

Versatile Hydrogen Sulphide Scavenger Facilitates Improved Safety when Dealing with Sour Wells

Eric Davidson, D. Nelson McMillan, Alexandra Morrison, Halliburton

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Abstract

Eight years ago a major drilling fluids service company introduced a novel, environmentally friendly, hydrogen sulphide scavenger to the market place. The requirement was for a zinc free, non toxic, rapidly reacting additive to be used in water based mud. The product specifically developed for this application was a water soluble compound that performed very successfully in wells in the Caspian region with very high H₂S content (~36% in the gas phase).

Use of this additive has been refined and it now can be used to give virtually instant sulphide removal from sour slops, sour water/brine produced during underbalanced or managed pressure drilling and, with great advantage, in oil based mud. A particularly valuable feature is that the content of active sulphide scavenger in mud (water based or oil based) can be easily monitored to give a record of the capability of the mud to absorb sulphide. Thus, unlike traditional methods that involve monitoring the concentration of active sulphide brought to surface, it is possible, proactively and easily, to monitor and control the concentration of scavenger in place to prevent H₂S being brought to surface. This is considered to be a major contribution to the improvement of safety when drilling sour wells.

The paper describes the mode of action of the scavenger, explains why this additive, designed for water based mud, is so effective in oil based mud and how the iron content of the mud is monitored.

Introduction

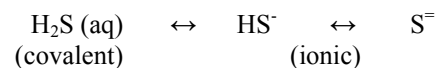
The issue of sour wells has been recognised as a major concern since the inception of the oil and gas extraction industry. H₂S in the mud system can cause major corrosion of steelwork but a much more important consideration is the risk to life.

Until the mid 1970s there was no satisfactory method for monitoring sulphide in the drilling mud system but at that time the Garrett Gas Train equipment and procedure were introduced^{1,2} and adopted as an API procedure.³

Effect of pH

Traditionally, the most common precaution to be used to control release of H₂S is to run the mud at high pH. The reason why high pH reduces the risk from H₂S is, of course,

well known but it has also been pointed out that reliance on high pH can be dangerous.^{4,5} The explanation for these apparent contradictions is quite simple. H₂S in aqueous solution can exist in two forms, ionic and covalent, as shown in the following equilibrium diagram



The covalent form is volatile and exerts a significant partial pressure, but sulphide in ionic form is non-volatile and stays in solution. The relative proportions of the sulphur in the ionic and covalent forms are a function of pH; the higher the pH the higher the proportion existing in the ionic state. The relationship between pH, sulphide concentration in the solution phase and partial pressure of H₂S in the vapour phase above the fluid has been explored and reported on extensively by Wendt.^{4,5}

Wendt estimated, as a first approximation, that at 50°C, if the concentration of sulphide in solution was less than 5000 ppm and if the pH of the solution was at least 12 then a partial pressure of H₂S of <20 ppm in the vapour phase could be achieved. This concentration was regarded by Wendt as “safe” for a working environment but it can only be maintained if the concentration in solution remains below 5000 ppm. Furthermore, with decreasing pH the tolerable dissolved sulphide concentration corresponding to the “safe” partial pressure of 20 ppm decreases markedly. For example, the maximum tolerable dissolved sulphide concentration at decreasing pH values would be as follows:

pH 11 - dissolved sulphide concentration 500 ppm

pH 10- dissolved sulphide concentration 50 ppm.

Below pH 10 even very low concentrations of dissolved sulphide can give rise to hazardous partial pressures of H₂S.

Modern regulations concerning exposure to H₂S are somewhat more stringent. Current European regulations⁶ quote 5 ppm as the long term exposure limit (10 ppm for short term – 15 min—exposure). Maintaining a target of 5 ppm would obviously be difficult. A preferable target would be zero but as pointed out by Wendt^{4,5} reliance solely on high pH cannot prevent the release of some hydrogen sulphide into the vapour phase. To achieve zero release of H₂S as vapour it

would be necessary to have recourse to scavengers that totally immobilise H₂S.

There is common belief that lime is an effective sulphide scavenger based on the following:



However, this equilibrium is highly reversible. If pH is reduced, for example due to an influx of a sufficient quantity of acid gases such as H₂S or carbon dioxide into the mud the partial pressure of the hydrogen sulphide in the vapour phase can increase, potentially to lethal concentration.

