

Solids Formation in MEA Triazine Contact Towers, Prevention and Advice.

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ABSTRACT

Triazines (Hexahydrotriazines) are one of the most used H₂S scavenger chemistries in the North American oil and gas industry, specifically MEA triazines. The chemistry and application methods are well known due to over 2 decades of use, it has gained a commodity status and is thus a highly cost effective H₂S treatment solution. Currently it offers one of the lowest cost per mass of H₂S removed available in the market. There are however risks when using triazines, one being the formation of polymeric solids. This is mainly due to “overspending” the Triazine (over exposure of the dithiazine to H₂S). The term “over spent” was commonly referred to the creation of Trithianes. Recent studies have shed more light on the triazine reaction pathways and provided a more realistic approach to solids formation.⁴

This paper will focus on the use of MEA triazines in static and dynamic systems, specifically co-current and counter-current flooded dynamic contact towers, and how solids form in them, what can be done to reduce or eliminate solids formation and design suggestions for systems that has far lower fouling risks. The solutions and suggestions discussed in this paper comes from field experience with these systems.

Keywords: MEA Triazine, H₂S Removal, H₂S Scavenging, Contact towers, Triazine solids, Triazine fouling, Dithiazine, Scavenger towers, Amorphous polymeric dithiazine, bubble towers, Trithiane

INTRODUCTION

Liquid H₂S Scavengers can be any liquid that physically or chemically remove H₂S from liquids or gas. There are numerous liquid H₂S scavengers currently being utilized in the North American oil

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and gas industry with MEA Triazines being the most popular for applications requiring < 2 tons of Sulfur removal per day and typical amine or Claus systems for >2 tons of Sulfur removal/day. In this paper focus will be placed on the non-oxidative and non-regenerative H₂S scavenger MEA Triazine and its application in contact tower systems, specifically looking at solids (polymeric dithiazine) formation.

Some of the reasons why solids form in these systems will be discussed in this paper. To better understand the discussion, a brief overview of the most commonly used MEA Triazine contact tower configurations will be presented first. After looking at why and how the solids form, a solution section will follow providing advice and suggestions on how to eliminate or reduce the occurrence of solids.

CONTACT TOWERS

Currently two types of contact tower systems are being used with MEA Triazine; batch bubble towers (static) and continuous bubble towers (dynamic).

Batch Towers (Static)

The batch systems are extremely simple in nature. They usually consist of a pressure vessel, a gas inlet and gas outlet. The sour gas enters the tower at the bottom, bubbles through a fixed volume of Scavenger and exits the tower as sweet gas. The fixed volume of scavenger is used until fully spent after which it is replaced with a fresh batch of scavenger. These towers are usually filled up to 70% of maximum capacity. Change-out frequency (in days) is determined by dividing the fill capacity by the expected scavenger usage per day. Theoretical usage (consumption/day) of the scavenger depends on the amount of H₂S to be removed daily and is related to the stoichiometric reaction ratio of Triazine to H₂S (theoretical uptake in gallons/lb of H₂S or liters/kg of H₂S). A simple schematic of a batch application can be seen in Fig 1. These contactors can also contain internal packing.

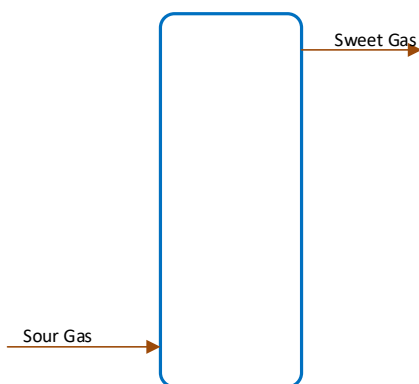


Figure 1: Batch Tower (Static)

Continuous Towers (Dynamic)

There are currently two main types of continuously fed contact towers (scavenger towers) utilized; co-current and counter-current. In both systems H₂S scavenger is injected continuously into the towers. Both systems are initially loaded with scavenger, at start-up the scavenger injection

pumps feed fresh scavenger into the tower at the estimated scavenger consumption rate. The main difference between them is; in the co-current system the liquid and gas flows upwards in the column and in the counter-current system the gas flows up through the scavenger whilst the scavenger flows down. There are numerous variations of these systems.

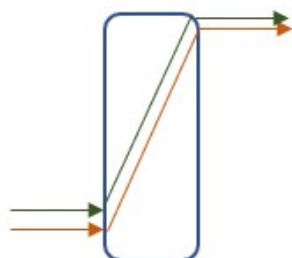


Figure 2: Co-Current

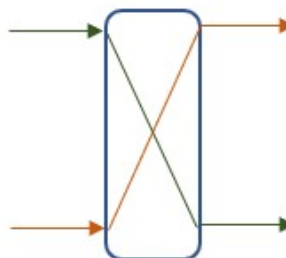


Figure 3: Counter-Current

For the purpose of this article a co-current system will be described as a continuously flooded tower that flows over to a post scrubber separator. Both the gas and scavenger exit the top of the tower and flows into a separator where the scavenger is separated from the gas. The spent scavenger is sent to a spent tank and disposed off. These types of configurations are very common in the industry. A simple schematic can be seen in Figure 4.

