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Comparison of Laboratory Based H₂S Scavenger Methodologies for Oil and Gas Production

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ABSTRACT

H₂S scavenger test methodologies used for the evaluation of scavenger products in oil and gas production can vary in design and purpose. The benefits and limitations of three different methods have been determined using established scavenger chemistries. The capacity, kinetics, and efficiency of the scavengers were evaluated by employing a variation of temperature, concentration, and, in some cases, pressure. The effect of pH was studied to determine the contribution of neutralization compared to a reaction where the sulfide is covalently bound (reversible versus non-reversible reactions). Additional observations were made on thermal stability and secondary effects, such as, solids formation from reaction products and scaling. Industry requires information on the capability of H₂S scavenger methods in order to select suitable products to implement in their production systems. The intent is to provide a perspective that helps them make technically informed decisions.

Key words: hydrogen sulfide, H₂S scavengers, capacity, efficiency, kinetics, mass balance

INTRODUCTION

H₂S is commonly found in oil and gas production streams and is either naturally occurring in the reservoir or its presence is due to sulfate-reducing bacteria metabolic activity. The presence of H₂S in oil and gas fields causes several operational and production difficulties. Firstly, H₂S is highly toxic thus fields that produce H₂S need strict operational practices in place to mitigate this risk. Secondly, H₂S is an acidic gas and cause corrosion (e.g. localized or sulfide stress cracking) of carbon steel metallurgies. The primary reaction product of H₂S corrosion is a mixture of polymorphous iron sulfide scales (mackinawite, troilite, pyrrhotite, greigite and pyrite) that deposit on the metal surface¹. Beneath these scales, there is the possibility of under deposit corrosion occurring. H₂S can react with any oxygen present due to leaks or injection of thermodynamic hydrate inhibitors (e.g. ethylene glycol or methanol) forming elemental sulfur. If the sulfur deposits on the metal surface, it will initiate very aggressive localized corrosion. Finally, crude oils produced with H₂S present, have lower commercial value compared to sweet crudes.

In addition to biocides, nitrate, corrosion inhibitors and iron sulfide dissolvers, H₂S scavengers are used to mitigate the risks presented by H₂S. H₂S scavengers react with H₂S in either the gas or liquid phase to form non-hazardous, non-reactive species. Monoethanolamine (MEA) triazine (hexahydro-1,3,5-tris(hydroxyethyl)-s-triazine) is the most widely used scavenger. It is less toxic than most aldehyde scavengers and reacts very quickly with H₂S^{2,3}. MEA triazine reacts irreversibly with H₂S to form dithiazine (5-hydroxyethylhexahydrodithiazine). One of the major concerns with MEA triazine is that there is a strong possibility of the by-product MEA reacting with excess H₂S to form an ethanolammonium sulfide species that in turn reacts with the dithiazine to form a largely insoluble polymer, commonly referred to as amorphous dithiazine⁴. An alternative triazine used in oil and gas production is monomethylamine (MMA) triazine (1,3,5-trimethyl hexahydro-s-triazine). MMA triazine has greater volatility than MEA triazine so is more suitable for dry gas applications.

Formaldehyde has been added to MEA triazine scavengers to increase the overall uptake capacity of a specific volume of the product. This comes with its own set of concerns as the excess formaldehyde requires additional safety considerations and laboratory testing indicates that solid by-product issues are increased.

Glycol hemiformals including ethylenedioxydimethanol (EDDM) are non-nitrogen containing H₂S scavengers. Some examples are non-bio accumulating (>60 % biodegradable in 28 days) and are environmentally acceptable for use offshore. Additionally, they have shown good performance in multiphase systems with scale and corrosion inhibitors also present in the production fluids⁵. Hemiformals react significantly slower than nitrogen-containing scavengers and may have lower capacity due to a longer reaction time. However, research indicates that their efficiency and reaction rate can be improved by mixing them with an organic acid metal complex and a tertiary amine⁶.

Oxazolidines contain nitrogen, but in contrast to triazine tend to have high thermal stability. Unlike various other scavenging chemistries, oxazolidines are not very selective and tend to react with most sulfur-containing compounds including mercaptans. Though effective in mixed production, oxazolidines favor low water cuts and may require mutual solvents to enhance solubility⁷. The most widely used oxazolidine is 3,3'-methylenebis(5-methyloxazolidine) (MBO) which, in theory has twice the molar uptake capacity of regular oxazolidines. Other H₂S scavenger chemistry includes Schiff bases, alkyl amines, glyoxal and organic acid metal complexes. However, these chemistries were not included in the study detailed in this paper.

A variety of H₂S scavenger test methods have been developed and discussed in several publications. The different methods will favor some chemistries over others, and it is essential to fully understand reaction mechanisms to evaluate the relevance of the results versus the field application. One of the simplest methods reported involves generating H₂S in a water sample via the addition of sodium

hydrosulfide and measuring the H_2S concentration with and without scavenger addition using a colorimetric method⁸. Similar methods generate H_2S through sodium sulfide (Na_2S) addition with the H_2S measured using gas detection tubes. To assess scavenger efficacy in acidic environments, one method uses iron (ii) sulfide (FeS) added to hydrochloric acid (HCl) in a vessel to generate H_2S ⁹. Excess H_2S is trapped in another vessel and is precipitated with cadmium sulfate as cadmium sulfide (CdS). The test is carried out with and without scavenger, and the capacity of the scavenger is determined based on the mass of FeS added and the amount of CdS that forms.

Another atmospheric pressure test developed for rapid screening of H_2S scavengers has been designated as “ H_2S Scavenger Titration Method”¹⁰. This method uses an amperometric molecular probe that measures molecular H_2S concentration and pH. The scavenger is titrated in small aliquots to the test solution saturated with H_2S (the H_2S level is left to stabilize between scavenger additions), until the H_2S concentration is zero. The output of this test is a graph of scavenger concentration plotted against sulfide concentration.

A method has been developed that uses a Continuous Stirred Tank Reactor (CSTR) or an autoclave to assess H_2S scavenger performance in high-temperature, high-pressure environments¹¹. This technique assesses scavenger efficiency in a multiphase (gas, brine and hydrocarbon) system and uses an ultra-violet analyzer spectrophotometer to measure the H_2S concentration before and after scavenger addition. This method measures scavenger efficiency in real-time and the data can be used to calculate the capacity of the scavenger to remove H_2S .

This paper provides details on three H_2S scavenger test methods and the results of standard scavenger chemistries, MEA triazine, EDDM, and MBO, which were evaluated in each test. The objective was to compare the methods to better define their purpose and determine if there are complementary relationships. Ultimately, the goal was to develop an understanding of how these methods can assist H_2S scavenger selection for oil and gas applications.

EXPERIMENTAL AND RESULTS

Bubble Tower Test

Method

Measured by mass flow meters, sour gas is dispersed via a fritted sparger through a column of fluid containing the neat scavenger chemistry. Temperature is applied using heat tape and maintained by a thermocouple connected to a controller. H_2S uptake is determined based on the time the inlet gas is introduced until breakthrough is obtained and is plotted as gas concentration versus time (Figure 1). The outlet gas concentration is analyzed by gas chromatography using a thermal conductivity detector (TCD) and the results reported as the volume of scavenger required to react with H_2S by weight. Prior to the test, the system is purged with nitrogen and allowed to thermally equilibrate. A schematic of a test with MEA triazine is shown in Figure 2.