Which raises a very important question: **is reliance on high pH an adequate protection when drilling sour wells?**

Use of Garrett Gas Train

The Garrett Gas Train (GGT) provides a sensitive and reliable method for measuring the free and soluble sulphide concentration of the circulating mud. The actual apparatus and method of use are described clearly in the literature for water based mud and for oil based fluid,^{1,2} and it is not proposed to deal with such details in this paper. Irrespective of the type of fluid under test the basic feature is the same; in each case the objective is to measure the free, dissolved H₂S and the sulphide that is tied up in soluble but ionic form by high pH or “neutralised” with lime. For water based mud the liquid fraction is separated by filtration. This filtrate will contain dissolved H₂S and the soluble sulphides.

To release the dissolved sulphides an aliquot of the filtrate is placed in the Gas Train and treated with 2.5M sulphuric acid to convert ionic sulphide back to covalent volatile H₂S. The hydrogen sulphide gas is swept by a stream of inert carrier gas and passed to a tube that gives a direct read-out of H₂S concentration.

The filtration step provides a significant advantage when sulphide scavengers involving zinc or iron are concerned. Both of these types of scavenger immobilise sulphide in the form of insoluble precipitated zinc or iron sulphide. In both cases it is possible, if the pH is lowered to about 3, the sulphide can be released in the covalent, volatile form⁷ which, of course, would distort the result. Filtration removes this potential.

In the case of oil based mud the method calls for an aliquot of mud (unfiltered) to be inserted into the Gas Train and treated with an organic acid (2M citric acid) plus demulsifier to break the invert emulsion. The expectation is that the weak acidity⁷ will not release sulphide from insoluble zinc or iron scavengers or from heavy metal sulphide that might be present in mud components.

In the cases of both types of mud the objective is to measure the sulphide that is free in solution (i.e., dissolved H₂S) or “fixed” by high pH. If this analytical method shows significant or high sulphide concentrations there may be cause for concern. As Wendt has shown,^{4,5} a sulphide loading of a few hundred ppm in the mud can be changed from a tolerable to a hazardous situation by a fairly small decrease in pH of the mud. Indeed, for optimal safety it can be said that the target

hydrogen sulphide content as measured by the GGT should be zero. **Also it can be argued that one of the shortcomings of the GGT method is that it measures only what comes to surface; it tells us nothing about capability of the mud to convert the sulphide into an inactive form downhole.**

Development of “New” Sulphide Scavenger

This “new” sulphide scavenger was first introduced about 8 years ago. The development was in response to a requirement for development of a new field in the Caspian region. Experience from adjacent oil fields in that part of Asia indicated that reservoirs were very hydrogen sulphide rich. The special aspect of this particular requirement was that the field was to be developed in accordance with the highest environmental standards and potentially toxic materials would not be acceptable in drilling mud or drill cuttings. In particular this ruled out sulphide scavengers based on zinc and various organic materials. This aspect is discussed in more detail in a previous paper⁸ and it is not proposed to repeat the detailed discussions concerning other possible scavengers in this paper. However, the section below contains a summary of some of the procedures contained in the original publication.⁸

In the interests of simplicity, and to avoid having to deal with complex, and perhaps variable, end products from the reaction between H₂S and organic reactants the preferred option was to exploit the well known affinity between iron and sulphide. Iron had two particular attractions: first, like zinc, it has a high affinity to sulphide and secondly it is much less toxic than zinc, as shown in Table 1.⁸

Table 1: Toxicity of zinc and iron to various aquatic organisms

Species common name	Water flea	Opossum shrimp	Bluegill	Rainbow trout
Salt water/fresh water	freshwater	seawater	freshwater	freshwater
Tox of iron LC50 (mg/L)	30,060	90,000	51,000	20,800
Tox of zinc LC50 (mg/L)	9,800	520	3,200	2,600
Exposure time (hr)	48	96	96	96

Note that higher LC50 concentrations indicate lower toxicity of compounds (i.e., they can be present at higher concentrations before 50% mortality of test organisms is observed).

Iron, unlike zinc, is not regarded as an environmentally unacceptable element.

