(4)

Even though, tests have shown that the its reaction with sulphide is very fast and efficient, it is impractical to use it as a pre-treatment during drilling operations as copper will plate out on any ferretic material and set up a corrosion cell. There are reports that these scavengers have caused a lot of corrosion problems in production fields due to this fact.⁵

Moreover, it can be concluded that copper compounds can be used to remove hydrogen sulphide where there will be no contact with any ferretic material, for instance if hydrogen sulphide is brought to the surface due to a large influx of the gas.

Hydrogen peroxide has also been suggested as an additive to mud at the flowline to convert hydrogen sulphide to free sulphur according to the reaction:

$$H_2O_2 + H_2S \rightarrow S^0 + H_2O \tag{5}$$

The chemistry of the reaction is sound but the practical application is very limited as the hydrogen peroxide is too reactive with other components of the system.⁵ Due to this, it will be impossible to have a satisfactory removal of hydrogen sulphide.

Another approach is the addition of zinc-containing chemicals and zinc oxide (ZnO), zinc carbonate (ZnCO₃) and basic zinc carbonate (Zn₅(OH)₆(CO₃)₂) are still being used for the job in the industry.¹⁶ The solubility of ZnO and ZnCO₃ rapidly increase at either high pH or low pH because of the amphoteric nature of zinc compounds but basic zinc carbonate is soluble at both ends of the pH scale.¹¹ If mud pH is higher than about 11 (as is frequently the practice in drilling), zincate ions form, which greatly increase the solubility of the basic zinc carbonate. Zincate ions form because of the abundant OH combine with the zinc ions.¹¹

$$Zn_{2+} + 3OH \rightarrow Zn(OH)_{3} -$$
(6)

$$Zn(OH)_{3-} + OH- \rightarrow Zn(OH)_{4-}$$
⁽⁷⁾

Due to this phenomenon, a zinc-base scavenger can dissolve completely in high pH muds giving high concentration of zinc or zincate ions for fast and complete precipitation of the sulphides. This makes the zinc-base scavengers efficient.

However, moderate to heavy additions of zinc-base chemicals causes detrimental effects to mud rheology, es-

pecially flocculation, and causes fluid loss. This is accentuated especially at high $pH.^{11}$

Iron compounds were also tested and put to practice up till the current time to remove sulphide during drilling or in the produced fluids. The only inorganic iron-base chemicals currently used as scavengers in drilling and produced fluids are iron oxides, which are insoluble in both water and muds. Reaction mechanisms between iron oxides and soluble sulphides that cause the formation of various iron-sulphur compounds may involve changes in oxidation state, precipitations, or combinations of both.

However, some drilling fluid specialists, especially Alvin³, Ray *et al*²⁰ and Garrett *et al*¹¹ have really researched into the scavenging technology of the iron oxides and they concluded that a synthetic magnetic iron oxide with the trade mark name *ironite sponge* (magnetite Fe₃O₄) is the best among the iron oxides for sulphide scavenging tasks. But, they observed in various tests that low pH speed the reaction of ironite sponge with hydrogen sulphide.

Laboratory tests of sulphide scavengers have used easily handled sodium sulphide crystals instead of highly toxic H_2S gas. In tests where basic sodium sulphide was added to the muds instead of H_2S gas and since iron oxide appears to react only with H_2S , the following reactions was proposed for a solution of sodium sulphide in water.

$$Na_2S + H_2O \leftrightarrow NaHS + NaOH$$
 (8)

 $NaHS + H_2O \leftrightarrow H_2S + NaOH$ (9)

$$Fe_3O_4 + 6H_2S \rightarrow 3FeS_2 \downarrow + 4H_2O + 2H_2$$
 (10)

Since both solution reactions would tend to go to the left at high pH, the small partial concentration of H_2S would explain the observed very low reaction rates of iron oxide with sodium sulphide in muds with pH of more than 8.

The much higher reaction rates observed in iron oxide can be caused by higher pressure and temperature.³

But the fact is that the precipitation of sulphides by the iron oxide is essentially an oxidation-reduction reaction between the gas and the solid, which actually proceeds faster at low pH and slow at high pH.²⁰ This limitation does not allow the ironite sponge to be tagged ideal by the specialists because it is unusual for a mud to have acidic pH ranges.

The search for ideal scavengers continued up to the recent development sulphide scavengers. Some of the findings done in developing/sourcing new scavengers, especially organic compounds and chelates, after the first generation of H_2S scavengers are briefly reviewed below.

