Effect of MMEA on the Performance of Tail Gas and AGE Units

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ABSTRACT

Methylmonoethanolamine (MMEA) is one of the secondary amines produced by the degradation of N-methyldiethanolamine (MDEA). It is frequently present in the MDEA solvents used in tail gas treating units (TGTUs) and is a possible contaminant in acid gas enrichment (AGE) as well. The presence of MMEA seems to be associated with SO_2 breakthrough events from the sulfur plant into the TGTU amine system. MMEA is a highly reactive amine with fast kinetics, and its presence even in relatively small concentrations (typically less than 1% by weight) is shown to cause tremendous loss of selectivity by increasing the absorption rate of carbon dioxide. This paper presents two case studies that establish MMEA as a cause for much lower-than-expected selectivity in a TGTU and loss of sulphur plant feed gas quality in two AGE applications.

Introduction

The secondary amines MMEA and DEA are fragments of the decomposition of MDEA. A detailed and intriguing discussion of MDEA degradation in TGTUs can be found in Critchfield and Jenkins (1999). These authors noted that secondary amines accumulate when MDEA degrades, and MMEA and DEA in particular are common fragments of degradation of the parent amine. Accelerated degradation appears to be associated with SO_2 breakthrough from the sulfur plant to the TGTU amine system. *Whenever there are organic acid heat stable salts (HSSs), there is almost always MMEA and often DEA as well*. Indeed, as a percentage of the original amine, the total concentration of secondary amine fragments is roughly twice that of the total organic acids present. Critchfield and Jenkins argue that two-carbon organic acids are probably derived from cleaving the ethanol arms of MDEA itself. There is usually more DEA than MMEA (roughly a 2:1 ratio) in a TGTU amine sample. MMEA as a contaminant at a concentration of 1 wt% is not rare, nor is DEA at 2 wt%. However, the presence of MMEA is potentially much more deleterious to tail gas treating, i.e., CO_2 slip, than DEA because the rate constant for the reaction of MMEA with CO_2 is surpassed only by piperazine. MMEA reacts 10 times faster than DEA and about 30 to 40% faster than even MEA at absorption conditions. Thus, MDEA solvent containing 1 wt% total secondary amine with a DEA to MMEA ratio of 2 to 1 reacts at roughly four times the rate of the same solvent containing only 1 wt% of DEA alone. There is potential then for MMEA-contaminated MDEA solvent to suffer a significant loss of its ability to slip carbon dioxide because of the highly reactive nature of the MMEA component. As borne out by the case studies to follow, the impact of MMEA on such applications as TGTUs and AGE units which require high selectivity for hydrogen sulphide can be quite severe. In contrast, as a contaminant, DEA has only a modest effect on selectivity.

It is fortunate that MMEA is a rather volatile amine. Although it seems to form rapidly as a result of an SO_2 breakthrough event, over time it is removed from the solvent by being stripped into the gas being treated. However, its removal rate is not high enough to prevent it from having a severely deleterious effect on process performance over a considerable period of time. Thus, unless SO_2 breakthrough is a very common and frequent event, the MMEA level is naturally kept in check although performance will suffer during, and for quite some time following, an SO_2 breakthrough.

Case Studies

The rest of this paper presents case studies of the effect of MMEA on the performance of a TGTU and two AGE units. In all cases it is found that MMEA even at 0.3 wt% causes significant loss in process performance. The TGTU case is of an actual operating unit; the AGE cases are hypothetical, but under conditions typical of real processing.