One option that was considered was a porous form of magnetite (Fe₃O₄). This approach has been frequently used in the industry since the early part of the last century but there are limitations; reported to be mainly completeness of reaction and reaction rate. Magnetite is a solid and obviously the potential reaction will be largely dependent on available external and internal surface area. Any reaction that proceeds beyond the surface layer will occur in the solid state so that rate of diffusion of the sulphide ion in the Fe₃O₄ lattice will be

rate limiting. There are reports that typically about 30/40% of the iron reacts², that reaction rate is favoured at pH of 8 or less and that high pH has a negative effect on rate⁹.

On the basis of findings from adjacent wells it was expected that the concentration of hydrogen sulphide in the produced fluid would be very high, at least 20% or greater. Since it was essential to minimise the chances of hydrogen sulphide gas being brought to surface it was considered that the ideal mud system would involve use of a high pH (pH ≥ 12) fluid together with a rapid action sulphide scavenger. With this requirement in mind it was considered that porous magnetite would probably be less than ideal and an alternative way of using the chemistry of iron should be examined.

Two main objectives were set for an “ideal” scavenger.

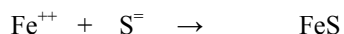
- very rapid reaction
- quantitative reaction with sulphide.

In other words, the sort of behaviour that might be expected from a soluble form of iron. Additional requirements for the iron compound were perceived to be as follows:

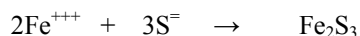
- soluble in water or highly saline brine
- remain in solution up to and beyond pH 12 without precipitation of iron hydroxide
- precipitate as iron sulphide on contact with even a low concentration of sulphide ions
- have minimal effect on mud properties before and after reaction with sulphide
- have good environmental and HSE acceptability before and after reaction with sulphide.

Soluble inorganic iron salts would not be acceptable as they would precipitate out at pH 7 or less, to produce gelatinous metal hydroxides, so the obvious line of investigation was to assess the acceptability of iron complexes⁸. The identity of potentially suitable compounds was narrowed down by calculations involving the stability constants of available iron chelates and the solubility products of iron hydroxide and iron sulphide.^{10, 11} This approach allowed some estimates to be made of pH limitations on the stability of a given complex and whether precipitation of the sulphide would be likely.

The first question to be addressed concerned the preferred oxidation state of the iron moiety. Trivalent iron had some attraction in that it can react with more sulphide than is the case for divalent iron. For example, divalent iron can react with sulphide on a mole per mole basis:



Whereas the reaction with trivalent iron is more complex, for example:



However, the trivalent iron proceeds to oxidise some of the sulphide to elemental sulphur as represented by the following equation;



In summary, the overall implication is that iron in the 3+ oxidation state would appear to be able to remove 50% more

sulphide than an equivalent weight of iron in the 2+ oxidation state, indicating the possibility of extra efficiency.

However, the hydroxides of Fe (III) have much lower solubility than those of Fe (II) and this made it more difficult to achieve the desired degree of stability required in solutions of high pH. As predicted, Fe (III) complexes involving simple amino carboxylic acids had very limited tolerance to high pH.

The iron complex ultimately selected was a chelated form of ferrous iron. The compound had excellent performance regarding toxicity and environmental risks. For example, this chemical finds use as a fertiliser for aquatic plants and as a food supplement for humans. According to North Sea OSPAR OCNS (Offshore Chemical Notification Scheme) classification this compound has a GOLD rating, which means that it falls within the most environmentally benign range of chemicals.

To establish the acceptability of this compound as a practical sulphide scavenger, two series of tests were completed.

1. potential impact on properties of the drilling mud
2. degree and rate of removal of the sulphide

Impact on Mud Properties

The tests were designed with the conditions of the probable first application in mind. That is, the water based mud formulation was optimised for 127°C. Then the properties of various combinations were tested as shown below:

- mud with no sulphide or scavenger
- mud with added sulphide
- mud with added scavenger
- mud with added sulphide and iron complex.

Conditions and concentrations were adjusted to be as near as possible to the expectations for the first applications, and all tests were done after hot rolling the fluids at 127°C.

This test work is described in greater detail in the original paper⁸ but in summary, neither the scavenger nor the scavenger plus sulphide had any significant detrimental impact on mud properties.

Degree and Rate of Sulphide Removal

A relatively simple procedure was adopted for investigating the rate and degree of reaction. Performing tests on base brine of appropriate pH was more useful than working with whole mud. In that way, complicating effects due to other components such as barite or polymers were avoided.

