

Interpreting H₂S Scavenger Laboratory Test Results Using A Kinetic Model

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ABSTRACT

Several test procedures have been developed to evaluate the performance of H₂S scavengers in the laboratory. One of these procedures is based on a semi-batch continuous stirred-tank reactor (CSTR) concept with a constant flow of a gas containing H₂S. This procedure has been implemented at high pressures and temperatures (HP/HT) to evaluate the effect of several parameters (e.g., temperature, pressure, oil type, brine chemistry, water cut, pH, CO₂/H₂S concentrations) on the scavenging capacity of different chemicals. However, in many field applications, H₂S scavengers are injected at suitable points in the system with the expectation of having the H₂S concentration reduced below target levels before the fluid reaches certain parts. Therefore, not only the scavenging capacity but also its kinetics need to be considered when selecting an H₂S scavenger for specific applications.

A kinetic model was developed and implemented to assist in the interpretation of H₂S scavenger test results obtained from the CSTR with continuous gas flow procedure. Using this kinetic model, parameters related to the H₂S scavenger reaction kinetics can be extracted and used for qualifying chemicals for a specific application. This kinetic model also simulates the effect of different test parameters on the experimental results and can be used to extrapolate laboratory results to field conditions.

Key words: Chemical Treatment, Hydrogen Sulfide, Scavenger

INTRODUCTION

H₂S scavengers (SC) are commonly injected into multiphase pipelines transporting oil, water, and gas when the H₂S concentration is relatively low (ppm levels) but higher than the maximum allowable H₂S concentration in systems located downstream, due to integrity, safety or tariff limitations. Under these situations, it is expected that the H₂S scavenger injected in some points of the system (e.g., subsea) be capable of reducing the H₂S concentration before reaching certain parts of the system (e.g., topsides). In this case, the H₂S scavenger should be selected not only based on its capacity, but also on its kinetics at the expected field conditions.

Therefore, including kinetic related parameters in H₂S scavenger evaluations is critical to make informed decisions when selecting a specific treatment program in the field. Depending on the scavenging kinetics, scavenger concentrations much higher than its calculated capacity may be required to reach a specific target H₂S concentration within a given residence time.

An experimental methodology based on a continuous stirred-tank reactor (CSTR) approach with constant gas flow has been developed and used extensively to evaluate different scavengers for multiphase applications. The effects of the most relevant parameters have been published, including scavenger pre-saturation with CO₂; scavenger degradation; water cut; oil type; temperature; gas mixture composition; and pH.¹⁻³

This experimental approach has been used to qualify H₂S scavengers based not only on its capacity to extract H₂S from the multiphase system, but also on its kinetics. Some parameters have been shown to affect the kinetics of the reaction more than the thermodynamics.¹⁻³

A kinetic model was initially developed for Triazine based H₂S scavengers, but has been recently expanded to cover other types of H₂S scavengers.¹ This paper presents how this kinetic model can assist in the design of the test matrix and interpretation of the laboratory data to extract kinetic parameters that could be used in extrapolating laboratory results to the field.

TYPICAL TEST PROTOCOL

Figure 1 shows schematics of a typical set-up implemented for evaluating H₂S scavengers at high pressure using the semi-batch CSTR methodology. The main difference between the current setup and the original conceptual design shown in previous publications¹⁻³ is conducting the reaction in a stirred autoclave and injecting the scavenger via a high-pressure syringe pump.

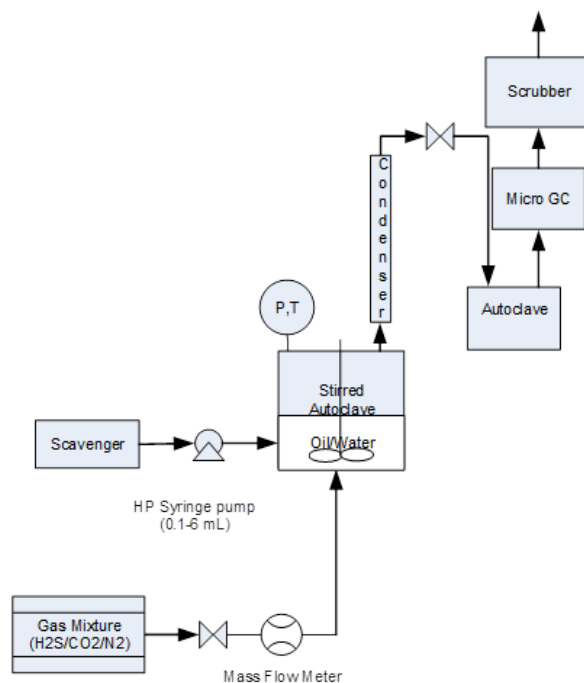


Figure 1: Schematics of a Typical Test Set-up for evaluating H₂S scavengers at high pressure using the semi-batch CSTR methodology

The typical procedure involves the following steps:

- Deaerate the autoclave
2. Load autoclave with a given volume of deaerated liquid(s), which could be brine and/or crude (or mineral) oil.
3. Start gas purge at a selected flow rate. Mass flow rate controllers are currently used to compensate for pressure and temperatures at different test conditions. In this paper, gas flow rates will be expressed in Standard cm³/min (SCCM).
4. Increase temperature and monitor pressure until they stabilize.