Tail Gas Treating

This refinery tail gas treating unit contains 20 feet of 2-in Pall Rings and handles 28 MMscfd of gas with 1.70% H_2S and 3.48% CO_2 in a stream of mostly nitrogen. The solvent is nominally 37 wt% MDEA. Ion chromatography shows the solvent contains the following heat stable salt contaminants: 0.33 wt% thiosulfate, 0.15 wt% formate, and 0.15 wt% sodium ion. In addition, another peak eluted on the IC, but it was unidentified and was assumed to be DEA with a concentration of 1.0 wt%. The entire TGTU was modeled using the ProTreat® mass transfer rate-based simulator. Table 1 shows simulation results for the virgin solvent (uncontaminated MDEA), solvent with the known HSS slate, and the same solvent with 1.0 wt% DEA. First, it can be seen that the presence of HSSs results in a somewhat more cleanly stripped solvent which leads to reduced H_2S leak from the unit. When the unidentified peak is assumed to be 1.0% DEA, the H_2S leak increases because of the factor of nearly 9 times higher CO_2 loading in the lean amine— CO_2 reacts with DEA and is harder to strip out. The H_2S backpressure is increased over the lean solvent. But none of these results agreed with measured unit performance.

Table 1   Effect of MMEA on TGTU Performance

Case	H_2S Leak (ppm)	% CO_2 Slip	Lean H_2S (Loading)	Lean CO_2 (Loading)
Virgin Solvent	73	93.4	0.00457	0.000035
w/ HSSs	61	93.9	0.00187	0.000016
w/ HSSs + 1.0 wt% DEA	89	93.4	0.00189	0.000139
Effect of MMEA at 1:2 Ratio with DEA				
w/ HSSs + 0.67 wt% DEA + 0.33 wt% MMEA	208	83.6	0.00164	0.000215
Effect of 2 wt% Secondary Amines				
w/ HSSs + 2.00% DEA	128	91.9	0.00178	0.000453
w/ HSSs + 1.33 wt% DEA + 0.67 wt% MMEA	219	76.5	0.00132	0.000739

The CO2 slip through this TGTU was consistently measured by the plant at 83%, and the H_2S leak was considerably higher than predicted by these three cases. When the assumed 1 wt% DEA is replaced, however, with the more likely 2:1 mix of DEA and MMEA, the simulated lean loading falls to 83.6% in an almost perfect prediction of the measurement, and the additional CO_2 absorption causes the H_2S leak to rise to just over 200 ppm—unfortunately there are no comparison H_2S data.

The effect of doubling the total concentration of the secondary amine degradation products (but keeping the 2:1 ratio of DEA to MMEA) shows a slightly higher H_2S leak, and even lower CO_2 slip. However, the resulting changes from doubling the MMEA content are not nearly as pronounced as they were from introducing a small amount of MMEA in the first place. To summarise, the presence of even a seemingly quite small concentration of MMEA, a known product of MDEA degradation, can have a surprisingly large and detrimental effect on the CO_2 being slipped through a TGTU.

Acid Gas Enrichment

Acid Gas Enrichment units are sometimes operated using an amine circuit that is completely separate from the rest of the units in a gas plant. The enriched gas feeds a sulphur plant and tail gas from the sulphur plant is then treated using amine held in a completely separate TGTU amine circuit. The possibility of an SO_2 breakthrough into the AGE amine is completely obviated. However, because the TGTU and the AGE both use well stripped MDEA as the solvent, there is the temptation to use a common regenerator and operate these two units on the same amine circuit. We have already seen the deleterious effect of an SO_2 breakthrough on TGTU performance. Thiosulfate can also be introduced in a stealthier manner by allowing the amine to be exposed to air. Here, the oxygen dissolved in either fresh makeup amine or an inadequately blanketed lean amine surge tank can react with residual H_2S in solution by the chemistry below (reference Kohl & Nielsen and ASRL):

$$2HS^- + 2O_2 = H_2O + S_2O_3^=$$
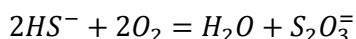
What are its possible effects on AGE? This question is answered by using the ProTreat® mass transfer rate-based simulator to examine two cases: one involves enriching an acid gas from 8% H_2S to a concentration that can be fed to a Claus sulphur plant; the other upgrades an already marginally acceptable acid gas from 34% H_2S to a higher quality sulphur plant feed.