Saturated sodium chloride brine at 1.2 sg was treated with potassium hydroxide to bring the pH up to 12. Then, a known quantity of sodium sulphide was dissolved in the brine to simulate the effect of absorbing H₂S in brine at high pH. In such circumstances, the hydrogen sulphide would be predominantly present in the ionic form^{1,2} therefore, adding sulphide that was already in ionic form simplified the test procedure and avoided the risks associated with working with H₂S gas.

The next step was to add the stoichiometric appropriate amount of scavenger under test and then monitor the decrease

in sulphide concentration over time. Order of addition was also tested, that is, treating the brine in advance with the scavenger and then adding the sulphide. This was carried out at 35°C. As expected, order of addition had no effect on the reaction.

In brief, the reaction rate of sulphide and the Fe complex was found to be extremely rapid and quantitative (Fig 1). In these tests, three samples of brine at pH 12 were treated with equivalent concentrations of sodium sulphide. Then, the samples of brine were treated with the stoichiometric equivalent quantities of either the soluble Fe complex, porous Fe₃O₄ or zinc oxide. The results are summarised in Fig 1.

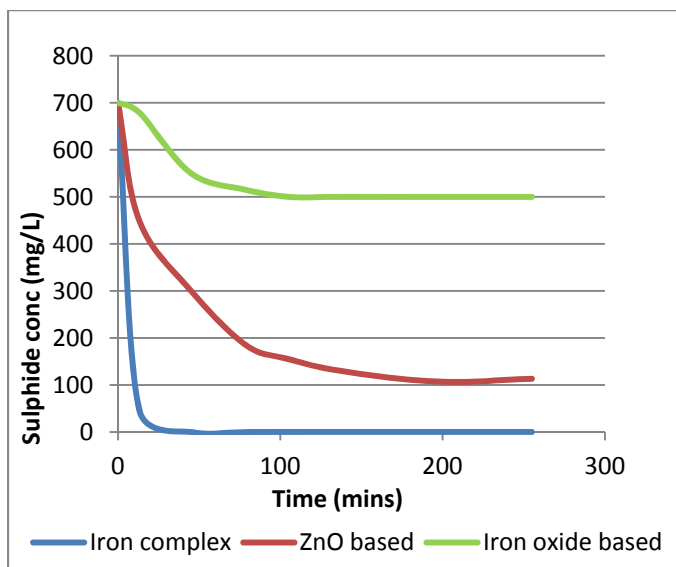


Fig 1. Reaction rates for three types of sulphide scavenger

The results shown in Fig. 1 are exactly what would be expected when comparing the action of a soluble scavenger with that of insoluble solids. In one case, the soluble iron is available for instant and complete reaction; the reaction is almost certainly of the extremely rapid ionic type. On the other hand, the solids have an initial fairly fast reaction, but the rate reduces rapidly and the reactions appear to be complete well before all of the scavenger has reacted. The speed of action of the iron complex is consistent with the prospect that all of the sulphide can be scavenged well before the mud returns to surface. This not so obvious for the zinc and iron oxide based scavengers.

Field Experience

This section is a brief description of tests and observations that are treated in more detail in a previous paper⁸.

Experience with wells drilled onshore in adjacent areas of the Pri-Caspian Basin suggested a high probability of encountering high concentrations of H₂S in the reservoir. The well was programmed so that the 8½-in section, which would drill into the expected limestone reservoir would use a

relatively simple water-based mud as the bottomhole static temperature (BHST) was expected to be only a little over 100°C. The formulation and mud properties are given respectively in Tables 2 and 3.

Table 2: Fluid formulation from first well where iron complex was used

Seawater, m ³	0.7
KOH (kg/m ³)	3.65
Lime (kg/m ³)	4.6
Filtration Control 1 (kg/m ³)	6.0
Filtration Control 2 (kg/m ³)	0.6
Filtration Control 3 (kg/m ³)	13.6
Viscosifier/Suspension (kg/m ³)	3.0
Iron complex (kg/m ³)	6.0
Alkalinity control (kg/m ³)	1.93
Deflocculant (kg/m ³)	0.94
Biocide (kg/m ³)	1.45
Barite (kg/m ³)	1036

Table 3: Fluid properties on the first well where iron complex was added to the fluid system