5. Record gas composition (H_2S , CO_2 , N_2) on-line (e.g, using a gas chromatograph, GC) until steady state.
6. Inject a given volume of H_2S scavenger.
7. Record changes in gas composition until returning H_2S to the initial value.

Figure 2 shows a typical test result.¹ The concentration of H_2S in the gas phase is shown on the vertical axis and the time is displayed on the horizontal axis. The following parameters are commonly used for data interpretation:

- Scavenging capacity ($\text{Kg H}_2\text{S/L SC}$), proportional to the red area in Figure 2a;
- Time required to reach a given percent of the scavenging capacity, for example 90% (Figure 2a)
- Time required to reach the minimum H_2S concentration ($t_{\min} [\text{H}_2\text{S}]$) (Figure 2a), as well as the mass of H_2S consumed per volume of scavenger ($\text{Kg H}_2\text{S/L SC}$) up to the point of minimum concentration (see yellow area in Figure 2b).
- Time to reach a specified capacity (e.g., 0.01 $\text{Kg H}_2\text{S/L SC}$ in in Figure 2a).
- Time to reach a specified H_2S concentration, after the minimum (e.g., 2.9% in Figure 2b)

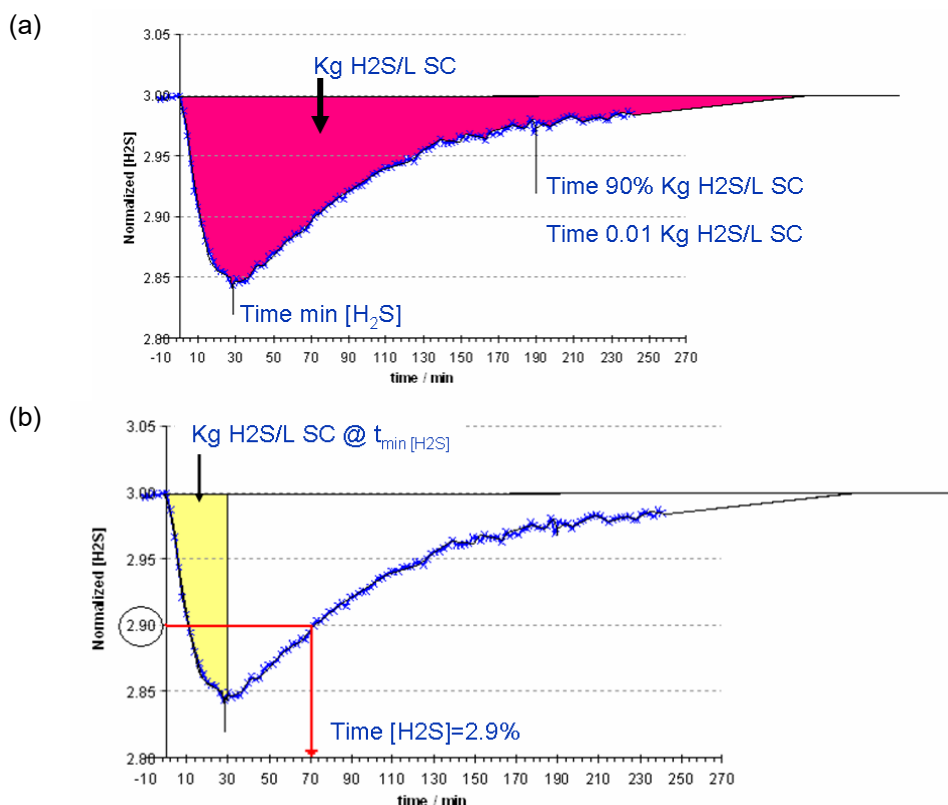


Figure 2. Typical experimental result and some parameters commonly used for data interpretation¹

MULTIPHASE H_2S SCAVENGING MODEL

Basis of the Model

summarizes the approach used for modeling Triazine based H_2S scavenger kinetics. As mentioned before, this model has been extended to other commercial H_2S scavengers.

