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Sulfur removal in amine plants

Jenny Seagraves, INEOS LLC, USA, discusses a number of design considerations to optimise organic sulfur removal with amine solutions, demonstrating how target sulfur levels can be achieved in the treated gas, with the possibility of eliminating the caustic polishing unit.

The current practice of gas treating with alkanolamine (amine) solutions is intended to maximise the removal of hydrogen sulfide (H_2S) and/or carbon dioxide (CO_2) from gas streams. Although requirements do exist for the removal of organic sulfur compounds such as carbonyl sulfide (COS), carbon disulfide (CS_2) and mercaptans (RSH), their removal is usually incidental in an amine unit, and near complete removal is typically achieved by a downstream caustic polishing unit. In response to stricter environmental regulations and to further reduce operating costs, more and more refiners and gas processors are focusing attention towards improving the organic sulfur removal capabilities of amine plants.

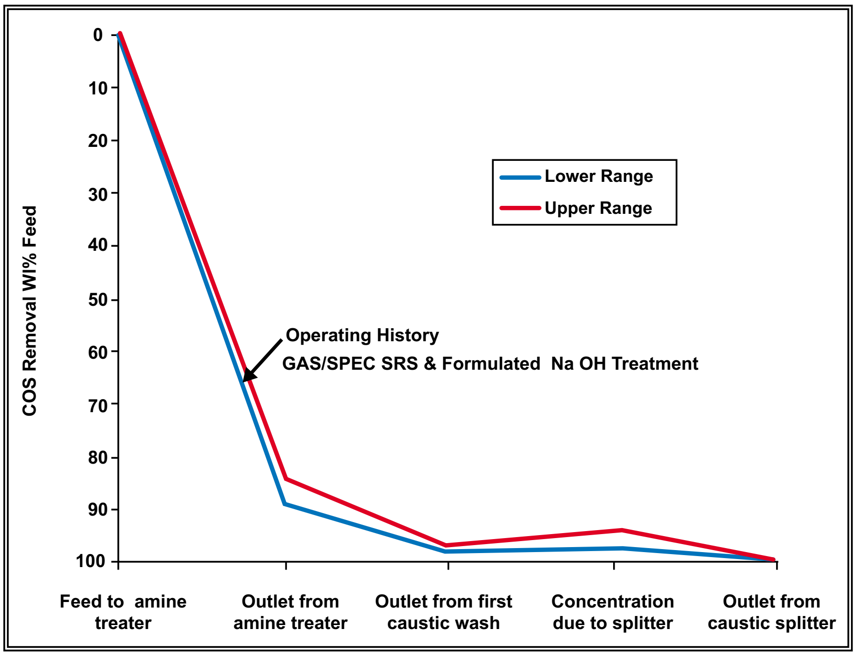

Figure 1. COS removal in a C_3/C_4 treater.

The need for more organic sulfur data

Sulfur compounds have different properties and these affect the mechanism by which they are removed. Unfortunately, sulfur compounds are often lumped together in their treatment, with the assumption that a single solvent or process can address the removal of all the sulfur species. In order to select the best solvent or process, the first priority is to obtain good estimates of the levels of different sulfur species present and also to determine if any fluctuations over time are expected.

Even with a good sulfur analysis, designers may be required to make decisions based on the limited data concerning sulfur removal efficiencies. Although COS has been the subject of detailed laboratory studies, more data is needed to complete accurate modelling for industrial applications. Detailed data for methyl and ethyl mercaptan has been very scarce until Jou et. al.[1,2,3] recently published solubility data in MDEA and DEA. Even so, there are numerous other sulfur species in natural gas streams for which no data is available. These include long chain mercaptans and heavy sulfur compounds. Fortunately, these sulfur species are present in trace quantities. However, as sulfur specifications are lowered, filling these data gaps will become increasingly important for proper design.

