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 (H₂S) requires care and planning to ensure the safety of rig personnel and protection of assets.

H₂S 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 H₂S gas exposure as defined by the Occupational Safety and Health Administration (OSHA). H₂S 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).

H₂S 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 (H₂S in Oil Industry. 2017).

When drilling in H₂S bearing formations, careful planning is required. Special consideration must be paid to personnel safety, drilling fluids, tubulars, blowout preventers, onsite equipment and H₂S scavengers. H₂S scavengers are added to drilling fluids when drilling in areas known to contain H₂S. Typically, H₂S 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 H₂S scavenger based on zinc ammonium carbonate (ZAC).

Table 1. OSHA defined H₂S gas exposure symptoms.

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Symptoms/Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00011–0.00033</td>
<td>Typical background concentrations</td>
</tr>
<tr>
<td>0.01–1.5</td>
<td>Odor threshold (rotten egg smell).</td>
</tr>
<tr>
<td>2–5</td>
<td>Prolonged exposure may cause nausea, tearing of the eyes, headaches or loss of sleep. Airway problems may occur in asthma sufferers.</td>
</tr>
<tr>
<td>20</td>
<td>Possible fatigue, loss of appetite, headaches, poor memory and dizziness.</td>
</tr>
<tr>
<td>50–100</td>
<td>Slight conjunctivitis and respiratory tract irritation after 1 hour of exposure. May cause digestive problems and loss of appetite.</td>
</tr>
<tr>
<td>100</td>
<td>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</td>
</tr>
</tbody>
</table>
Table 3. Water-based mud formulation.  

<table>
<thead>
<tr>
<th>Material</th>
<th>Addition Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap Water</td>
<td>340 mL</td>
</tr>
<tr>
<td>API Bentonite</td>
<td>10 lb/bbl</td>
</tr>
<tr>
<td>Xanthan Gum</td>
<td>0.5 lb/bbl</td>
</tr>
<tr>
<td>Lignite</td>
<td>5 lb/bbl</td>
</tr>
<tr>
<td>Scavenger Chemistry</td>
<td>1 - 3 lb/bbl</td>
</tr>
<tr>
<td>Sodium Sulfide</td>
<td>5.75 lb/bbl</td>
</tr>
</tbody>
</table>

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.
9. Test filtrate for H₂S 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 H₂S (zinc sulfide) compared to the base mud. At 1 lb/bbl treatment (as delivered), the industry standards did not remove enough H₂S to be considered safe. The ZAC removed almost all of the H₂S from the mud system.
As the amount of scavenger was increased, a decrease in H$_2$S 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$_2$S. It is quite likely that 3 lb/bbl ZAC was excessive for the amount of H$_2$S.

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.

<table>
<thead>
<tr>
<th>Material</th>
<th>Addition Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Oil</td>
<td>191 lb/bbl</td>
</tr>
<tr>
<td>10.5 ppg CaCl$_2$ Brine</td>
<td>83.6 lb/bbl</td>
</tr>
<tr>
<td>Organoclay</td>
<td>8 lb/bbl</td>
</tr>
<tr>
<td>Emulsifier</td>
<td>6 lb/bbl</td>
</tr>
<tr>
<td>Rheology Modifier</td>
<td>2 lb/bbl</td>
</tr>
<tr>
<td>Lime</td>
<td>8 lb/bbl</td>
</tr>
<tr>
<td>Barite</td>
<td>116 lb/bbl</td>
</tr>
<tr>
<td>Scavenger Chemistry</td>
<td>1 - 8.5 lb/bbl</td>
</tr>
<tr>
<td>Sodium Sulfide</td>
<td>5.5 lb/bbl</td>
</tr>
</tbody>
</table>

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$_2$S content via Garrett Gas Train.

Figure 4 shows that the scavengers were able to reduce the amount of H$_2$S 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$_2$S when its dosage was doubled. The ZAC removed almost all of the H$_2$S 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$_2$S
- The same material functions in both water and oil-based systems
- Reduced logistics with single additive

Acknowledgments

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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

lb/bbl = pounds per barrel

SBM = Synthetic Fluid-based OBM

References and Background Reading


https://www.onepetro.org/conference-paper/SPE-6655-MS