AGE of 8% H_2S Gas

The unit treats 30 000 Nm³/h of water-saturated acid gas containing 8 mol% H_2S, 90 mol% CO_2 and 1 mol% each of methane and ethane at 1 barg. The solvent is 45 wt% generic MDEA but we will allow for up to 2 wt% of the secondary amines DEA and MMEA either in a 2:1 ratio, or with DEA alone. There are two important measures of treating success in AGE: the first is the H_2S content of the enriched gas; the other is the H_2S leak from the absorber. The first is to be maximized, the second minimized.

Table 2 shows that the presence of HSSs and even 1.0 wt% DEA does not much alter the CO_2 slip compared with virgin (uncontaminated) solvent. Heat stable salts drive the lean loading of H_2S somewhat lower, resulting in a reduction in H_2S leak from the absorber. The presence of 1.0 wt% DEA essentially negates the slight benefit of the HSSs. However, if the secondary amine products of MDEA decomposition are in fact DEA and MMEA in the 2:1 ratio reported by Critchfield and Jenkins[1], more CO_2

is absorbed, and the H_2S leak rises. The enriched gas drops from 43–44% H_2S to 37% H_2S, the CO_2 slip decreases from 88% to 85% and the H_2S leak increases from 20 ppmv to 46 ppmv. If the solvent actually has 2 wt% total secondary amine with DEA to MDEA in a 2:1 ratio, what was a fairly satisfactory acid gas drops to only 33% H_2S. Contamination can turn a fairly well enriched gas into a very marginal one.

Table 2   Effect of MMEA on Enrichment of 8% H_2S Gas

Case	H_2S Leak (ppmv)	CO_2 Slip (%)	Enriched Gas (Dry Basis) H_2S (mole%)	CO_2 (mole%)
Virgin Solvent (45 wt% MDEA)	20.9	88.2	43.0	57.0
w/ HSSs	15.6	88.6	43.7	56.3
w/HSSs + 1.0 wt% DEA	19.9	88.8	44.3	55.7
Effect of MMEA at 1:2 Ratio with DEA				
w/HSSs + 0.67 wt% DEA + 0.33 wt% MMEA	46.4	85.2	37.4	62.6
Effect of 2 wt% Secondary Amines				
w/ HSSs + 2.00 wt% DEA	25.2	89.0	44.6	55.4
w/ HSSs + 1.33 wt% DEA + 0.67 wt% MMEA	129	82.3	32.9	67.1

AGE Upgrading for 34% H_2S Gas

The conditions for this case are the same as for the 8% H_2S gas already described except that the H_2S content of the acid gas feed to the AGE is now 34% which required the solvent flow to be increased from 1,250 USgpm to 3,500 USgpm. As can be seen in Table 3, the virgin solvent is capable of achieving

Table 3   Effect of MMEA on Enrichment of 34% H_2S Gas

Case	H_2S Leak (ppmv)	CO_2 Slip (%)	Enriched Gas (Dry Basis) H_2S (mole%)	CO_2 (mole%)
Virgin Solvent (45 wt% MDEA)	67.4	82.6	75.3	24.7
w/ HSSs	2.9	83.3	76.1	23.9
w/HSSs + 1.0 wt% DEA	3.1	83.8	76.6	23.4
Effect of MMEA at 1:2 Ratio with DEA				
w/HSSs + 0.67 wt% DEA + 0.33 wt% MMEA	3.7	73.6	66.8	33.2
Effect of 2 wt% Secondary Amines				
w/ HSSs + 2.00 wt% DEA	3.0	83.5	76.3	23.7
w/ HSSs + 1.33 wt% DEA + 0.67 wt% MMEA	4.1	66.7	61.4	38.6

an H_2S leak from the absorber of 67 ppmv, but with HSSs, the lean amine H_2S loading is driven so low that about 3 ppmv H_2S leak can be achieved even when there is as much as 2 wt% DEA in the solvent. Under all four sets of conditions without MMEA, the enriched gas is 75–76% H_2S. But when MMEA is

present, H_2S in the enriched gas falls by 10 to 15 full percentage points depending on the MMEA concentration. This is *a very significant loss in Claus feed gas quality* (and a significant increase in gas volume flow to the Claus unit because of the extra carbon dioxide) which is caused by a seemingly small amount of MMEA contamination of the solvent. *MMEA is a very important contaminant in MDEA*.

MMEA Volatility

The presence of MMEA can seriously degrade the performance of such treating units as TGTUs and AGEs where high selectivity is of paramount importance. Along with DEA, it appears to be formed as a degradation product from MDEA when SO_2 breakthrough events from the sulphur plant into the TGTU amine system occur. MMEA is a fairly volatile amine, having a vapour pressure roughly 100 times that of MDEA. Thus, MMEA will be gradually removed from the solvent and leave with the gas from the absorber assuming the generation rate from SO_2 breakthrough is not continual. In fact, as Jenkins and Critchfield report, SO2 breakthrough would eventually render the solvent ineffective by protonating all of the amine. However, many amine unit systems these days are equipped to run with continuous heat stable salt removal (HSSR) units. It is not inconceivable to have the HSSR removing the thiosulfate as it is being generated resulting in a steady state level of thiosulfate that is constant and balancing the SO_2 incursion into the system.

TGTUs do not usually have surge capacity beyond what is naturally contained in the tower sumps, heat exchangers, and piping. Total residence time in the system is typically 15–25 minutes. With a solvent flow of 600 USgpm as in the case study presented here, the solvent in the TGTU amounts to about 12,000 USgal or about 100,000 pounds of which about 500 pounds are MMEA (0.5 wt%). The vapourisation loss from the system was simulated to be about 1.5 lb/h, so about a month would be needed to remove 90% of the MMEA. Thus, provided there is a single SO_2 incursion event, the system should recover by itself in a reasonable short period of time. However, breakthrough events do not usually occur in isolation, so although this degradation product will be continuously removed, it will also tend to be repeatedly formed. Therefore, one should expect to find a measureable level of MMEA in any TGTU that suffers from periodic SO_2 breakthrough, despite MMEA's volatility.

Processing Ramifications

Besides degrading amine unit performance, the Claus performance itself is reduced and the additional CO_2 pickup that enters the sulfur plant can build over time, limiting the processing capacity of the sulfur block and ultimately throttling back the upstream hydrocarbon producing units. The financial penalty can be enormous.

Concluding Remarks

Secondary amines are a product of MDEA decomposition which appears to be associated with SO_2 breakthroughs from a sulphur plant into TGTUs and, if on a common amine circuit, into AGEs as well. Indeed, this has been an argument in many camps for not integrating the TGU and AGE systems. Tail gas cleanup can be seriously impacted by the presence of even a relatively small concentration of MMEA (although it is not much affected by DEA). CO_2 slip can be much reduced from what a clean solvent would provide, and the consequence is abnormally high H_2S leak from the unit. In AGE units a design based on clean solvent may suggest satisfactory enrichment of acid gas. However, if a small

amount of MMEA is present, the enriched gas may turn out to be completely unsuitable and a modified sulphur plant may be needed.

For the first time, it is now conceivable to construct end-of-run TGU or AGE simulations that properly account for degraded and HSS contamination. The cost of poor amine and sour water system hygiene, unreliable air demand control, and TGU front-end can be more than just cleaning up the heat stable salts that result from SO_2 or oxygen incursion into the amine. Loss of tail gas unit (and corresponding SRU) processing capacity from MMEA formation will result until the amine system inventory is dumped and recharged with fresh MDEA. Mass transfer rate-based simulation using the ProTreat® simulator will reveal these issues during the design phase when there is the opportunity to take measures to deal with the problem, rather than after the plant is built when correcting problems is much more expensive.

References

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