

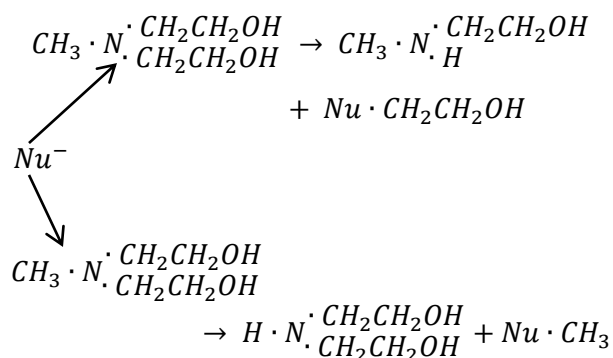
The CONTACTOR™

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Effect of MMEA Contamination on Selectivity in TGTUs

The secondary amines methylmonoethanolamine (MMEA) and diethanolamine (DEA) are fragments of the decomposition of *N*-methyl-diethanolamine (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 SO₂ 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.

Clark (2015) has suggested the following mechanism for the degradation reactions:



Here Nu⁻ is a nucleotide such as sulfate, cyanide and thiocyanate ion. In the first reaction, attack by the nucleotide forms MMEA while the second forms DEA. There is usually more DEA than MMEA, however, (roughly a 2:1 ratio) in a TGTU amine

sample. The mechanism suggests that if the cleavage kinetics for the CH₃-N and the N-CH₂CH₂OH bonds are equal, there should be twice as much MMEA as DEA. This is the opposite of what is generally observed, so one can only assume that the kinetic constants differ by a factor of about four.

MMEA as a contaminant at a concentration of 1 wt% is not rare, nor is DEA at 2 wt%. But the presence of MMEA is potentially much more deleterious to tail gas treating, i.e., CO₂ slip, than DEA because the rate constant for the reaction of MMEA with CO₂ 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 study to follow, the impact of MMEA on such applications as TGTUs (and AGE units as will be discussed in the March issue) which require high selectivity for hydrogen sulphide can be quite severe (Keller, 2012). In contrast, as a contaminant, DEA has only a modest effect on selectivity.

Fortunately, MMEA is a rather volatile amine. Although it seems to form rapidly as a result of an SO₂ 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 SO₂ 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 SO₂ breakthrough. Any anionic heat stable salt can potentially cause this effect.

Case Study

This refinery tail gas treating unit contains 20 feet of 2-in Pall Rings and handles 28 MMscfd of gas with 1.70% H₂S and 3.48% CO₂ 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 simulated treating for the virgin solvent (uncontaminated MDEA), solvent with the known HSS slate, and the same solvent with 1.0 wt% and 2.0 wt% DEA. Table 2 shows corresponding simulated solvent lean loadings. First, it can be seen that the presence of HSSs results in a somewhat more cleanly stripped solvent (Table 2) which leads to reduced H₂S leak from the unit. When the unidentified peak is assumed to be 1.0% DEA, the H₂S leak increases because of the factor of nearly 9 times higher CO₂ loading in the lean amine—CO₂ reacts with DEA and is harder to strip out. The H₂S backpressure is increased over the lean solvent. But none of these results agreed with measured unit performance. The CO₂ slip through this TGTU was consistently measured by the plant at 83%, and the H₂S leak was considerably higher than predicted by these three cases.

Table 1 Effect of MMEA on TGTU Performance

Case	H ₂ S Leak (ppmv)	CO ₂ Slip (%)
Virgin Solvent	73	93.4
w/ HSSs	61	93.9
1 wt% Secondary Amines		
w/ HSSs + 1 wt% DEA	89	93.4
w/ HSSs + 0.67 wt% DEA + 0.33 wt% MMEA	208	83.6
2 wt% Secondary Amines		
w/ HSSs + 2.00 wt% DEA	128	91.9
w/ HSSs + 1.33 wt% DEA + 0.67 wt% MMEA	219	76.5

Table 2 Effect of MMEA on Lean Loadings

Case	H ₂ S Loading	CO ₂ Loading
Virgin Solvent	0.00457	0.000035
w/ HSSs	0.00187	0.000016
1 wt% Secondary Amines		
w/ HSSs + 1 wt% DEA	0.00189	0.00189
w/ HSSs + 0.67 wt% DEA + 0.33 wt% MMEA	0.000139	0.000139
2 wt% Secondary Amines		
w/ HSSs + 2.00 wt% DEA	0.00178	0.000453
w/ HSSs + 1.33 wt% DEA + 0.67 wt% MMEA	0.00132	0.000739

When the assumed 1 wt% DEA is replaced, however, with the more likely 2:1 mix of DEA and MMEA, the simulated CO₂ slip falls to 83.6% in an almost perfect prediction of the measurement, and the additional CO₂ absorption causes the H₂S leak to rise to just over 200 ppm—unfortunately there are no comparison H₂S data.

The effect of doubling the total concentration of the secondary amine degradation products shows an even lower CO₂ slip, but the change from doubling the MMEA content isn't nearly as great as from having a first small amount of MMEA.

As shown by ProTreat® mass transfer rate-based simulation, 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 CO₂ being slipped through a TGTU.

References

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