

Laboratory simulation of gas sweetening

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Abstract:

In this article, a new testing equipment and protocol in order to evaluation H₂S scavengers for direct chemical injection into gas pipelines is described. The testing protocol address several shortcomings in previous accepted tests which did not take into account the formation of a spray of the product, or tested the product in its final formulation.

Introduction:

Sour oil and gas fields, those containing high levels of H₂S, require expensive infrastructure in order to maintain safe working standards for employees and mitigate high corrosion risks [1, 2, 3]. Furthermore, sour oil and gas receive a penalty at the refinery and can be sold for considerably less per barrel compared to a sweet product, thus urging the need for H₂S removal. Increasingly more oil fields are turning sour. In the case of offshore resources this is mostly due to the presence of sulfate reducing bacteria, which are either naturally present in the reservoir or have been introduced during secondary flooding. Onshore, particularly in the USA, the exploitation of new resources includes increasing numbers of sour fields [4]. H₂S removal is an estimated worldwide market consisting of US\$500 million [5].

H₂S scavenging refers to the introduction of a chemical which reacts non-reversibly with H₂S, thus removing it from the oil or gas stream, is an increasing popular way of dealing with this problem. The main types of scavengers available on the market are triazines [6], particularly 1,3,5-Tris(2-hydroxyethyl)hexahydro-s-triazine, hereafter MEA Triazine [7]. MEA Triazine, reacts rapidly with four equivalents of H₂S when it is the only acid gas present to form 5 (2-hydroxyethyl)-hexahydro-1,3,5-dithiazine [8]. MEA Triazine has fast kinetics, works well across a broad temperature range, and can be manufactured cheaply. However, there are some significant drawbacks to the use of Triazine. The high pH of the water based triazine solutions can lead

of carbonate scaling [9], and further reactions of the dithiazines form an insoluble polymer which can lead to blockages [10]. For these reasons, many companies are interested in developing new H₂S scavengers.

There are several methods available for sweetening gas. H₂S can be removed via a contact tower, or through continuous direct chemical injection [11]. Logistical challenges, and room for potential error in running a field trial mean that pre-field laboratory evaluation of products are essential. There are several standard laboratory tests, such as the gas breakthrough test and the Parr reactor. Furthermore, there is increasing interest in using sulfide detecting electrodes to measure the kinetics of scavenging reactions [12, 13].

These tests are all able to assess the performance and capacity of the H₂S Scavenger by measuring the depletion rate of H₂S. Each of these tests has been developed as a laboratory simulation of a different field applications. The gas breakthrough test is a simulation of a contact tower. The Parr reactor [14] which is able to assess the performance and capacity of scavenger at elevated temperatures and pressures, provides information about multiphase and downhole scavenging. However, in the case of direct injection there is still a gap between laboratory prediction of scavenger performance and actual results from field use [15]. While it is known that the method of injection plays a large role in the distribution and thus performance of the scavenger [16], none of the laboratory based methods incorporate this function. Industry has recognized the need to better predict the field performance of scavengers, particularly for direct chemical injection and this has led to the development of simulation software also being able to take into account flow conditions in the pipe [15]. There are reports of several large scale device which have been developed to simulate different types of oil and gas installations, covering applications such as sea floor pipelines [17] injection of scavengers into the multiphase [7] and gas pipelines loops [11, 15] which can evaluate the performance of scavengers. However, each experiment involves considerable amounts of oil or gas and scavengers, which are all not at insignificant cost so can only be considered for late stage development work. What is missing in this field is a lab scale test, which incorporates the physics of spraying chemicals, gas flow and mass transfer processing involved in the direct injection treatment of sour gas fields. In this article we describe the development of such a device and how it can be used to overcome these problems.