Mud Density (sg)	1.95 to 1.98	
Plastic Viscosity (cps)	28 to 35	
Yield Point (lb/100ft ²)	22 to 30	
Gels (Pa)	10 sec	3 to 12
	10 min	12 to 28
pH	8.8 to 10.9	
API Fluid Loss (ml/30 min)	<5.0	
HPHT Fluid Loss (ml/30 min @ 120°C, 500 psi)	<20.0	

In addition to hydrogen sulphide, CO₂ was also expected to be present in the reservoir. An alkalinity control agent was added to control the CO₂ as well as an excess of lime. A Garret Gas Train was run daily and on bottoms-up to monitor the levels of these acid gases in solution. The new iron complex scavenger was included in the mud and proved to be so effective that hydrogen sulphide was never detected in any of these tests. CO₂ was found to be present and was measured to a maximum of 3000 mg/l after one wiper trip. At the time, the apparent absence of any detectable H₂S called into question whether the formation actually did contain sulphide as expected. Such doubts were instantly dispelled after the first core was taken and brought to surface under strict hydrogen sulphide safety procedures; high concentrations of hydrogen sulphide were bleeding out of the core.

The subsequent well tests gave very similar results. The produced oil content contained 6% hydrogen sulphide and 2% CO₂. During core testing hydrogen sulphide was measured at concentrations varying from 20 to 28% in the gaseous phase.

Scavengers for Oil Based Mud

Scavenging H₂S from oil based mud is superficially complicated by the presence of two phases in which the gas is soluble. Hydrogen sulphide, under normal conditions, is three times more soluble in oil than in water¹² although this relationship can be disturbed by adjusting the pH of the

aqueous phase. Furthermore, oil (except in very unusual circumstances) comprises the majority of the liquid phase. Thus, there are good superficial reasons for expecting that any sulphide scavenger intended for oil based mud would need to mainly target the oil fraction, or even tackle each phase separately.

Early attempts to optimise sulphide scavengers for oil based mud tended to concentrate on the oil fraction. For example, Garrett² investigated the possible use of oil soluble zinc salts such as zinc naphthenate. This approach produced some reaction but it was very slow. A rather surprising observation was that in these tests zinc oxide was more effective than the oil soluble zinc compound. Tests on samples of oil based mud contaminated with hydrogen sulphide and then treated with the stoichiometrically appropriate quantity of zinc naphthenate or zinc oxide were carried out over extended periods. After a contact period of 96 hours zinc oxide had reduced the sulphide by 54% and the equivalent value for zinc naphthenate was 14%. When an eight fold excess of the scavengers was used zinc oxide achieved a 90% sulphide removal after 5 hours contact time and 100% removal after 22 hours. The same test involving zinc naphthenate removed only 70% after 96 hours of contact.

The slow reaction of the organic compound with sulphide in the oil phase was not very surprising. It is generally observed that organic chemical reactions tend to be much slower than reactions in the inorganic solution state. However, the removal of sulphide by the wholly inorganic zinc oxide was also unacceptably slow. Ideally we would hope to match the performance of the iron complex in water based mud: that is, sufficiently fast to ensure removal of sulphide before the mud returned to surface.

On the basis of the test work done with water based mud and porous Fe₃O₄ or zinc oxide there was little prospect of a faster performance in oil based mud. However, consideration of the physical chemistry of the distribution of the hydrogen sulphide between the oil and aqueous phases suggested that the iron complex could be effective in that type of fluid.

It is a general principle of physical chemistry that when two immiscible phases are in contact and there is a third phase which is soluble in both of the other two, then, at equilibrium, the third phase will be distributed between the other two according to the chemical activity of the third phase. At low concentration it is an acceptable approximation to use concentration rather than activity. Therefore, since we know that hydrogen sulphide is three times more soluble in oil than in brine¹² we can calculate the so called partition coefficient ($K_{O/B}$) which is the ratio of the concentration of hydrogen sulphide in oil and the concentration of hydrogen sulphide in brine. For oil and brine the approximate value of $K_{O/B}$ for hydrogen sulphide (conc in oil/conc in water = $K_{O/B}$) is 3.¹²

An implication of the existence of the partition relationship is that if the hydrogen sulphide is removed (chemically or mechanically) from either of the phases then hydrogen sulphide will migrate to the depleted phase to maintain the ratio of three. Iron complex in the aqueous phase provides a mechanism for rendering the sulphide insoluble and inactive, so there was the expectation that to maintain

equilibrium, hydrogen sulphide would diffuse from the oil phase into the brine. In other words, it was expected that the iron complex in the water phase might “suck” the hydrogen sulphide from the oil phase. Also because the water phase is dispersed in the continuous oil phase in the form of very small droplets the interfacial area between the two phases is very large; thus facilitating rapid exchange of H₂S from the oil to the aqueous fluid containing the sulphide scavenger.