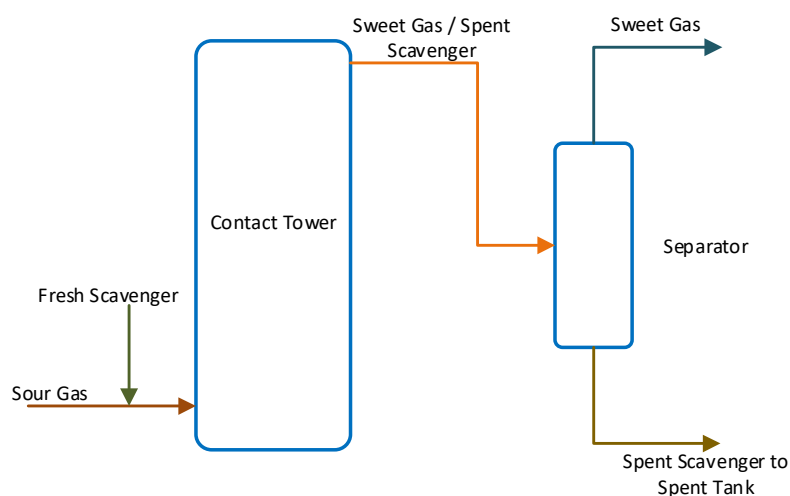


Figure 4: Co-current system with post scrubber separator.

On average, the majority of the well-designed Triazine continuous flooded bubble towers achieve system efficiency (or utilization) values of 70-85%. Efficiency relates to the amount of Triazine used to remove a certain amount of H_2S per day compared to theoretical values (based on stoichiometric ratios). Tower (Column) heights varies from 8 ft S/S (Seam to Seam) up to 30 ft S/S (9.14 meters S/S) with internal diameters ranging from 24" to 160" (60.96 to 403.2 cm). These contactors also use a wide variety of sparger or distributor designs, which does have an influence on overall system performance.¹ There are numerous factors that influence system efficiency,

they will not be discussed in this paper but further reading is advised.^{1,2} Operating conditions vary greatly with pressures ranges of 50 – 2000 psi (344.7 – 13789 kPa).

MEA Triazine Reaction

The reaction of MEA Triazine and H₂S is well documented. The Nitrogen atoms in the Triazine molecule are substituted with sulfur atoms. Nitrogen substitution up to two occurs resulting in dithiazine (5-hydroxyethylhexahydrodithiazine) formation. No measurable quantities of Trithiane are formed (3rd Nitrogen substitution) although the industry believed for a long time that the Trithiane is causing solids formation. The exact reaction path of the dithiazine to form solids has been under investigation the last couple of years with the latest reaction theory presented below:^{3,4}