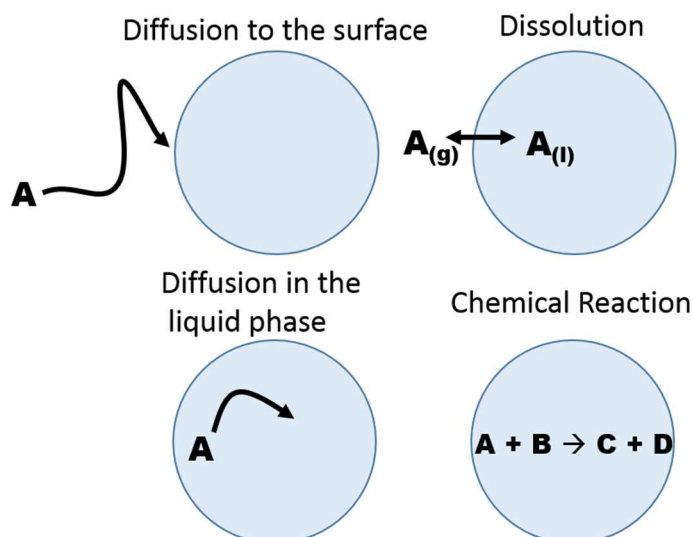


Figure 1. Mass transfer processes involved for aqueous-based reaction where one reactant is a gaseous species

In order to better understand the features behind the scavenging process, we consider the multiple steps involved in an absorption followed by reaction process. These are depicted in Figure 1. Within this model, the different mass transfer processes, which need to occur before a reaction between the H₂S and the scavenger can take place, are illustrated. In the first step, the gas phase reactant diffuses to the surface of the droplet. In step 2, the reactant dissolves in the droplet, in this example water. Step 3 describes the diffusion of the reactant inside the droplet until meeting a reagent. In the final stage, the reaction takes place. Additional to the steps shown here, one should also keep in mind that the reacted products also diffuse within the droplet and that over time a concentration gradient of reacted product forms [18], hindering the scavenging process. This adds additional mass transfer steps to the reaction, creating further deviations from measured chemical kinetics. The kinetics of the chemical reaction is only covered in the final step. We believe that kinetic measurements of the reaction of the scavenger with H₂S, in dilute conditions, such as those made with the sulfide detecting electrode [13] do not provide sufficient information to rank new scavenger products and only covers part of the process in the field. It is particularly important to make tests on the final formulation of the product, including any surfactants which may be present in order to better predict the real scavenger performance.

To this end we present, to the best of our knowledge, for the first time, a simple laboratory method to measure the effectiveness of H₂S scavengers used in direct chemical injection. We have striven to capture the essential physics of the direct injection process without overcomplicating the experimental protocol, leaving an easy interpretation of results.

Method:

A schematic presentation of the experimental setup is depicted in Figure 2. The experimental set-up is similar to apparatus described for CO₂ capture by amine solutions. [19, 20, 21]. A test is performed by first filling the glass chambers with N₂ gas containing 1000ppm H₂S. Once a stable reading has been achieved on the H₂S sensor, the pump is turned on and the H₂S scavenger solution begins to spray. After a certain period of time, the reading on the H₂S sensor reaches a new stable value and the test is stopped. All pipes and the glass chambers are cleaned with water, and 0.1 M citric acid, and then dried between experiments. For non-water based scavenger solutions the equipment is cleaned with acetone and dried before rinsing again with water to