Table 1. Solubility of methyl mercaptan in amine solvents

Solvent	Henry's constant @ 40 ˚C MPa	Source
50 wt% GAS/SPEC CS-Plus	1.2 - 2.2	6
50 wt% GAS/SPEC CS-2010	1.8 - 2.6	6
50 wt% MDEA	6.1	6
50 wt% MDEA	6.2 - 10.6	1
35 wt% DEA	6.0	3
35 wt% DEA with acid gas	8.6 - 34.3	3
50 wt% MDEA with acid gas	15.1 - 26.3	1
50 wt% MDEA with acid gas	9.8 - 14.0	6

Mechanism of COS and CS_2 removal

According to Kohl and Nielsen[4], COS and CS_2 removal is achieved by three mechanisms in amine solutions:

- Hydrolysis (reaction with water) to form H_2S and CO_2, which may be subsequently absorbed.

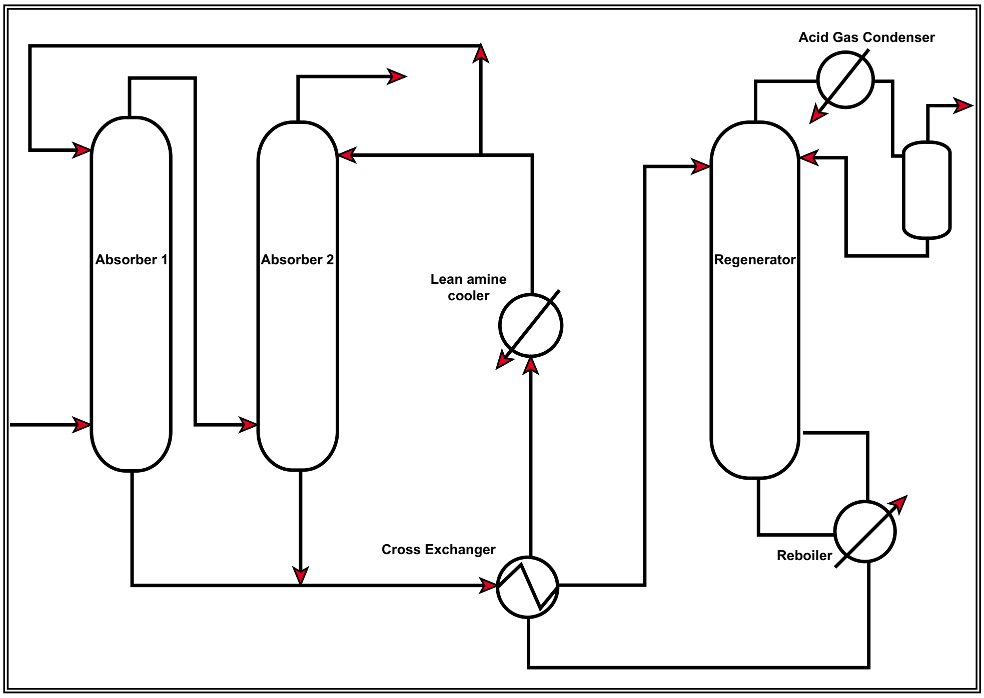

Figure 2. Conceptual design for optimum organic sulfur removal.

- Direct reaction with the amine to form a relatively stable compound (that may or may not be regenerable).
- Physical solubility in the solution.

Of the above, only hydrolysis and direct reactions play a significant role in COS removal. Since COS and CS_2 are very similar in structure to CO_2, they follow the same reaction mechanism as CO_2. COS has been studied extensively and the removal efficiency is better understood than CS_2. Sharma[5] found that primary and secondary amine reactions with COS are:

$$2\ RNH_2 + COS \longrightarrow RNHCOS^- + RNH_3^+$$

$$2\ R_2NH + COS \longrightarrow R_2NCOS^- + R_2NH_2^+$$

Tertiary amines such as methyldiethanolamine (MDEA) act as a base catalyst for the hydrolysis. The reaction is:

$$R_3N + H_2O + COS \qquad R_3NH + + HCO_2S^-$$

Although the mechanism of COS is very similar to CO_2, the rate of COS reaction with amine is substantially lower. Sharma[5] indicates that the reactivity of COS is approximately 100 times slower than CO_2. Therefore, complete removal of COS usually requires high removal of CO_2. The efficiency of COS removal depends on the reactivity of the amine, the absorption temperature and the contact time. The relative effectiveness of various amines for COS removal is:

GAS/SPEC$^+$ CS-Plus >> MEA > DGA™ > GAS/SPEC SRS, DEA > DIPA > MDEA

Primary amines such as monoethanolamine (MEA) and Diglycolamine™ (DGA) will undergo direct reactions with COS to form degradation compounds, which may decrease the solution acid gas carrying capacity overtime. INEOS GAS/SPEC CS-Plus shows superior reactivity toward COS but is also susceptible to degradation by COS. Diethanolamine (DEA), GAS/SPEC SRS and diisopropanolamine offer moderate COS removal with some CO_2 slip, but do not form COS degradation products in any appreciable amounts. MDEA has the lowest reactivity toward COS and is generally not considered to be a good solvent for COS removal.

Mechanism for mercaptan removal

Mercaptans do not react with amines but are removed primarily by physical absorption in the solvent. Since all amine solutions are comprised mostly of water on a mole % basis and mercaptan solubility in water is very low, amine solutions are generally not an efficient solvent for mercaptan removal.

Mercaptans are much weaker acids than H_2S and CO_2, and short chain mercaptans such as methyl and ethyl mercaptans form weakly bonded mecaptide salts in solution. Therefore, more basic amines tend to give better absorption characteristics for methyl and ethyl mercaptan than less basic amines such as MDEA. On the other hand, long chain mercaptans are expected to behave much more like hydrocarbons and may be better removed by amines or solvents that exhibit higher hydrocarbon solubility. Unfortunately, high hydrocarbon solubility is generally not a desired characteristic for a solvent, particularly in liquid hydrocarbon treating applications.

The presence of H_2S and CO_2 interferes with the absorption of mercaptan in amines. Acid gases reduce the alkalinity of the amine solution, which reduces mercaptan absorption. The data of Jou, et. al.[1,2,3] show that the solubility of methyl and ethyl mercaptan in MDEA and DEA are reduced by two to three fold when H_2S and/or CO_2 are present. Data from the INEOS GAS/SPEC laboratory also demonstrate the same effect. Henry's constant was obtained by the equation $\varphi\ P_i/x_l$, where φ is the fugacity coefficient, P_i is the mercaptan partial pressure, and X_i is the mole fraction in the liquid phase. Therefore, a smaller Henry's constant value indicates better solubility.

Process considerations for COS removal

Improvement in total sulfur removal may be accomplished in an existing unit by changes in solvent or by changes in operation. Increasing the number of trays or the mass transfer area will enhance COS removal. If maximum CO_2 removal is desired, selection of a more reactive amine will yield the best results. However, some of the more reactive amines also form degradation products. In these cases, periodic reclaiming of the solution should be considered in the design.

Operational changes such as increasing the lean amine temperature will increase the reaction rate of the COS with the amine. However, the temperature should be maintained such that H_2S removal is not affected and the maximum absorber temperature is not exceeded. The author has observed lean amine temperature as high as 150 °F in order to enhance the COS reactions. The guideline for maximum temperature in the amine absorber is 185 °F to minimise corrosion, due to acid gas flashing. If higher lean amine temperature is used, a water wash should also be incorporated to minimise amine losses due to vaporisation.

In applications where maximum sulfur removal and minimum CO_2 removal is desired, some selectivity may have to be sacrificed. Plant data indicate that in a selective MDEA application, COS removal is approximately 10 - 33%. Processes other than amines should be considered if both selective H_2S and COS removal are required.

Another possibility in optimising COS removal is the use of a non standard amine design. It has been suggested by Butwell[7] that H_2S and CO_2 removal competes with the COS removal. Therefore, improved COS removal can be achieved by contacting the gas with lean amine in the second stage after the H_2S and CO_2 have been removed in the first stage.

A casestudy in COS removal

One of the earliest casestudies of COS removal was given by Pearce and Bacon[8]. In this example, a refinery system switched from MEA to MDEA to decrease amine degradation and increase selectivity of removal of H_2S over CO_2. One particular C_3/C_4 liquid hydrocarbon stream had a feed to the amine unit with a COS content of less than 100 ppm COS. The specification was less than 50 ppb in the treated product.

The plant started up on generic MDEA with approximately 20 wt% aqueous solution followed by a one stage caustic scrubber. The initial COS removal was considerably less than adequate; although the main unit showed a 33% removal of COS, the conventional caustic scrubber showed little or no removal. The GAS/SPEC technical service group was then called into the refinery. It was found that the problem could be greatly reduced by converting the generic MDEA system to GAS/SPEC SRS solvent and upgrading the caustic scrubber to formulated caustic. The outlet COS was reduced to 100 ppb; however, this was still above the specification. A second column was put into service also utilising formulated caustic, with the required specification then being met.

The performance of the total COS removal system after the system stabilised is shown in Figure 1. The GAS/SPEC SRS solvent achieved 85% removal of COS. The formulated caustic was improved to 97%. Removal after the formulated caustic polishing unit was 99.95%.

Process considerations for mercaptan removal

In existing amine plants, mercaptan removal is almost always very low. This is the result of designs that strive to remove the targeted amounts of H_2S and/or CO_2 with the lowest possible circulation rate. Therefore, when mercaptan removal is needed, the only option is to increase circulation or to reduce the absorption temperature. Increasing the amine concentration may help, but the maximum amine concentration is limited by viscosity and/or corrosion considerations. In these cases, a change in amine solvent may provide small improvements to mercaptan removal. However, more dramatic improvement may require significant changes in plant design.

The concept of a two stage absorption amine unit can be extended to mercaptan removal. The advantage of utilising a second absorption stage for mercaptan removal is that the solubility of mercaptan is better in the absence of acid gas. Also, there is better control of the absorption temperature favouring maximum mercaptan removal. It is difficult to control temperatures in the first absorption column if significant amounts of H_2S and/or CO_2 are present. The exothermic reaction of the amine and acid gases will result in a significant temperature rise that further reduces mercaptan solubility. In some cases, the absorber temperature will increase by as much as 100 °F due to this exothermic reaction. Hence, the overall mercaptan removal is limited by the absorption of H_2S and/or CO_2 and their influence on the temperature of the absorption column. If practical, further improvements can be realised if the sweet gas from the first stage can be compressed prior to the second stage. This will help to reduce the overall circulation requirements. Figure 2 illustrates a conceptual design for enhanced mercaptan removal.

The concept of a two stage absorber design also opens up possibilities to various regeneration schemes. The amine from the second stage can be combined with the rich from the first stage and regenerated in a traditional stripping column. However, since the acidic sulfur components from the second stage is so low, other regeneration methods such as ion-exchange or electrochemical methods may also be employed for the liquid stream from only the second absorber. This could reduce the overall regeneration requirements of the amine unit.

Conclusion

Stricter environmental regulations, the cost of caustic treating and the cost of spent caustic disposal are forcing many gas processors and refiners to consider non traditional alternatives to address their total sulfur removal needs. Although amines have long been considered ineffective for organic sulfur removal, there has been increased interest to re-evaluate this process to maximise sulfur removal. Several strategies have been presented to help improve the organic sulfur removal capabilities of amine plants. Solvent selection, absorption temperature control and two stage absorption schemes are possible options.

While plant operators would like to eliminate their caustic polishing unit altogether, this may or may not be possible given that organic sulfur removal varies depending on the specific species present. Prediction of organic sulfur removal is difficult because of the scarcity of data. While success may be possible in some cases, it is unlikely that success can be guaranteed for every application. Each application must be assessed separately to determine whether the targeted removal is feasible and if economics favour a change in solvent, absorption temperature control and/or an alternative design configuration.

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Notes

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