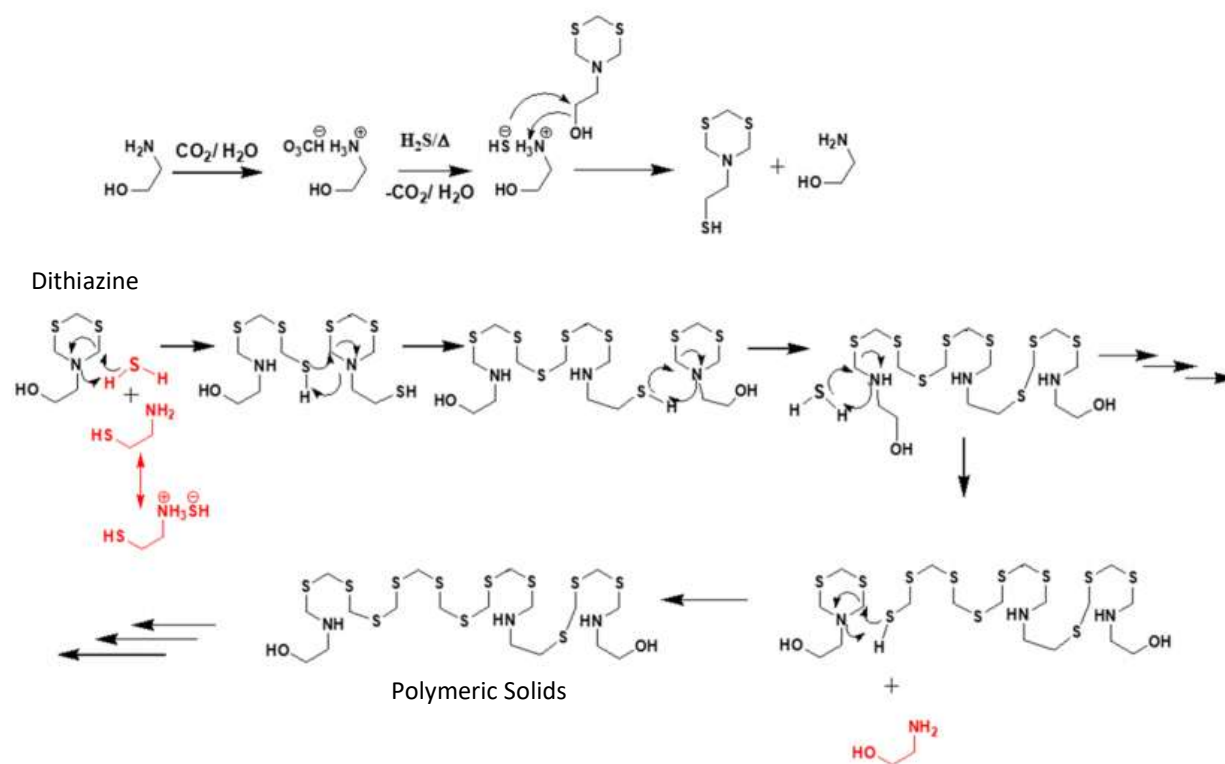


Figure 5: Dithiazine reaction to polymeric solids^{3,4}

It should be noted that when the industry determines theoretical scavenger usage, the stoichiometric ratio of 1:2 is used most often (1 mole of Triazine reacting with two moles of H₂S). However, a stoichiometric ratio of 1:4 is possible if the system contains no CO₂.⁴

As can be seen from Fig 5, it is proposed that dithiazine reacts with MEA and H₂S to initiate the polymerization process to eventually form a complex polymeric structure (amorphous polymeric dithiazine)¹. Taylor et al⁴ suggests that after this initial reaction, the polarization reaction will continue without any H₂S present.

This polymeric material is highly insoluble in most organic and inorganic solvents and acids. This solid will result in fouling of processing equipment, contact towers, pipelines etc. In severe cases solids deposition will result in the shut-in of entire systems.

Triazine and H_2S reaction kinetics are fast and will thus react first before any other reactions with H_2S occur (thus in a solution of Triazine and Dithiazine, the H_2S will be consumed by the Triazine reaction first). This is important to keep in mind for the sections to follow.

SOLIDS FORMATION – STATIC TOWERS

Solids formation (fouling) in static scavenger towers are common. Some static towers are filled with packing which complicates matters substantially when the tower needs to be cleaned. To understand why fouling occurs in contactors it is important to understand how the scavenger removes the H_2S from the gas. In Figure 1 it was shown that these systems are very simple in nature, gas is bubbled through a static volume of scavenger. The gas bubble distribution achieved in the column depends on numerous factors including the scavenger viscosity, superficial gas velocity, sparger design, system pressure, gas density etc.^{1,2} For the purpose of this article we will use gas hold-up as a parameter that summarizes the gas dispersion through the tower.

Gas hold-up is the fraction of the total volume occupied by gas, basically providing us a simple parameter to show how effectively the gas is distributed into the liquid. A high gas hold-up indicated that a high percentage of the total fluid volume is occupied by the gas, this indicates that we can disperse the gas into relatively small bubbles which rises much slower than big bubbles (Stoke's law). The slower the bubbles rise the more bubbles will occupy the space at the same time, hence a larger gas hold-up value. The larger the gas hold-up, the larger the interfacial contact area and thus an improved mass transfer is expected. In summary, the better gas bubble size distribution achieved, the better overall H_2S removal will be (in general).

In a static bubble tower application, the tower is filled to approximately 70% of max vessel volume. The 30% space left will be occupied by the gas, in general we assume the gas hold-up of the system will be slightly less than 30%. Gas with a certain concentration of H_2S will be bubbled through the volume of scavenger. Based on the amount of H_2S present in the inlet gas, a certain amount of scavenger will be consumed (reacted to form dithiazine). In the ideal world (no fluctuation in inlet gas volume and H_2S concentration), one would expect a linear decline of unreacted Triazine and a linear increase in dithiazine (Figure 6.) To illustrate this, we assume we have 2000 gallons of fresh scavenger in a static tower. The inlet gas contains 50 lbs/day of H_2S that needs to be removed. Assuming we need 50 gallons of MEA Triazine to remove the 50 lbs of H_2S , this will result in a system change-out frequency of 40 days (2000 gallons/50 gallons/day).