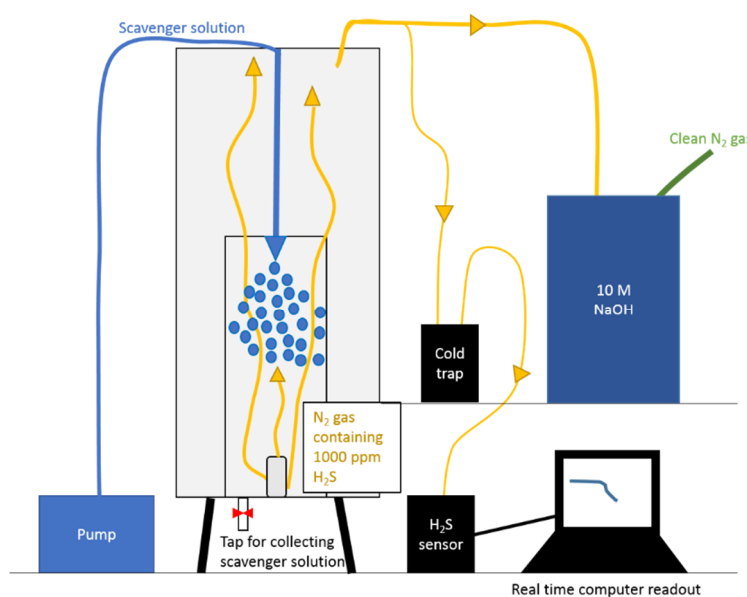


Figure 2. Sketch of the gas phase scavenging apparatus

remove any solvent traces.

Prior to measuring with scavengers we first testing the baseline absorption of water was determined, as we are primarily working with water-based scavengers. The chamber was filled with 1000 ppm H₂S gas with a rate of

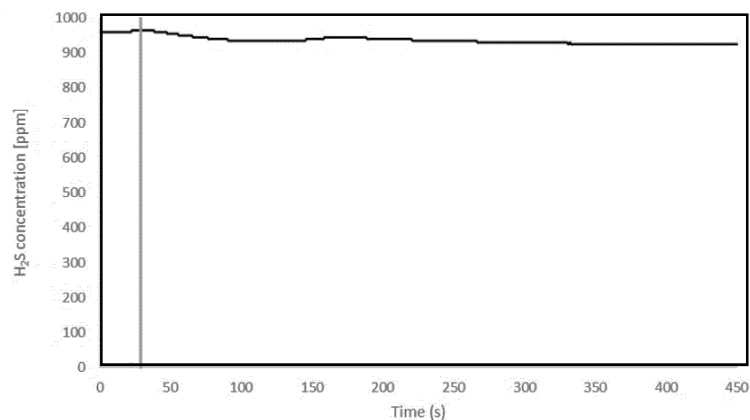


Figure 3. Measurement of the baseline of H₂S absorption when spraying water

40 L/min and then sprayed with demineralized water at 70 mL/min. The pH was measured to be 9. The results are displayed in Figure 3. The grey line indicates turning on of the pump and the beginning of spray.

What can be seen from the baseline measurements (Figure 3) is, that there is some absorption of H_2S by water. Because all lines of the pump are primed with fluid (in this case water, but in other cases scavenger) spray begins exactly the same time as turning on the pump. A drop in H_2S value from 960 to 920 ppm, or a 4% reduction is observed. This result shows that absorption is not a major factor in the H_2S removal, and a large dynamic range of the measurements in which to differentiate scavengers is available.

Results and discussion:

In order to gain a more fundamental understanding of the experimental device initial experiments with 0.1M NaOH as a cheap and non-toxic model scavenger were performed. First, a parameter screening to identify what the dominate influences are on product performance was performed. An example curve is shown in Figure 4.

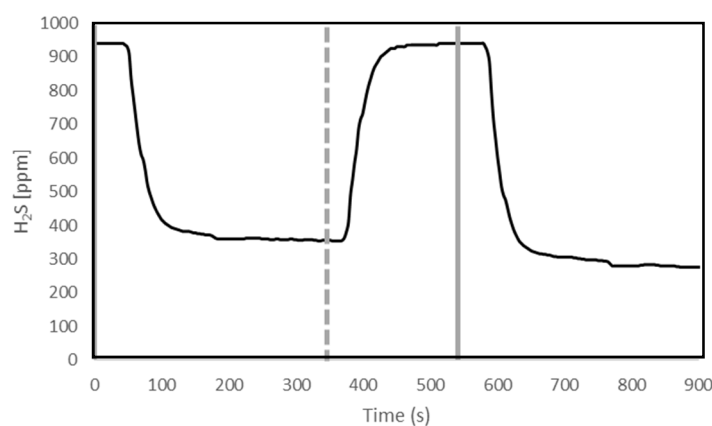


Figure 4. Model experiment with Sodium Hydroxide as H_2S Scavenger

A typical experimental curve is displayed in Figure 4, wherein the grey lines indicate the time at which the pump was started and spraying commenced and the dashed line indicates stopping of the spray. It is worth to discuss some of the features in more detail. Firstly, the buildup of H_2S concentration in the reaction chamber can be observed as the air is slowly replaced. The gas is sampled from the top of the chamber, and at the beginning of the experiment the sampling lines are also filled with air. This results in the apparent time lag between starting the spray, and the initial decrease of H_2S concentration. We also notice that on the repeat experiment the maximum value of H_2S concentration reached is slightly lower. This hysteresis comes from the non-saturated scavenger solution which has collected at the bottom of the chamber, or droplets which remain on the walls. We can see this results in a $\sim 10\%$ reduction in the maximum concentration of H_2S measured in the chamber. To remove this effect, it was decided to completely clean and dry the apparatus after each experiment.

Having clarified the negligible effects of adsorption of just water spray, and established an experimental and cleaning protocol, we now focused on identifying the effects of physical features of the spray itself. We were particularly concerned that differences in concentration and viscosity of different products would make comparisons difficult. To understand these effects, extensive parameter screening using 0.1 M NaOH solutions of different concentrations and viscosities was performed.

The dominant factor is the ratio of scavenger to H_2S regardless of droplet size, product viscosity, concentration, gas flow, liquid flow rate etc., all of which will be discussed in the section below. From this, it can be concluded that a good mixing of product and H_2S inside the reaction area is obtained. Therefore, in order to compare the effectiveness of different products it is only necessary to keep the molar flux constant, and dilution of the formulation in order to do this will not unduly skew results.

In Figure 5, it can be seen that under the same liquid dosing conditions, increasing the gas flow decreases the percentage of H_2S removed. This is not surprising as the total amount of H_2S passing through the system is increased.

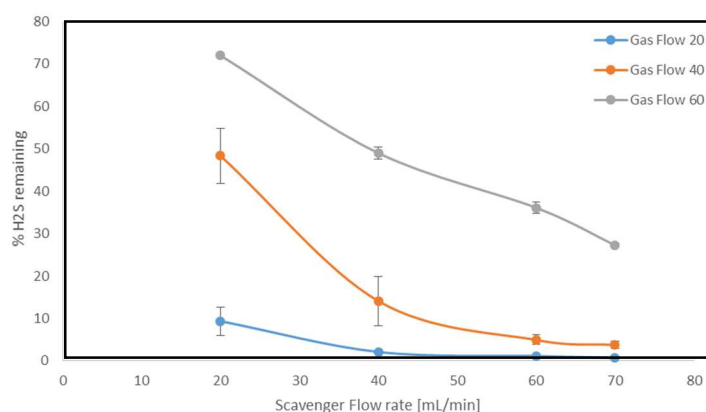


Figure 5: Effect of gas flow rate on scavenging process

If we re-plot the same data in terms of the ratio of moles of scavenger to moles of H_2S we can see that irrespective of the gas or liquid flow rates used, the most important factor is this ratio (shown in Figure 6).

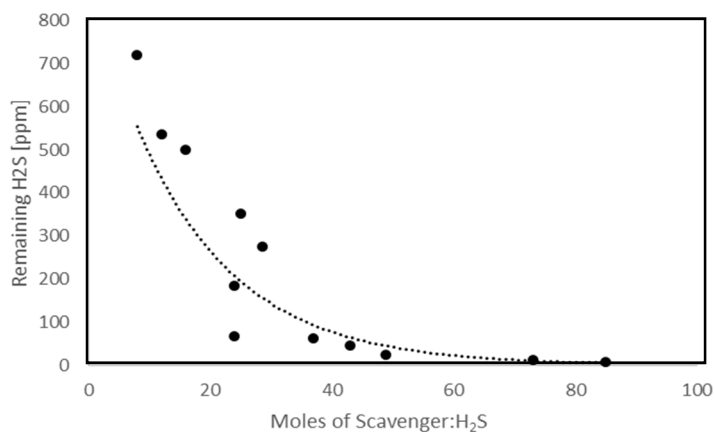


Figure 6. The effect of the ration of the molar flux of scavenger to the molar flux of H_2S on the scavenging performance

As shown in Figure 6, the most important factor for the determination of the scavenger is simply the molar flux which is used. As long as we are using excess of scavenger, it makes relatively little difference if the scavenger is diluted, or used at different flow rates, or if the formulations have different viscosities and differences in the spray profile of the product. Therefore, in order to compare the performance of different scavengers we dilute them to the same concentration and spray them at the same flow rate. It is worth to note that while this ratio is the dominant controller for the scavenging performance it is not possible to compare scavenging performance at different gas flow rates due to different dynamics (i.e. diffusion speeds, contact times).

To understand the effect of concentration, NaOH solutions of different concentrations at different flow rates were sprayed, so that the total molar flux remained the same. The spray pattern was characterized using the Malvern SprayTech [22]. Spray patterns were measured using the same flow rates and same nozzles as used in the scavenging experiments and the results are included in table 1.

Concentration [M]	0.05	0.1	0.2
Flow Rate [mL/min]	80	40	20
Molar Flux [mole/min]	0,004	0,004	0,004
d<50> spray profile [μm]	45	60	60

Table 1. Parameters used for the concentration study and the descriptors for the spray profile of the different flow rates.

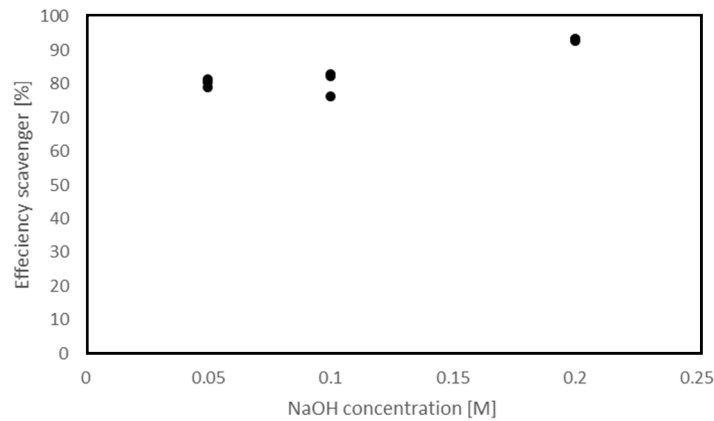


Figure 7. Efficiency of NaOH as a scavenger using different flow rates and different concentrations, but keeping the molar flux of NaOH constant

The results of the concentration study (Figure 7) show no significant differences between the efficiency of the scavenger with regards to concentrations. It was previously thought that spraying a lower concentration of scavenger at higher flow rates would result in smaller droplets with larger surface area. Contrary to expectations there is even a slight increase on scavenger performance at higher concentrations and low flow rates. The d_{50} , the median droplet size, of the spray measured for each of these conditions shows that whilst at the highest flow rates we see a decrease in the median spray size, there was no measureable difference between droplet sizes at the lower flow rates. This leads us to conclude that due to the relative small volume of the reaction chamber, and the high gas rates leading to good mixing conditions the droplet size is not a limiting factor in the scavenger's performance in this test.

The nozzles we are using are scaled down version of those typically found in the field, which are capable of delivering 0.5L/min, compared to our 50mL/min of scavenger solutions. Measurement of the droplet sizes produced with these larger nozzles varied between $d_{50} = 60\mu\text{m}$ for the water solutions and $d_{50} = 115\mu\text{m}$ for water glycerin mixture (Viscosity = 18 mPas). Therefore we do not expect, also for larger scale applications that droplet size differences due to viscosity will play a major role in Scavenger performance.

