Fast, feasible and safe method for evaluation of H_2S Scavenger performance in acidizing laboratory

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Abstract

Hydrogen sulfide (H_2S) is hazardous and toxic gas that leads to worker fatality. Nonetheless, hydrogen sulfide can also impair the formation permeability by creating precipitations that plug the pore throats. Therefore, removal of hydrogen sulfide content from formation or flow back fluids had become a necessity. Many research have been conducted to investigate techniques that can reduce hydrogen sulfide in wellbore or prevent of producing it, and one of these techniques is using hydrogen sulfide scavengers. In this paper have tried to discuss about scavengers in acid stimulation treatment and extend an experimentally method to evaluate their performance. A simple, fast procedure was developed to evaluate hydrogen sulfide scavenger performance. Iron sulfide and Hydrochloric acid 10% was used to produce hydrogen sulfide. The gas was transferred through the acid solution and the performance of the solution to scavenging the gas was evaluated due to the measurement of Cadmiun sulfate precipitation in next flask. Effect different parameters were investigated on the hydrogen sulfide capturing performance. The results show that a little change in temperature, pH and concentration of additives have significant effect on hydrogen sulfide capturing.

Keywords: H_2S scavenger, acid stimulation, triazine-based, aldehyde, FeS, acidizing additives.

Introduction

Major problem in oil and gas operations result from the formation of hydrogen sulfide in the reservoir, which results in increased corrosion and iron sulfide forming leading to higher operating costs and reduced revenue. This operating cost including hydrogen sulfide corrosion of drill pipe, protective casing strings and other related equipment. The gas also constitutes a serious environmental and health hazard. Operational reports indicate that a spike of hydrogen sulfide is sometimes evolved while flowing back the acidizing treatment. Formation of H_2S in acid returns highly undesirable because it creates a significant risk of stress corrosion cracking with any susceptible materials present in the well.

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Many research have been conducted to investigate techniques that can reduce hydrogen sulfide in wellbore or prevent of producing it, and one of these techniques is using hydrogen sulfide scavengers. The treatment of Hydrogen sulfide scavengers in fluid to combat hydrogen sulfide effects provides the best common medium for overall control. H_2S scavengers are chemicals that favorably react with H_2S gas to eliminate it and produce environmental friendly products. These products depend on the type and composition of the scavenger and the condition at which the reaction take place. The products of the reaction between H_2S and scavenger should not damage the formation by creating precipitation or hindering function of another additive. The function of hydrogen sulfide scavengers used during well stimulation is critical. The scavengers must be reliable because the safety of personnel and equipment depends on it.

Hydrogen sulfide sources: Hydrogen sulfide originates from several sources in water, oil and gas wells. Thermal decomposition of drilling mud additives can produce hydrogen sulfide [1]. Sulfate reducing bacteria are those bacteria and archaea that can obtain energy by oxidizing organic compounds or molecular hydrogen (H_2) while reducing sulfate (SO_4^{2-}) to hydrogen sulfide (H_2S). Sulfate reducing bacteria (SRB) can utilize organic substances such as acetate, bio-polymers and sulfate ion from water to produce hydrogen sulfide [2,3]. Thermo catalytic reduction of the sulfate ion in the formation water in contact with hydrocarbons will produce hydrogen sulfide [4].

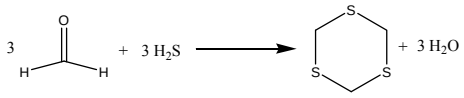
Hydrogen Sulfide Scavengers: One general approach for removing hydrogen sulfide from, or at least substantially reducing the amount of hydrogen sulfide is to expose the hydrogen sulfide to a treatment liquid containing an agent which chemically react with hydrogen sulfide, a so called a hydrogen sulfide scavenger. There are some hydrogen sulfide scavengers that are used in the acid stimulation treatment. H_2S scavenger selected should meet the following criteria for good performance:

1. Scavengers should be effective in scavenging H_2S kinetically and thermodynamically.
2. Ideally the scavengers can be used with treatment acid without changing the acid mineral reaction kinetics and thermodynamics.
3. The scavengers are compatible with additives in the treatment system, such as iron control agent, corrosion inhibitors, surfactants, mutual solvents, anti-sludge agents/demulsifiers, and other additives for operational needs.
4. Scavengers (either original products or reaction products after scavenging) do not cause further formation damage or the operational problems (e.g. Corrosion) in the treatment.
5. HSE and economically acceptable.

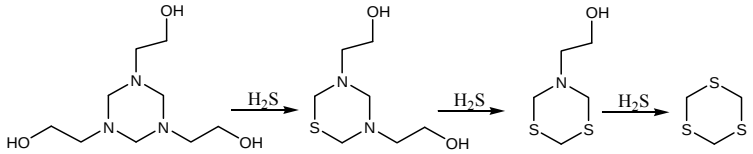
H_2S scavengers are able to react with H_2S and produce stable products. There are two main categories in H_2S scavengers chemicals:

1. Metal-based H_2S scavengers: these chemicals produce solid s that cause damage to the formation
2. Organic-based H_2S scavengers: aldehydes and triazine can react with H_2S and produce soluble products.