Charles and others⁷ observed that chemical techniques applied to oilfield waterflood operations (which are the main cause of biogenic sulphides in the industry) involve basically the use of neutralizers, oxidizers, and scavengers. Historically, neutralizers-such as sodium hydroxide, ammonia, and amines-were used first in an attempt to remove hydrogen sulphide from produced fluids. These materials are inexpedient because the hydrogen

SULPHIDE SCAVENGERS IN OIL AND GAS INDUSTRY ...

M.K. AMOSA, I.A. MOHAMMED, AND S.A. YARO

sulphide can be easily regenerated within the oilfield waterflood systems when pH changes. Chemical oxidizers can remove hydrogen sulphide from oilfield waterflood operations but can produce undesirable side effects, such as corrosion and the formation of unwanted solids. Examples of oxidizers include chlorine, chlorine dioxide, hypochlorite, hydrogen peroxide, and thiosulphate.⁷

They also reported that some attempts to use metallic salts and oxides as scavengers in oilfield waterfloods have resulted in the formation of undesirable solid, metallic sulphides. Metallic salt coatings on zeolite filter agents have been suggested as an alternative.

Charles *et al*⁷ compared hydrogen peroxide and some chlorine-containing chemicals with the scavenging ability of acrolein and formaldehyde in the waterflood system. They reached a conclusion thus: "Hydrogen peroxide was able to provide some control, although some concern for concurrent accelerated oxygen corrosion in actual field systems is anticipated. The chlorine-containing chemicals (chlorine dioxide and sodium hypochlorite) appear to remove the hydrogen sulphide effectively in acidic and neutral waters but begin to decline in effectiveness under alkaline conditions. These chlorine-containing materials formed particulates (colloidal sulphur) during these experiments, which can be corrosive."

The final conclusion was that both formaldehyde and acrolein are aldehydes and the best performance of these sulphide scavengers can be seen in surface cleaning operations in the treatment of oilfield water flood systems. Good performance results depend on the nature of the system and the mechanism of the scavenging process. Once, these concepts are identified within a given system, economic judgments can be made.⁷

It can be observed from the above researches that formaldehyde, apart from being used as scavenger in muds and produced fluids and gases, can also be applied in the surface cleaning of waterflood systems.

However, in the case of possible processes based on organic reactants such as acrolein, formaldehydes and others, there were outstanding questions concerning health, safety, and environmental aspects of the reactants and reaction products. For instance, it is established fact that formaldehyde has a limited use in the oil industry because it is carcinogen.¹⁸

It is recommended that more of the aldehyde family should be put into test in order to decide whether some other aldehydes can be used as safe scavengers.

Sitz *et al*²¹ has once worked on amine-aldehyde condensates and they concluded that these condensates are suitably used for hydrogen sulphide removal from the produced fluids to meet the sales specification for the maximum allowable hydrogen sulphide concentration in the gas of 4 ppm. But one of the drawbacks associated with the products is their expensiveness considering the large amount of fluids to be treated.

They highlighted that nitrate solutions, acrolein, caustic scrubbing, formaldehyde and amine-aldehyde condensates are best applied as scavengers (for sweetening purpose) in produced oil, water and gas.²¹

Nasr-El-Din et al18 has also investigated that with pipelines or refinery operations, surface cleaning is the major goal of the operation. It was observed that several different suppression technologies have been developed for surface cleaning operations. Suppression chemicals that contain aldehydes were developed of which most efficient agent is formaldehyde, which reacts stoichiometrically with hydrogen sulphide to produce trithiane, a very insoluble material. But one of the biggest drawbacks associated with these organic chemicals, apart from the fact that they undergo very complex chemical reactions and expensiveness of some them, is their toxicity to humans, for instance the carcinogenic altitude of formaldehyde mentioned previously. Besides, they also observed that these chemicals are best applied in refinery operations such as gas sweetening or other surface cleaning operations.18

In a US Patent filed by Frenier¹⁰, he investigated that chelating agents such as ammonium salts of ethylenediaminetetraacetic acid (ammoniated-EDTA), hydroxyethylethylenediaminetriacetic acid (ammoniated-HEDTA), and ammoniated-DPTA are all useful as sulphide scavengers up to the temperature of 200 °C but their scavenging ability decrease at temperatures below 100 °C.¹⁰ Summarily, these chelating agents are not suitable as scavengers in drilling operating conditions where there can be temperature of up to 500 °C depending on the depth of the well.