In order to determine the effect of viscosity on scavenging performance trials using different concentrations of NaOH and glycerin solutions were made. The results are shown in Figure 8. Again, the concentrations were chosen so that the flux of NaOH (conc. x flow rate) remained constant and only the viscosity, and droplet sizes were varying.

Concentration [M]	0,1	0,115	0,145	0,145
Flow Rate [mL/min]	80	70	45	45
% Glycerin	0	50	66	75

Viscosity ¹ [mPas]	0.89	2.5	17.7	35.5
1/viscosity [kg/ms]	0.001	0.0004	6×10^{-5}	3×10^{-5}
Molar Flux [mol/min]	0.008	0.008	0.008	0.007
d<50> spray profile [μm]	45	80	110	-

Table 2. Solutions of NaOH and glycerin used to determine the viscosity dependence of scavenging performance.

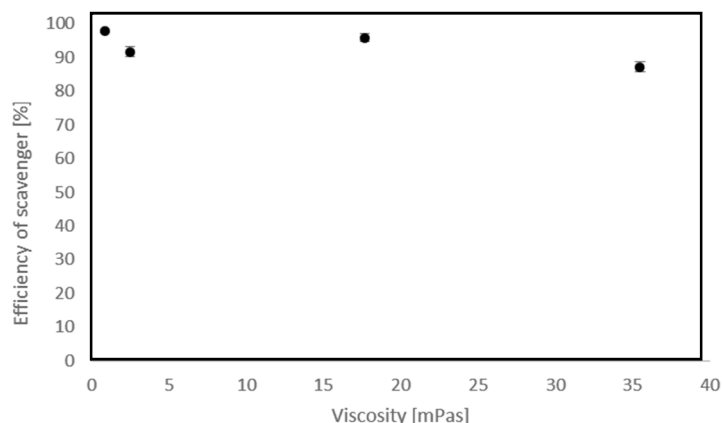


Figure 8. Effect of NaOH solutions with different viscosity on scavenging performance.

What we again notice is that there is virtually no difference in overall scavenger performance with regards to viscosity. Viscosity can affect the droplet size, and we do see increase in the median droplet size with increasing viscosity for the solutions we measured. The viscosity should also affect the diffusion rates of H₂S and scavenger inside the droplets. Both these factors are expected to contribute to a negative scavenging performance. However, our results show virtually no difference in scavenging performance, that is, all differences are within the reproducibility margin of our experiments. In this particular testing set up, we can conclude that these factors are minor effects.

Having established that droplet size, concentration and viscosity do not play a major role in the measured scavenging process in this test, we are able to make dilutions to our scavenger solutions in order to compare different products of the same concentration, rather than being restricted to testing only the final formulations of commercial products.

¹ Values of viscosity glycerin-water mixtures taken from literature [24].

Considering the four step model proposed for adsorption followed by chemical reaction, we can identify each of the steps with a physical-chemical parameter of the experiment. Step 1, the diffusion to the droplet will depend on the gas flow rates. We do not expect this to differ by changing the product. Step 2, dissolution of H₂S into the droplet will depend on H₂S solubility, the mass transfer resistance, or interfacial properties and the droplet surface area. We have observed that the droplet size, and thus surface area, does not play an observable role in the scavenging performance in this test. Therefore, any difference occurring between products at this step, can only be caused by changes to the interface, i.e. addition of a phase transfer catalyst, or H₂S solubility. For the studies of water formulated scavenger solutions we do not need to consider the impact of solubility as it remains constant for all our formulations. The third step of the adsorption/scavenging process involves the diffusion of the reactants inside the droplet. If this was a major factor we would expect that as viscosity increases, and diffusion rates decrease the scavenging performance would also decrease. However, due to limitations of our pump, and in order to maintain a decent spray we are automatically limited in the range of viscosities which could be used. We can estimate using the Stokes Einstein relation for estimating diffusion constants that the differences in the diffusion rates of H₂S between these samples is proportional to 1/viscosity. These values span two orders of magnitude and are written in table 2. However in the range investigated, for our system this was also not observed to be a critical factor.