Hence, it seemed a promising line of investigation to test the iron complex on oil based mud.

Iron Complex and Oil Based Mud

The first, and perhaps most important, point to check was the compatibility of the iron complex and sulphide with oil based mud. Table 4 shows results for formulations and tests.

Table 4: Effect of iron complex and sulphide on OBM mud properties

Component	Concentration	Mix 1	Mix 2	Mix 3
Diesel	bbl	0.555	0.555	0.555
Emulsifier 1	Lb/bbl	7.0	7.0	7.0
Emulsifier 2	Lb/bbl	3.0	3.0	3.0
Viscosifier	Lb/bbl	2.5	2.5	2.5
Fluid loss additive	Lb/bbl	8.0	8.0	8.0
Lime	Lb/bbl	4.0	4.0	4.0
Water	bbl	0.095	0.095	0.095
CaCl ₂	Lb/bbl	16.4	16.4	16.4
Barite	Lb/bbl	419.0	419.0	419.0
Iron complex	Lb/bbl	8.0	---	8.0
Na sulphide	Lb/bbl	--	13.0	13.0
Hot rolled 90°C	Units			
PV	cP	29	30	30
YP	Lb/100 ft ²	11	8	7
10 sec gel	Lb/100 ft ²	5	3	3
10 min gel	Lb/100 ft ²	10	7	8
Electrical stability	volt	575	556	458
HTHP Fluid loss 90°C	ml/30 min	3.0	4.4	3.8

The data in the table show that the properties of the mud were very constant when treated with sulphide, the iron complex or a combination of the two. Such variations as were apparent were relatively insignificant and the mud could be easily treated to correct the minor deficiencies.

Field Experience with Oil Based Mud

In this case preliminary laboratory tests on the removal of sulphide from mud tests were omitted. Since it was expected that inclusion of iron complex in the mud would cause no significant problems it was considered an acceptable risk to embark on field trials with no further preliminary tests.

Initial application was in the North Sea and following very successful results (i.e., no hydrogen sulphide returned to surface) use has spread around the globe. The scavenger has been found to be particularly useful in the North Caspian area.

A recent paper has covered in detail the introduction of a routine field based method for monitoring the concentration of active iron complex in the mud system.¹³ The requirement for this method (which is applicable to water or oil based mud) was necessary for better control over the concentration of scavenger used, allowing for better control over costs and

safety. For safety it is necessary to maintain an adequate concentration of scavenger in the mud, particularly after a gas influx, etc., but to avoid working with an excessive concentration, to control cost.

The recent paper¹³ provides details of the operations in Kazakhstan and fully describes the analytical method for the determination of free iron (The method is also reproduced as the Appendix below). A chart taken from the original paper¹³ showing the good control over the active scavenger concentration that is provided by the analytical method is reproduced in Fig 2 below.

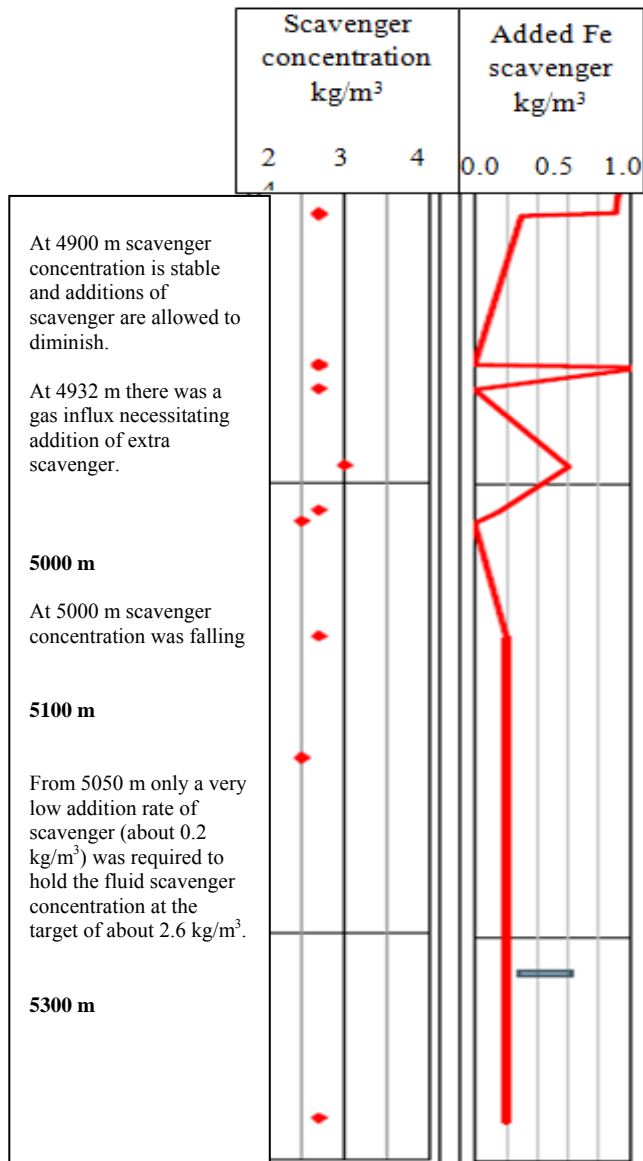


Fig 2 Scavenger addition rate trends and scavenger concentration trends in the fluid while drilling through the reservoir section

A major advantage of the ability to monitor the scavenger content of the circulating mud was that it was possible to be proactive with respect to controlling production of H₂S back to surface. In the event of detection of gas influx the concentration of scavenger could be immediately reinforced to prevent depletion.

As can be seen from the analytical method described in the Appendix, the method for monitoring the scavenger (i.e., via its iron content) is very simple even for operation in the field. Also the high effectiveness of the iron provides a measure of the ability of the mud to fix sulphide in situ, downhole. For example, it is known that free iron and H₂S cannot coexist. If there is adequate free iron in the fluid then return of H₂S to surface will be impossible.

This capability represents a much greater level of safety than can be offered by the standard method of using the GGT to monitor the concentration of “available” sulphide in the mud returned to surface.

Application of the Scavenger to Novel Situations

Low toxicity, very rapid reaction and water solubility have made this scavenger very suitable for use where very rapid removal (or prevention) of volatile sulphide is required. Two significant cases involve sour (or potentially sour) slops being returned from offshore and returns from underbalanced drilling operations.

Slops

In the case of operations offshore for a major Norwegian oil company, there are strict codes of conduct regarding transport of water and/or slops back to the shore. Fluids and containers must all be tested before being transported. Relevant excerpts from the instructions are:

1. If no hydrogen sulphide gas (H₂S) is detected, we recommend that the hazardous waste water/slop is pre-treated as standard precaution prior to any backloading. It is our recommendation that 2.5 kg of “iron complex” and 1.5 kg of biocide is added per m³ of liquid waste prior to backloading.
2. If H₂S is detected, it is recommended that a drilling fluid service representative is contacted, and given the measured concentration and total volume of waste water/slop. The representative will then make up a recipe for further treatment of H₂S on the rig. Upon completion of treatment and no detectable H₂S, it is recommended that 1 kg of “iron complex” and 1.5 kg biocide per m³ of waste water/slop is added as precaution prior to transferring liquid hazardous waste to offshore supply vessel.

Underbalanced Drilling

This was a situation for which conventional sulphide scavengers were totally unsuitable. Underbalanced drilling operations under way in Saudi Arabia involved the use of drill water as the power fluid but the power fluid plus produced water returned to surface was very rich in H₂S (up 500 ppm). Accordingly, the water needed to be treated immediately on

return to surface and only a very short time for reaction was available. Initial attempts to use conventional insoluble scavengers such as zinc oxide/carbonate or porous iron oxide failed. The insoluble solids merely fell out of suspension. However, the iron complex applied in solution form was a totally satisfactory solution to the problem.

Conclusions

- The sulphide scavenger that was developed for water based mud has been found to be equally effective on oil based mud.
- Because the scavenger is based on an iron complex it is a simple matter to monitor the soluble iron content of the mud.
- The soluble iron concentration provides a measure of the ability of the mud to scavenge sulphide.
- Standard methods of monitoring H₂S in drilling mud traditionally have mainly involved measuring the concentration of the gas or available sulphide brought to surface. This new method concentrates on the ability of the mud to absorb H₂S; for example while there is free iron in the mud, sulphide will be captured. Thus, by monitoring the capability of the mud to absorb H₂S it is possible to minimize the chances of gas being brought to surface. This ability represents a major improvement in the safety of working on sour wells.

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Appendix: Field method for monitoring available iron content in the mud

To help ensure adequate scavenging of hydrogen sulphide during drilling operations, an excess of the unreacted Fe(II) complex must be maintained within the mud. Verification of this excess required the development of a suitable field test method. A method was designed to measure the excess of iron based H₂S scavenger in invert oil emulsions.

Scope

Determination of residual iron scavenger in an oil based mud by the API CHEMets Iron in Brine Test Method: (measuring free iron in mg/L).

Reagents

Emulsion breaker: N-propoxy propanol (PNP)

Equipment

Proprietary Iron Test Kit (#K-6002), high shear mixer, mixing cups, API filtration apparatus (low-pressure), graduated cylinders (10 mL, 25 mL), disposable syringes (5 mL, 25 mL).

Procedure

1. A standard curve was developed by mixing solutions of deionized water with varied concentrations of iron scavenger. Suggested concentrations: 0.0, 0.5, 1.0, 1.5, 2.0, 2.5 lb/bbl. These solutions were hot rolled at 150°C, for one hour (Fig A1).
2. The proprietary Iron Test kit was used to determine the mg/L iron for each prepared sample in step 1. Using these data, a standard curve was then constructed, correlating the measured iron (mg/L) and the scavenger (lb/bbl) in deionized water.
3. Next, treat one (1) bbl of mud with 1% by vol. demulsifier plus 20 mL of PNP; then mix 15 minutes with high shear mixer, and collect the filtrate. This step is to break the emulsion and recover free iron in the water-phase of the filtrate.
4. Perform an API filtration test to acquire enough filtrate for analysis. Ensure filtrate is clear; if not, treat filtrate with flocculent and/or centrifuge, and repeat filtration to remove the suspended solids.
5. Determine the mg/L free iron on water-phase of the mud filtrate using proprietary Iron Test Kit (K-6002).
6. This iron value measured, in the mud filtrate, is then correlated with a concentration of scavenger found in

deionized water determined in the calibration curve.

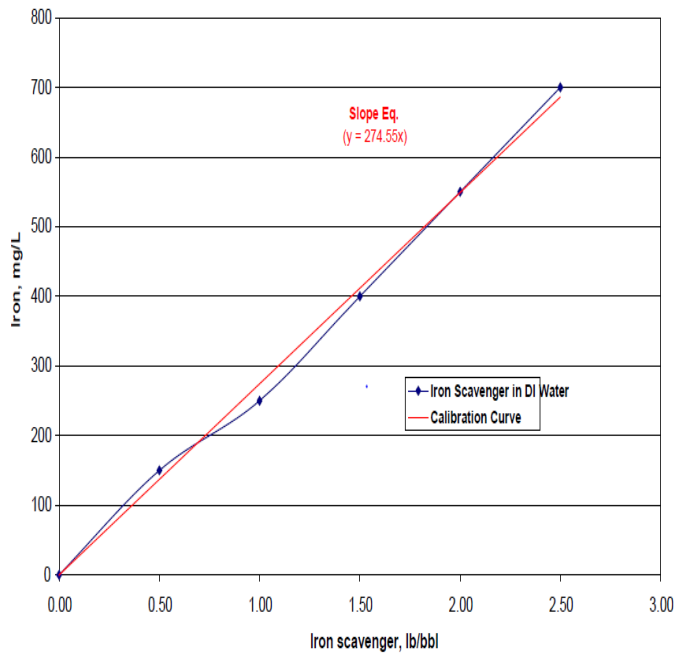


Fig A1. Calibration curve relating iron complex concentration and iron concentration

Table A1: Data for calibration curve

Scavenger in DI Water (lb/bbl)	Iron (mg/L)
0.00	0
0.50	150
1.00	250
1.50	400
2.00	550
2.50	700