Alan *et al*² observed that triazine based scavenger is well established and effective when applied to oilfield process problems but the drawback is that at temperatures lower than 40 °C, triazine/H₂S scavenging rates become increasingly low. They further investigated that stabilized chlorine dioxide is an efficient scavenger at a wide range of temperatures in produced fluids. But these investigations were carried out in mitigating SRB-generated sulphides in long transport pipelines and storage tanks. They noted that chemical products such as aldehydes, nitrites, peroxides, chelated iron, amines, triazines and chlorine dioxide are efficiently applicable in sweetening processes, i.e., for scavenging sulphides in produced fluids and that the chemicals are not really applicable in drilling operations.

Norman et al¹⁹ also observed that although inorganic materials which have been tried as sulphide scavengers include copper compounds, sodium nitrite, hydrogen peroxide, sodium chlorite and chlorine dioxide. All have at least one or two disadvantages. Some compounds are harmful, corrosive or have corrosive by-products, may be unstable or potentially explosive and may require special handling technique. And that the organic scavengers have been tried include formaldehvde. which glutaraldehyde and particularly glyoxal as well as glyoxal/surfactant mixtures. They investigated that none of these materials is particularly satisfactory. They are very slow in reaction with hydrogen sulphide, are unstable at high temperature and pressure and solidify at low temperatures and on long term storage. Some are also expensive, bearing in mind the large volume of hydrocarbon-water mixture to be treated. If a slow reacting hydrogen sulphide scavenger is used, for example glyoxal, it may be necessary either to introduce it at a point which

would allow the maximum reaction time or to substantially increase the dosage.

They further searched for a suitable scavenger which will be stable at extreme conditions of well deepness of about and beyond 8 000 feet (2 438.4 m) and at elevated temperatures of 54 °C and above and elevated pressures of up to 5 200 psi (538 bar) and above. They finally selected ammonium bisulphite and they investigated that the material, but despite its high solubility in water, it works best as a scavenger when the weight ratio of scavenger to hydrogen sulphide is considered. The weight ratio of scavenger to hydrogen sulphide can be as low as 2:1 when long reaction times (e.g. 20 hours) are used, but for shorter time (e.g. minutes) a weight ratio of 7.4:1 or greater is required. Even in trying to achieve satisfactory results, weight ratio of scavenger to sulphide as high as 20:1 has been found.14 However, careful observations must be made as to whether the rheological properties of a mud will not be upset when larger concentrations of the scavenger are applied. Scavengers generally are required in small in small amounts. As majority of these scavengers are expensive, the proper method for adding them is important both practically and economically.

Also, an ideal scavenger must have a characteristic of instant and complete removal of sulphides in a system and this is contrary to what was observed in ammonium bisulphite tested.

Though in some areas where hydrogen sulphide may be encountered during drilling operations it has become a practice to use oil-base muds, but this seems to provide protection for the metal goods only. The solubility of hydrogen sulphide oil is greater than it is in water and more pressure dependent, therefore more hydrogen sulphide could be carried in an oil mud downhole and release all at once when pressure is removed causing a large volume of free hydrogen sulphide at the surface.⁵ This will potentially cause health hazards to the personnel working on the field. For this reason, application of hydrogen sulphide scavengers is pertinent even when using an oil-base mud for the safety of personnel to be ensured. Garrett *et al*¹² has tested some chemicals to be best applied in oil-base muds. The only concern raised concerning the application of scavengers in oil-base muds is in the aspect of their solubility in the muds.

Garrett *et al*¹² investigated two hydrogen sulphide scavengers (zinc oxide, an inorganic, insoluble, white powdered chemical containing 80 wt% Zn, and zinc naphthenate, an organic, oil-soluble, dark-brown liquid of mixed molecular composition containing approximately 12 wt% Zn) on an oil-based mud.

After the tests, they concluded that the inorganic compound is a good candidate for an H_2S scavenger for oil muds. It is readily available, low in cost, and high in the percentage of zinc. This compound scavenged all the H_2S in a quicker way than the zinc naphthenate by converting the active sulphides into a more inert form and the mud was tested "zero sulphide" after the analysis.

Nonetheless, a more efficient and environmentally benign sulphide scavenger was revealed as Eric⁹ disclosed in a US patent published in 2004 that ferrous gluconate could have an efficient sulphide removal from drilling

SULPHIDE SCAVENGERS IN OIL AND GAS INDUSTRY ...

fluids. Though Eric performed some tests to investigate the desulphurization effects of the ferrous complex, major tests were performed on knowing the effects of the ferrous gluconate on the rheology of the drilling fluid and concluded that it has no adverse effect on it. The desulphurization showed that the complex has the ability to scavenge hydrogen sulphide efficiently.

Amosa⁴ later carried out more researches on the ferrous gluconate so as to determine the feasibility of sulphide uptake and also corrosion control by the addition of the ferrous gluconate to drilling fluids in hydrogen sulphide bearing wells. Since there has not been any work done yet to represent the realistic rig-site drilling conditions to test the stability of ferrous gluconate (in terms of its H₂S scavenging and corrosion inhibition effects) especially at HTHP conditions, it was felt that a research looking at temperatures and pressures of up to 350 °F (176 °C) and 6 000 psi (413 bar) would be worthwhile so as to examine if the iron complex can be stable, and still retain its expected scavenging and corrosion inhibition properties at such conditions.

The proposed/probable reaction of ferrous gluconate with sulphides is shown in equation 11^4 :

Fe
$$(C_6H_{12}O_7)_2 + S^2 \rightarrow FeS + 2 [C_6H_{12}O_7]^2$$
 (11)

Ferrous gluconate + Sulphide \rightarrow Ferrous sulphide + gluconate

Amosa⁴ performed tests on the desulphurization effect of the complex at various temperature conditions of 25 °C, 35 °C, 45 °C and 55 °C and agitated for a total time of 140 minutes. Same tests were also carried out on magnetite (*ironite sponge*) for comparison sake. The scavenger concentration to sulphide concentration was in the ratio of 1:1 for all the test conditions. The sulphide content was measured at 20 minutes interval of agitation and it was observed that temperature condition as low as of 25 °C can efficiently aid in the scavenging ability of the complex. It was also observed that the higher the temperature of the medium, the higher the rate of reaction between the scavenger and the sulphide. This was observed throughout the test conditions for both ferrous gluconate and magnetite. The mud was tested zero-sulphide content within 40 minutes of agitation when at 25 °C but the zero-sulphide content was achieved within the first 20 minutes of agitation at temperature of 55 °C (Table 3). The ferrous gluconate was able to scavenge the sulphide at 100% efficiency whereas magnetite's efficiency was only about 30%.⁴

It is an usual practice in drilling fluid technology that a scavenger's corrosion inhibition ability be evaluated so as to observe if the scavenger can assist in mitigating against corrosion of drilling tools. Knowing fully well that hydrogen sulphide is one of the causes of corrosion of drilling equipment, then the normal trend will be that the lower the sulphide content in the mud, the lower the corrosion rate of the drill tools. Various tests were carried out to evaluate the corrosion inhibition efficiency of the ferrous complex at various conditions of temperature and pressure of 150 °F/3000 psi (65.5 °C/206.8 bar), 275 °F/5 000 psi (135 °C/ 344.7 bar), and 350 °F/6 000 psi (176.6 °C/ 413.6 bar).⁴ Same tests were also carried out on magnetite (*ironite sponge*) for comparison sake.

SULPHIDE SCAVENGERS IN OIL AND GAS INDUSTRY..

M.K. AMOSA, I.A. MOHAMMED, AND S.A. YARO

Table 3. Comparative sulphide uptake of ferrous gluconate and magnetite											
Time Taken (mins)	Remaining sulphide content with ferrous gluconate at 25 °C (mg/l)	Remaining sulphide content with magnetite at 25 °C (mg/l)	Remaining sulphide content with ferrous gluconate at 55 °C (mg/l)	Remaining sulphide content with magnetite at 55 °C (mg/l)							
0	700	700	700	700							
20	30	690	0	620							
40	0	620	0	490							
60	0	600	0	440							
80	0	600	0	420							
100	0	600	0	410							
120	0	600	0	410							
140	0	600	0	410							

Source: Amosa (2009)

Table 4. Dependency of corrosion rates of the N-80 steel on 50 mg/l sulphide and various conditions of temperatures and pressures without any scavenger (control test)

Operation Conditions of Temperatures and Dressures	Corrosion Rate (mm/y)									
operating conditions of temperatures and Pressures	pH = 5.5	pH = 7.5	pH = 9.5	pH = 11.5						
150 °F and 3 000 psi	0.518	0.401	0.287	0.101						
275 °F and 5 000 psi	1.432	1.125	0.804	0.282						
350 °F and 6 000 psi	1.887	1.462	1.046	0.364						

Source: Amosa (2009)

Table 5. Comparative Inhibition of 50 mg/l sulphide using the two scavengers Test Conditions: 350 °F (177 °C) – 4 hr – 6 000 psi (41.4 MPa), Sulphide:Scavenger ratio; 1:1, 1:2, 1:3 & 1:4																
рН	рН 5.5				7.5			9.5				11.5				
	Scav. G Scav.M		Sca	av.G	.G Scav.M		Scav.G		Scav.M		Scav.G		Scav.M			
Inhibitor Concen. (mg/l)	Corro- sion Rate (mm/yr)	I.E. (%)														
50	0.527	72.1	0.950	49.7	0.349	76.0	0.764	47.8	0.191	81.7	0.642	38.6	0.039	89.3	0.261	28.8
100	0.018	99.0	0.788	58.2	0.013	99.1	0.660	54.9	0.010	99.1	0.544	47.9	0.004	99.0	0.242	34.0
150	0.018	99.0	0.626	66.8	0.013	99.1	0.550	62.4	0.010	99.1	0.446	57.4	0.004	99.0	0.219	40.4
200	0.018	99.0	0.471	75.1	0.013	99.1	0.434	70.3	0.010	99.1	0.342	67.3	0.004	99.0	0.194	47.2

Higher condition of temperatures and pressures contributed to higher corrosion inhibition efficiencies as observed during the corrosion tests.⁴ Ferrous gluconate exhibited almost 100% corrosion inhibition efficiency as compared to the 47% efficiency exhibited by magnetite at alkaline pH which is best for drilling fluids. It was observed that the corrosion rates were very low and pitting corrosion on the coupons was markedly reduced in the results obtained at operating condition of 350 °F/6 000 psi (176.6 °C/ 413.6 bar) as shown in Table 5 compared to the corrosion rates obtained in the control tests in Table 4. The same trend of results was obtained in the case of other operating conditions of 150 °F/3 000 psi (65.5 °C/206.8 bar) and 275 °F/5 000 psi (135 °C/ 344.7 bar).⁴

The use of ferrous gluconate as scavenger in other media such as crude oil and produced fluid is being investigated. From the foregoing, it seems the search still continues for an *ideal scavenger* for use in the Oil and Gas industry applications.

7. Conclusions and Recommendations

- Hydrogen sulphide scavengers are employed in more than one field applications like drilling operations and sweetening processes; and the type of scavenger needed for a particular application depends whether it can act better in that medium.
- Although there have been many findings on sulphide scavengers, each one of them has one or more limitations, ranging from attributed exorbitant prices to Health, Safety and Environmental (HSE) problems.
- Ferrous gluconate has been recently found to be efficient and environmentally benign but the laboratory tests still need be translated into real rig-site operation. It should also be tested in other media other than drill-

SULPHIDE SCAVENGERS IN OIL AND GAS INDUSTRY ...

ing fluid so as to evaluate its hydrogen sulphide scavenging ability in these media.

- Optimization studies on the reaction between ferrous gluconate and hydrogen sulphide need be done.
- There exist more research needs to develop or source for hydrogen sulphide scavengers, perhaps embodying complementary mixtures of chemicals or a compound specifically investigated to fit the needs and match more closely the qualities of an *ideal scavenger*.
- Thorough testing is necessary for any particular sulphide scavenger sourced or designed so as to know if it has satisfactory scavenging ability in every applications; and if it will not adversely affect the rheology (when used in drilling mud) at various conditions of temperatures and pressures. Otherwise, the researcher on the particular scavenger should state the medium where the scavenger is mostly fit for application.

References

- Al-Humaidan, A. Y., Nasr-El-Din, H. A., "Optimization of Hydrogen Sulphide Scavengers Used During Well Stimulation" SPE Paper, Intl. Symp. On Oilfield Chemistry, Texas, Feb. 16-19, 1999, Pp 2.
- Alan, A. G., Read, P. A., Wilson, R. D., "Evaluation and Field Application of A New Hydrogen Sulphide Scavenger", 10th Int'l Oilfield Chemical Symp., Norway, March 1-3, 1999. Pp 1-4.
- Alvin, S., "H₂S Need Not be Deadly, Dangerous, Destructive," SPE Journal 5202, November, 1974, Pp 150.
- Amosa, M. K., "Comparative Analysis of Hydrogen Sulphide Scavenging Effects of Ferrous Gluconate and Magnetite in Oil and Gas Drilling Fluids", Unpublished MSc Thesis, Ahmadu Bello University, Zaria, Nigeria, 2009.
- Carney, L. L., and Jones, B., "Practical Solutions to Combat the Detrimental Effects of H₂S During Drilling Operations", *SPE Journal* 5198, Nov., 1974. Pp 115-117.
- Carter, D. R., and Adams N. J., "Hydrogen Sulphide in the Drilling Industry" SPE Journal, Symp. On Deep Drilling and Production, Texas, April 1-3, 1979, Pp 125-128.
- Charles, L. K., John, L. B., and Martin, W. P., "Factors Contributing to the ability of Acrolein to scavenge corrosive hydrogen sulphide" *SPE Journal* 11749, Pp 647, Oct., 1985.
- DHEN (NIOSH), "Occupational Exposure to Hydrogen Sulphide", Publication No. 77-158, Pg 61, May 1977.
- 9. Eric, D., (2004): "Method and Composition for Scavenging Sulphide in Drilling Fluids and Composition", United States Patent 6746611, pp 1-6.
- Frenier, W. W.," Process and Composition for Inhibiting High-Temperature Iron and Steel Corrosion", US Patent 5096618, Pp 3, March 17 1992.
- Garrett, R. L., Clark, R. K., Carney, L. L., and Grantham, C. K., "Chemical Scavengers for Sulphides in Water-Base Drilling Fluids," *SPE Paper, Annual Mtg.*, Houston, June, 1979, Pp 787-794.
- Garrett, R. L., Carlton, L. A., and Denekas, M. O., "Methods for Field Monitoring of Oil-Based Drilling Fluids for Hydrogen Sulphide and Water Intrusions," SPE Journal, Pp 93, March, 1990.
- Hudgins, C.M., McGlasson, R. L., Mehdizadeh, P., and Rosborough, W.M, "Hydrogen Sulphide Cracking of Carbon and Alloy Steels," Corrosion, pp. 238-251, August, 1966.
- 14. Jiang, L., Jones, T.G.J., Mullins, O.C., and Wu, X. "Hydrogen Sulphide Detection Method and Apparatus", US Patent 6939717, pp 1-2, Sept., 2005.
- 15. King, F. W., "Taking H2S from Liquid Sulphur Why and How", *The Oil and Gas Journal*, June 3, 1974, Pp 11.
- KMC Oiltools, "Drilling Fluid Engineering Manual", Version 1, Kuala-Lumpur, 2006. Section 12, pp. 1-12, Section 11b, pp 26-30.
- M-I L.L.C., "The Drilling Fluid Engineering Manual", Version 2.0 4/01, Chapter 19, Pp 12-13, 2001.
- Nasr-El-Din, H.A., Al-Humaidan, A.Y., Fadhel, B.A., Frenier, W.W., and Hill, D., "Investigation of Sulphide Scavengers in Well Acidizing Fluids," SPE Journal 80289, Louisiana, Sept., 3 2002, Pp 3.
- Norman B., and Robert, M., "Scavenging of Hydrogen sulphide", US Patent 5601700, pp 1-4, February, 1997.

Ray, J. D., Randall, B. V., and Parker, J. C., "Use of Reactive Iron Oxide to Remove H2S from Drilling Fluid", *Journal of Petroleum Technology*, 1979, pp 1-2.

- Sitz, C. D., Barbin, D. K., and Hampton, B. J., "Scale Control in a Hydrogen Sulphide Treatment Program" SPE Journal 80235, Texas, February, 5-7, 2003, pp 1-5.
- 22. Tung, N. P., Hung, P. V., Tien, P. D., and Loi, C. M., "Study of Corrosion Control Effect of H₂S Scavengers in Multiphase Systems" *SPE Journal* 65399, 2001 Int'l Symp. On Oilfield Chem., Houston, Texas, 13-16 Feb., 2001, Pp 1-3.

*

Authors:

M.K. Amosa, Department of Chemical Engineering, Ahmadu Bello University, Zaria, Nigeria, Corresponding author. Tel.: +2348052041750, +2348033981797

E-mail: dhakisalafi@live.com

I.A. Mohammed, Department of Chemical Engineering, Ahmadu Bello University, Zaria, Nigeria.

S. A. Yaro, Department of Metallurgical and Materials Engineering, Ahmadu Bello University, Zaria, Nigeria.