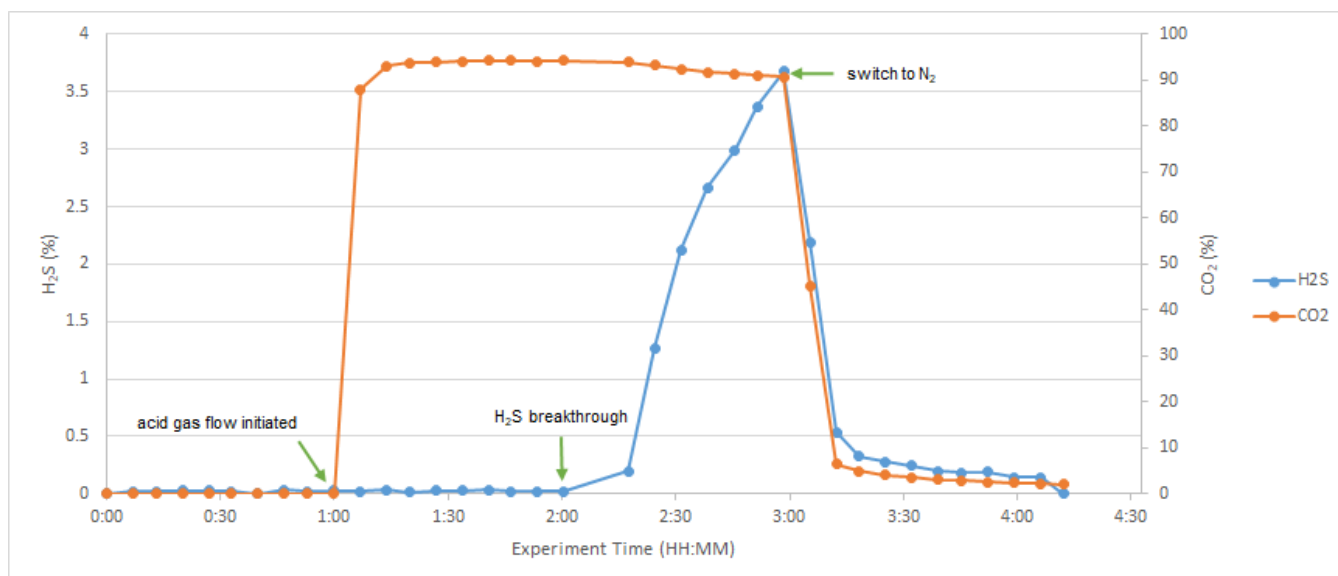


Figure 1: Graph of Outlet H₂S Concentration Versus Experimental Time for the Bubble Tower Test

The bubble tower test results presented herein were performed at room temperature with sparging H₂S and CO₂ (60 mL/min each). As listed in Table 1, the test products were MEA triazine, MBO, and EDDM. Upon the completion of each test, a flow of nitrogen replaces the acid gas in order to stop the interaction of H₂S with the test fluid and to allow the experimenter to disassemble and clean the test apparatus safely.

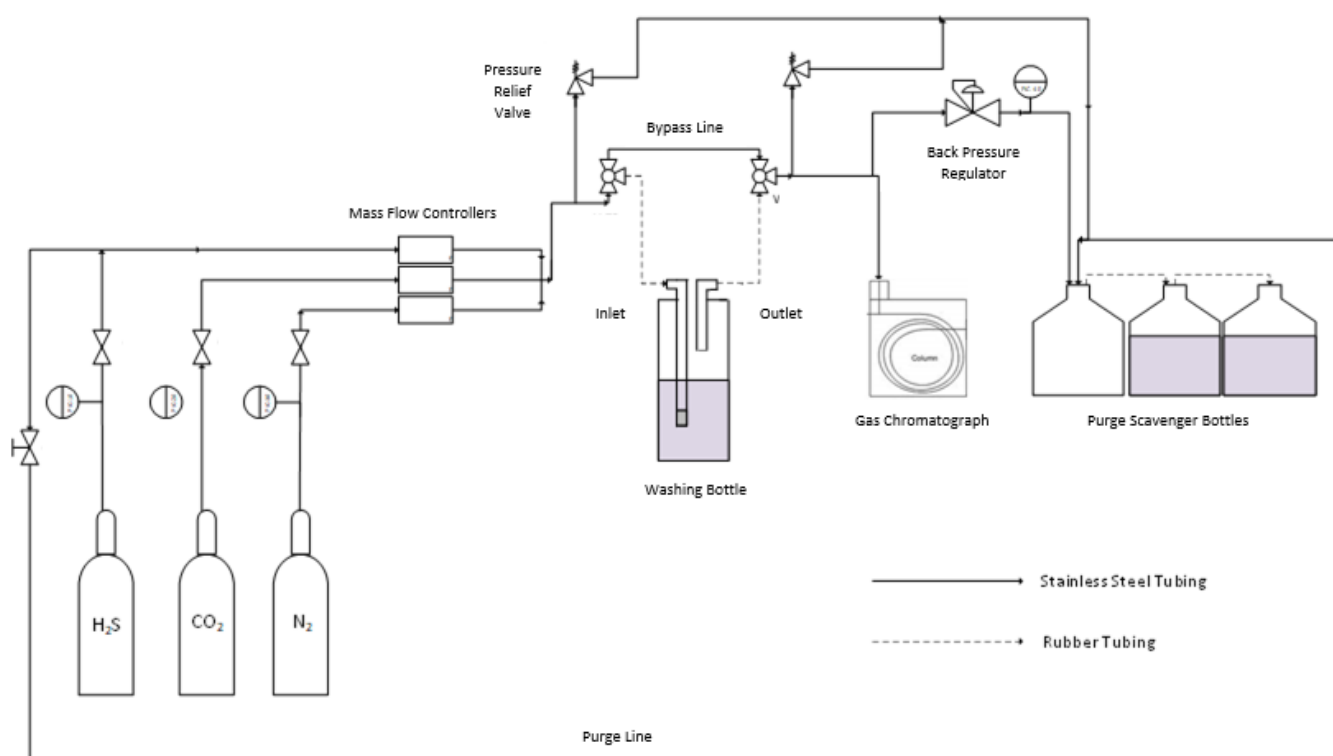


Figure 2: Bubble Tower Test Setup

Results

The results in Table 1 and Figure 3 below show that MEA triazine achieves complete scavenging until breakthrough at just over two hours, whereas, both MBO and EDDM exhibit immediate breakthrough with MBO being much lower and having approximately 0.5% or less H_2S throughout the test period. No solids were observed in any of the tests nor was foaming observed in the MEA triazine or EDDM tests. However, MBO did exhibit enough foaming to stop the test slightly short of the test period for the other two chemistries tested. EDDM is a near-neutral pH chemistry and, thus, exhibits slower reaction kinetics as it does not neutralize H_2S as MEA triazine and MBO does.

Table 1: Bubble Tower Test Parameters and Capacity Results for MEA Triazine, MBO, and EDDM

Chemistry	Activity (wt.%)	Temperature ($^{\circ}\text{C}$)	Capacity (mg H_2S /mL scav.)
MEA triazine	40-45	room temp.	65.5
MBO	>99	room temp.	immediate breakthrough
EDDM	~95	room temp.	immediate breakthrough

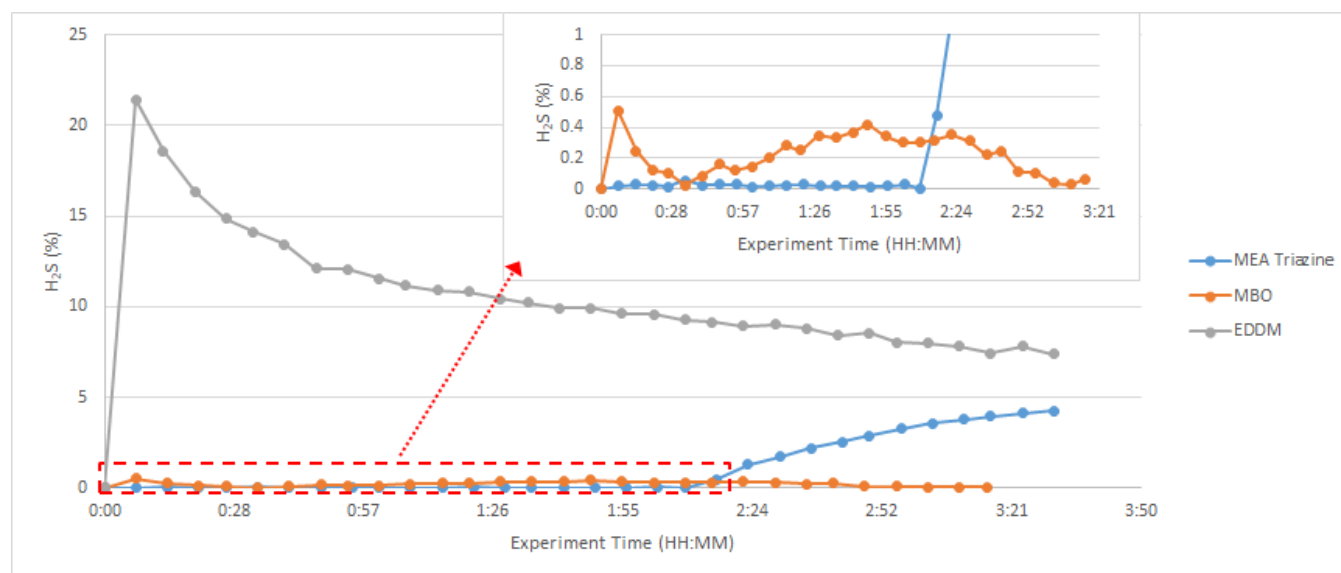


Figure 3: Graph of H_2S Concentration for MEA Triazine, MBO, and EDDM for the Bubble Tower Test (inset: magnified section of the baseline)

Once equilibrated, the CO_2 concentration for the MBO test was relatively constant, indicating the reaction specificity of the scavenger chemistries for H_2S (Figure 4). Conversely, the reduction in CO_2 for the MEA triazine test is attributed to the reaction of MEA (a by-product of the reaction of MEA triazine and H_2S)¹², whereas, the lower CO_2 in the EDDM test is due to the dilution effect of the H_2S that has been scavenged.