Reaction of formaldehyde as H2S Scavenger with Hydrogen sulfide is as below:



For example reaction of a triazine based H_2S Scavenger is as below:



Materials and Methods

For generating H_2S, HCl acid 10% was put into the dropping funnel; 1g FeS was placed into the two-necked flask, which has hose that was used to draw off the evolved gas (Figure 1).

$$FeS + 2HCl \rightarrow FeCl_2 + H_2S$$

Produced H_2S from the reaction enters a H_2S Scavenging flask that contains variable solutions. The H2S Trapping flask contains Cadmium Sulfate solution ($CdSO_4$) as absorbent at a concentration of 5 wt%. Generated Hydrogen sulfide will be calculated from consumed FeS using stoichiometric equations. Produced H_2S passes through Scavenging flask and the remained H2S enters Trapping flask and finally reacts with $CdSO_4$ and produced yellow precipitate of CdS as below reaction.

$$H_2S + CdSO_4 \rightarrow CdS\downarrow + H_2SO_4$$

CdS precipitates separated using filter paper, dried in oven at 150°C and then measured using a high precision balance. For safety issues, 6% NaOH solution was set to neutralize H_2S released from the reaction system as the last flask before vacuum Buchner flask. Place the reactor into system and start stirring reactor and absorbers while purging with Vacuum pump.

The amount of FeS, 10% HCl, aqueous solution of $CdSO_4$ and NaOH solution was constant during the all tests. On the other hand recipe of H2S Scavenging flask was variable in each test. For high temperature tests, H_2S Scavenging flask was put in 90ºC bath during scavenging reaction to determine temperature effect on the scavenger reaction. In order to study of pH effect on Scavenging reaction, $CaCO_3$ was added to 15% HCl to change pH (pH = 4.5).

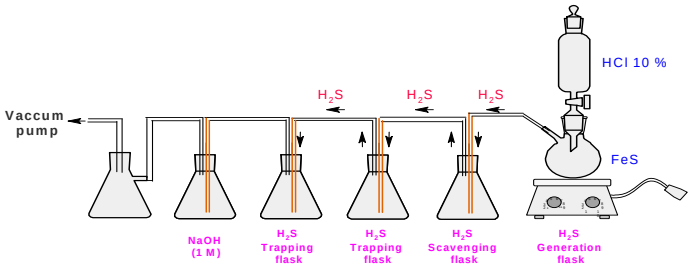


Figure 1: Experimental set-up

Results and discussion

Different parameters were investigated during this laboratory procedure. Table 1 depicts the lab tests and their results.

Table 1. Experimental results

Test No.	Description	Initial FeS (mol)	Remained FeS (mol)	Scavenged H2S	Scavenging Efficiency %
1	Water	0.0114	0.0029	0.0008	9.53
2	Water + HSO*	0.0114	0.0017	0.0038	39.35
3	HCl 15%	0.0114	0.0030	0.0012	13.8
4	HCl 15% + HSO	0.0114	0.0045	0.0006	18.75
5	HCl 15% +Additives	0.0114	0.0030	0.0018	21.64
6	HCl 15% +Additives +HSO	0.0114	0.0021	0.0012	32.54
7	15 % HCl + Additives (T=90°C)	0.0114	0.0018	0.0012	12.95
8	15 % HCl + Additives + HSO (T=90°C)	0.0114	0.0024	0.0053	58.73
9	15 % HCl + Additives (pH=4.5)	0.0114	0.0032	0.0018	22.35
10	15 % HCl + Additives + HSO (pH=4.5)	0.0114	0.0029	0.0053	62.62
11	15 % HCl + Additives (pH=4.5,T=90°C)	0.0114	0.0022	0.0013	14.25

12	15 % HCl + Additives + HSO (pH=4.5,T=90°C)	0.0114	0.0023	0.0022	24.40

*HSO: H_2S Scavenger

Scavenging Efficiency could be calculated using below equation:

$$Scavenging\ Efficiency\ (\%) = \frac{Scavenged\ Hydrogen\ Sulfide\ (mol)}{Generated\ Hydrogen\ Sulfide\ (mol)} * 100$$

Conclusion

The performance of hydrogen sulfide scavenger was examined and the following results were concluded:

- A simple, fast procedure was developed to screen hydrogen sulfide scavengers used during well stimulation.
- The efficiency of capturing hydrogen sulfide was found to be a function of pH and concentration of additives.
- Temperature had an overall increase in the scavenging efficiencies at a pH of 0.
- However temperature and pH had an increasing influence on scavenging efficiency, but these two objects simultaneously had an unacceptable effect on scavenging efficiency.

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