¹ This section

In general, the H₂S scavenging kinetics when a liquid scavenger is directly injected into a multiphase flow pipeline can be separated in three steps:

1. Step 1: Transport of the liquid scavenger into the liquid phases.
2. Step 2: Transport of H₂S from the gas to the crude oil and aqueous phases.
3. Step 3: Chemical reaction between the scavenger and dissolved H₂S.

Step 1: Liquid Scavenger Mass Transport. This step assumes that the liquid scavenger injected into a multiphase line partitions between the produced water and crude oil phases, as shown in the equations below.



where SC_(i) represents the total scavenger being injected into the pipeline. SC_(w) and SC_(o) represent the scavenger dissolved in the aqueous and oil phase, respectively. The equilibrium constants K_i are related to the corresponding forward k_i and backward kinetic constants k_{-i}

$$K_i = \frac{k_i}{k_{-i}} \quad (4)$$

For a water-soluble scavenger (e.g., Triazine based), it can be assumed that K₁ >> 1, K₂ << 1, and K₃ << 1. If we define the partition coefficient of the scavenger between oil and water, P_{o/w}, as the ratio between the scavenger concentration in oil [SC_(o)] and water [SC_(w)]

$$P_{o/w} = \frac{[SC]_o}{[SC]_w} = K_3 \quad (5)$$

Then the concentration of scavenger in the water phase can be estimated using the following equation

$$[SC]_{(aq)} \approx \frac{Q_{sc}}{P_{o/w}Q_o + Q_w} [SC]_{(i)} \quad (6)$$

where Q_{sc} represents the effective scavenger rate injected in the pipeline, assumed to be much smaller than the water (Q_w) and oil (Q_o) flow rates, and [SC]_(i) is the concentration of active component in the scavenger.

These equilibria can be considered scavenger and mass transport dependent, but H₂S independent. The kinetics will be highly influenced by the chemical injection method (e.g., atomizers, mixers, nozzles) and flow characteristics (e.g., velocities of the different phases, flow pattern, etc.).

Step 2: H₂S Mass transport and Dissociation. The transport of H₂S_(g) from the gas phase to the liquid phase can be represented as





where $H_2S_{(w)}$ and $H_2S_{(o)}$ represent the H_2S dissolved in water and oil phases, respectively.

$H_2S_{(w)}$ will be in equilibrium with its ionic species (HS^- and $S^{=}$) and, therefore, the total dissolved sulfur species are pH dependent:



At pH below 6 (typical of oil production brines saturated with CO_2 and H_2S), the dominant specie is undissociated H_2S . At higher pH values, $[HS^-]$ increases and becomes the dominant specie in the pH range between 8 to 12.

In general, increasing pH above 6 increases significantly the total amount of H_2S that can be absorbed in water. Increasing temperature decreases H_2S solubility, but its impact in total dissolved sulfur species is more significant at lower pH values.¹

The chemical composition of the aqueous phase and presence of other acids (e.g., CO_2 , organic acids) affects the solution pH and may have an important effect on the total H_2S species dissolved. This should be considered when interpreting H_2S scavenger performance, since the alkaline nature of some of these commercial products tend to increase the solution pH and, therefore, reduce the H_2S concentration in the gas by an absorption process. It is important to distinguish this effect (which is reversible) from the irreversible H_2S scavenging reaction.

These equilibria can be considered as H_2S and mass transport dependent, but scavenger independent. As in step 1, the kinetics will be highly influenced by the flow characteristics (e.g., velocities of the different phases, flow pattern, etc.) and presence of mixers or turbulence enhancers.

Step 3: Chemical reactions. This step includes the homogeneous chemical reaction between the scavenger and dissolved H_2S , as well as other reactions that may affect the H_2S scavenging kinetics.

It is assumed that the dissolved scavenger reacts irreversibly with the dissolved H_2S to produce stable soluble products. Depending on the scavenger, the reaction may preferentially take place in the water and/or oil phase, as indicated in the equations below:



Several scavengers can react with H_2S molecules in several steps, depending on the temperature. Therefore, the above reactions may have stoichiometric coefficients on H_2S higher than one.

The homogeneous reactions are considered to be scavenger and dissolved H_2S dependent, but mass transport (Steps 1 and 2) independent.

For this paper, a model based on Triazine based scavenger reacting solely in the water phase will be considered. The kinetics of the scavenging reaction was assumed to follow the reaction path published for different triazines with Na_2S in alkaline solutions^{4,5}.

At the typical pH of oil and gas production systems, where the Triazines are protonated and HS^- is a dominating specie, equation (12) can be separated in the following reactions: