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Zinc Ammonium Carbonate for Controlling Hydrogen Sulfide Gas During Drilling

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Abstract

An approach to controlling hydrogen sulfide gas is presented that utilizes zinc ammonium carbonate as the scavenger. Results are compared to standard hydrogen sulfide scavenger chemistries used in the drilling process.

A low solids water-based mud containing API Bentonite, xanthan gum, and lignite was created as a basis for evaluation. The pH of the formulation was adjusted to 10.5. The hydrogen sulfide scavengers were added to the formulation and mixed for one hour. Due to the dangers of handling hydrogen sulfide gas in the lab, sodium sulfide nonahydrate was used as a substitute. Samples were hot rolled for five hours at 150 degrees Fahrenheit. Filtrate was collected using the API fluid loss method and analyzed via Garrett Gas Train to determine the effectiveness of the scavengers.

The sodium sulfide nonahydrate was added to the mud base at 5.75 lb/bbl for testing. A mud not containing a scavenger was used as the baseline for the testing. The results of the testing indicate that zinc ammonium carbonate is an extremely effective scavenger when compared on an as-is basis to triazine, a scavenger commonly used in the industry today. Zinc ammonium carbonate at 1 lb/bbl virtually eliminated the presence of sodium sulfide in the filtrate water, removing 99.9% of the sodium sulfide present. At the same dose rate, triazine only removed 63% of the sodium sulfide present.

The study introduces another very effective and efficient alternative that can be used in controlling hydrogen sulfide for the protection of personnel and assets.

Introduction

Drilling for hydrocarbons in areas that contain hydrogen sulfide (H_2S) requires care and planning to ensure the safety of rig personnel and protection of assets.

H_2S gas is an extremely toxic gas that can cause immediate death if present at levels as low as 1,000 parts per million (ppm). Detection levels on rigs in excess of 10 ppm are considered actionable emergencies. Table 1 shows the short-term symptoms and effects of H_2S gas exposure as defined by the Occupational Safety and Health Administration (OSHA). H_2S is also extremely corrosive to most metals and can cause cracking in drill pipes and tubing and can also destroy testing tools and wirelines (Alkamil et al. 2018).

H_2S encountered when drilling is naturally formed by the thermal conversion of decayed organic matter (kerogen) that is trapped in sedimentary rocks. High-sulfur kerogens release hydrogen sulfide during their decomposition which is trapped in oil and gas reservoirs until they are encountered during the drilling process (H_2S in Oil Industry. 2017).

When drilling in H_2S bearing formations, careful planning is required. Special consideration must be paid to personnel safety, drilling fluids, tubulars, blowout preventers, onsite equipment and H_2S scavengers.

H_2S scavengers are added to drilling fluids when drilling in areas known to contain H_2S. Typically, H_2S scavengers are used in water-based drilling fluids (WBM) but are sometimes used in oil-based drilling fluids (OBM) as well.

The focus of this paper will be on a new H_2S scavenger based on zinc ammonium carbonate (ZAC).

Table 1. OSHA defined H_2S gas exposure symptoms.

Concentration (ppm)	Symptoms/Effects
0.00011–0.00033	Typical background concentrations
0.01–1.5	Odor threshold (rotten egg smell).
2-5	Prolonged exposure may cause nausea, tearing of the eyes, headaches or loss of sleep. Airway problems may occur in asthma sufferers.
20	Possible fatigue, loss of appetite, headaches, poor memory and dizziness.
50-100	Slight conjunctivitis and respiratory tract irritation after 1 hour of exposure. May cause digestive problems and loss of appetite.
100	Coughing, eye irritation, loss of smell after 2-15 minutes. Drowsiness after 15-30 minutes. Throat irritation after 1 hour. Symptoms will gradually increase with prolonged exposure. Death

	possible after 48 hours of exposure.
100-150	Loss of smell (olfactory fatigue or paralysis).
200-300	Severe conjunctivitis and respiratory tract irritation after 1 hour. Pulmonary edema may occur with prolonged exposure.
500-700	Staggering, collapse in 5 minutes. Serious eye damage in 30 minutes. Death after 30-60 minutes.
700-1,000	Rapid unconsciousness within 1-2 breaths. Death within minutes.
1,000-2,000	Near instant death.

Scavenging Mechanism and Benchmarks

BYK has developed a 26% active, zinc-based liquid H_2S scavenger. The liquid material is based on zinc ammonium carbonate which precipitates hydrogen sulfide into zinc sulfide. Figure 1 illustrates the reaction that takes place between the ZAC and the H_2S.

The most likely species of zinc ammonium carbonate is $Zn(NH_3)_2(CO_3)_2$. This solution will readily react with the hydrogen sulfide to form the insoluble precipitate, zinc sulfide as shown in Figure 1.

$$\mathbf{Zn + H_2S \rightarrow ZnS\ (\downarrow) + H_2}$$

Figure 1. Reaction with zinc ammonium carbonate.

By virtue of being in a liquid state the reaction is more rapid than those exhibited by powdered zinc-containing H_2S scavengers. Solubility and the available surface area of zinc containing particles will influence the reaction rate.

To demonstrate its effectiveness, the ZAC material was tested in a simple WBM. Two industry benchmarks, zinc oxide and a water-based triazine, were evaluated to determine relative effectiveness. The properties of the H_2S scavengers tested can be seen in Table 2.

Table 2. Properties of ZAC and industry benchmarks.

Chemistry	Activity	Solvents
ZAC	26%	Water
Zinc Oxide	98%	Dry Powder
Triazine	40%	Water

Performance Comparison in a WBM

In the first set of experiments a WBM was prepared. The formulation used is listed in Table 3. In each case the muds were hot rolled for five hours at 150°F. Two dosages were made for each type of H_2S scavenger along with a base mud. The muds were treated with 5.75 lb/bbl of sodium sulfide to simulate hydrogen sulfide contamination. Sodium sulfide was used as a safer test route than directly using H_2S. Sodium sulfide is basic and converts from Na_2S to S^{--}, HS^-, and H_2S depending on the pH of the drilling fluid (Amosa et al. 2010).

Table 3. Water-based mud formulation.

Material	Addition Level
Tap Water	340 mL
API Bentonite	10 lb/bbl
Xanthan Gum	0.5 lb/bbl
Lignite	5 lb/bbl
Scavenger Chemistry	1 - 3 lb/bbl
Sodium Sulfide	5.75 lb/bbl

Sample preparation and testing procedure:
1. Mix the tap water and xanthan gum for 10 minutes.
2. Add the bentonite and mix for 10 minutes.
3. Add the lignite and mix for 10 minutes.
4. Adjust pH to approximately 10.5 using sodium hydroxide.
5. Add the required amounts of scavenger products and mix for one hour using a Multimixer.
6. Add sodium sulfide to each sample. Close and seal aging cell immediately.
7. Hot roll the sample for 5 hours at 150°F.
8. Collect filtrate via API fluid loss test.
9. Test filtrate for H_2S content via Garrett Gas Train.

The API filtrate was collected for each sample over thirty minutes. The Garrett Gas Train method was used to determine the amount of sodium sulfide remaining in each mud after the brief hot rolling.

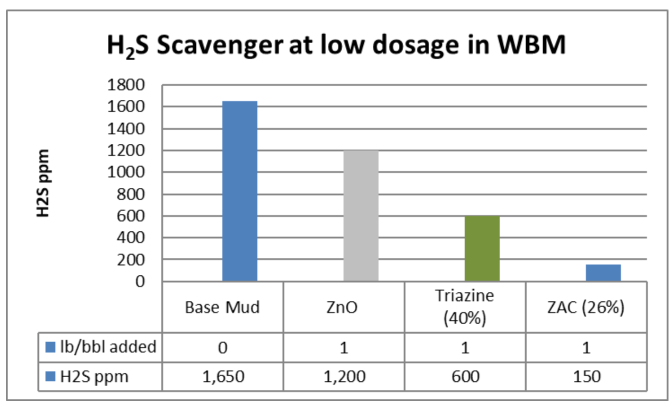

Figure 2. Treating at 1 lb/bbl scavenger.

In Figure 2 above, it is shown that each scavenger reduces the total amount of H_2S (zinc sulfide) compared to the base mud. At 1 lb/bbl treatment (as delivered), the industry standards did not remove enough H_2S to be considered safe. The ZAC removed almost all of the H_2S from the mud system.

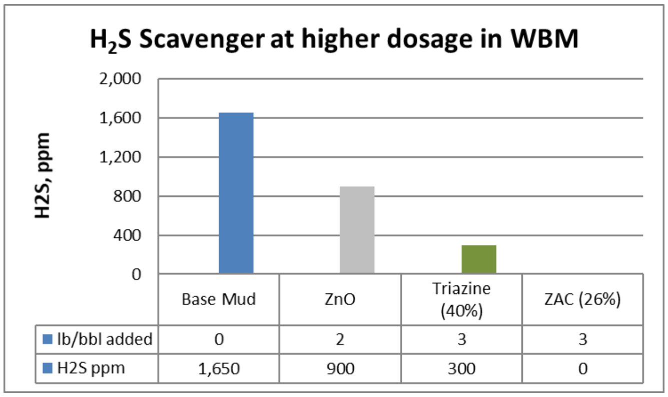

Figure 3. Treating with a higher dosage.

As the amount of scavenger was increased, a decrease in H_2S was observed as seen in Figure 3. 2 lb/bbl of Zinc Oxide reduced the toxic gas to 900 ppm while the triazine lowered it to 300 ppm. At 3 lb/bbl the ZAC completely eliminated the H_2S. It is quite likely that 3 lb/bbl ZAC was excessive for the amount of H_2S.

It should be noted that both zinc containing additives can flocculate clay-containing WBMs. A similar behavior occurs when calcium (Ca^{++}) from lime is added to the mud. This is easily countered with standard water-based mud thinners.

Performance Comparison in an SBM

The study also evaluated a slightly lower concentrated version of ZAC in a 10 lb/bbl synthetic-based mud. The active substance of the ZAC is identical, but the concentration is 15% active. Table 4 shows the formulation used for testing. Figure 4 shows the performance versus the same high purity Zinc Oxide used in the WBM testing.

Table 4. Synthetic-based mud formulation.

Material	Addition Level
Base Oil	191 lb/bbl
10.5 ppg $CaCl_2$ Brine	83.6 lb/bbl
Organoclay	8 lb/bbl
Emulsifier	6 lb/bbl
Rheology Modifier	2 lb/bbl
Lime	8 lb/bbl
Barite	116 lb/bbl
Scavenger Chemistry	1 - 8.5 lb/bbl
Sodium Sulfide	5.5 lb/bbl

Sample preparation and testing procedure:
1. Mix the oil, brine and clay for 10 minutes.
2. Add the emulsifiers and lime and mix for 15 minutes.
3. Add the barite and mix for 15 minutes.
4. Mix the mud on the Silverson for 10 minutes.
5. Add the required amounts of Zinc Oxide and Zinc Ammonium Carbonate.
6. Add Sodium Sulfide to each sample. Close and seal aging cell immediately.
7. Hot roll the sample for 5 hours at 150°F.
8. Test for H_2S content via Garrett Gas Train.

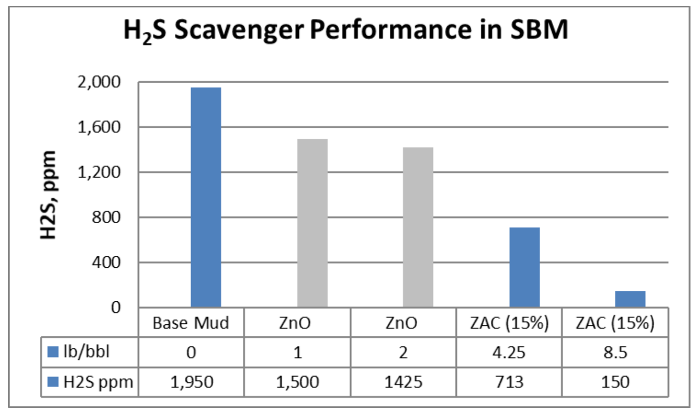

Figure 4. Performance in SBM.

Figure 4 shows that the scavengers were able to reduce the amount of H_2S compared to the base mud. Increasing the level of Zinc Oxide from 1 to 2 lb/bbl showed minimal effect. Whereas, ZAC showed a substantial decrease in H_2S when its dosage was doubled. The ZAC removed almost all of the H_2S from the mud system.

Since the 15% ZAC is more dilute, we should also point out the active content. At 4.25 and 8.5 lb/bbl treatment, there is only 0.64 and 1.3 lb/bbl of "active substance" being added to the mud system.

Conclusions

- Zinc Ammonium Carbonate is effective at removing H_2S
- The same material functions in both water and oil-based systems
- Reduced logistics with single additive

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Nomenclature

H_2S = *Hydrogen Sulfide*
ppg =*pounds per gallon*
ppm =*parts per million*
OSHA =*Occupational Safety and Health Administration*
WBM =*Water-based Drilling Fluids*
OBM =*Oil-based Drilling Fluids*
ZAC =*Zinc Ammonium Carbonate*
1b/bbl =*pounds per barrel*
SBM =*Synthetic Fluid-based OBM*

References and Background Reading

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