This means within our test, the critical factors which we can examine are the mass transfer resistance of the interface (step 2), and the kinetics of the scavenging reaction (step 4).

In order to check the reliability/reproducibility of our measurements, we performed the same test, under the same conditions 4 times and compared the results. They are shown in table 3.

Scavenger used:	Liquid flow rate:	Gas flow rate:	H ₂ S final value
50% MEA Triazine solution	40 mL/min	40L/min	216
50% MEA Triazine solution	40 mL/min	40L/min	228
50% MEA Triazine solution	40 mL/min	40L/min	206
50% MEA Triazine solution	40 mL/min	40L/min	234

Table 3. Test reproducibility

From these measurements we obtain an average result of 222 ppm, and an interval of uncertainty of 28 ppm. This means that only differences between measurements of approximately 50 ppm, or 5% of the dynamic range of the measurement should be considered as significant. This relatively small level of uncertainty allows us to compare and rank different scavengers accurately.

Commercially available scavengers (MEA and MMA) Triazines were tested in the house testing set-up. The comparative graphs, shown in Figure 9, show the performance of both triazines under the same conditions.

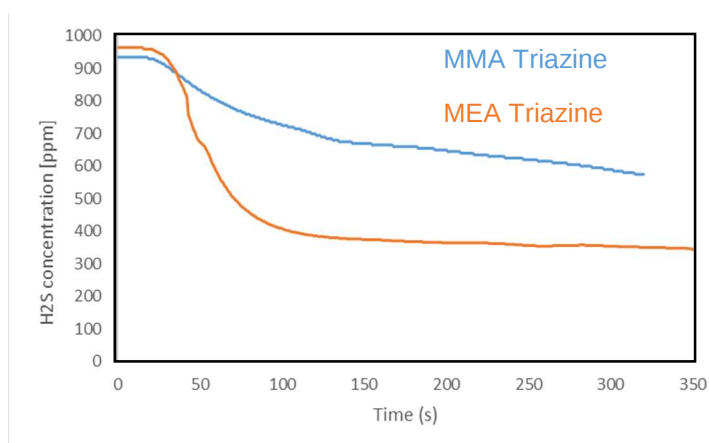


Figure 9. Comparative testing of MMA and MEA Triazines in the developed gas phase test

It can be seen that at the same molar ratio of H₂S to Scavenger the MEA scavenger is approximately twice as effective as the MMA scavenger. Here we recover the same results compared to traditional testing methods such as the bubble tower test. We also observe that the time required for the MEA Triazine to establish the steady state, that is a constant H₂S concentration is much shorter compared to the MMA Triazine. Previously published reactions rates show that the MEA Triazine has faster reaction kinetics than the MMA variant [23].

Conclusions:

Using fairly simple principles we have been able to develop a novel test method for ranking H₂S scavengers intended for use via direct injection in the gas phase. Unlike previous applications test, i.e. gas breakthrough test, or par reactors, this test combines for the first time spray properties of different scavengers, with a measurement of adsorption and reaction of H₂S with the scavenger.

We have determined, at least in the condition of good mixing, that the chemical kinetics and mass transfer resistance are the two dominant factors determining performance. Dilution or decreasing viscosity do not appear to be useful strategies to improve scavenger performance according to our test. For a given chemical, the most important factor for scavenging performance is how much of the chemical can be introduced at a given time.

Acknowledgements:

We sincerely thank the whole technical team: Romy Uhlmann for making all formulations to be tested, Christian Portaluppi for measuring the kinetics of the scavengers using the electrode method and providing support for the application testing, Rulldolf Schilb for building up of the equipment. We also thank Siegfried Steigler from Clariant Crop Services for support with spray characterization measurements. We thank James Begeal (Oil Services US) and AntonioPedro (Oil Services Brazil) for useful insights into field based H₂S

Scavenging. Additionally we thank Rudolf Strobel from Lechler for providing useful insights into industrial nozzles.

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