

The CONTACTOR™

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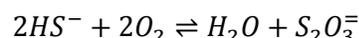
Effect of MMEA Contamination on Acid Gas Enrichment

In the February issue of *The Contactor™* we discussed the effect of fragments from MDEA degradation on tail gas treating unit performance. The effect on acid gas enrichment (AGE) units can be even more striking. This is this month's subject.

As elaborated in the preceding issue, the attack of certain nucleotides (anions) can fragment MDEA into DEA and MMEA. As a contaminant MMEA at a concentration of 1 wt% is not rare, nor is DEA at 2 wt%. But MMEA is potentially much more harmful to good CO₂ slip than DEA because the reaction rate constant for 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 (their usual proportion) reacts roughly four times as fast as the same solvent containing only 1 wt% of DEA alone. MMEA-contaminated MDEA can be expected to produce much lower carbon dioxide slip. This can be quite striking in AGE units because poorer CO₂ slip also lowers the H₂S content in the gas to the SRU. The objective, after all, is to maximize the H₂S concentration in the SRU feed. A case study will demonstrate the effect.

AGE 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 SO₂ 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 SO₂ 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 H₂S in solution by the chemistry below:



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% H₂S to a concentration that can be fed to a Claus sulphur plant; the other upgrades an already marginally acceptable acid gas from 34% H₂S to a higher quality sulphur plant feed.

AGE of 8% H₂S Gas

The unit treats 30,000 Nm³/h of water-saturated acid gas containing 8 mol% H₂S, 90 mol% CO₂ 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 H₂S content of the enriched gas; the other is the H₂S leak from the absorber. The first is to be maximized, the second minimized.

Tables 1 and 2 show that the presence of HSSs and even 1.0 wt% DEA does not much alter the CO₂ slip compared with virgin (uncontaminated) solvent. Heat stable salts drive the lean loading of H₂S somewhat lower, resulting in a reduction in H₂S 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 (1999), more CO₂ is absorbed, and the H₂S leak rises. The enriched gas drops from 43–44% H₂S to 37% H₂S, the CO₂ slip decreases from 88% to 85% and the H₂S 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% H₂S. Contamination can turn what was a fairly well enriched gas into a very marginal one.

Table 1 Absorber Performance— 8% H₂S Gas

Case	H ₂ S Leak (ppmv)	CO ₂ Slip (%)
Virgin Solvent	20.9	88.2
w/ HSSs	15.6	88.6
1 wt% Secondary Amines		
w/ HSSs + 1 wt% DEA	19.9	88.8
w/ HSSs + 0.67 wt% DEA + 0.33 wt% MMEA	46.4	85.2
2 wt% Secondary Amines		
w/ HSSs + 2.00 wt% DEA	25.2	89.0
w/ HSSs + 1.33 wt% DEA + 0.67 wt% MMEA	129	82.3

Table 2 Enrichment from 8% H₂S Gas

Case	Enriched Gas	
	H ₂ S (mol%)	CO ₂ (mol%)
Virgin Solvent	43.0	57.0
w/ HSSs	43.7	56.3
1 wt% Secondary Amines		
w/ HSSs + 1 wt% DEA	44.3	55.7
w/ HSSs + 0.67 wt% DEA + 0.33 wt% MMEA	37.4	62.6
2 wt% Secondary Amines		
w/ HSSs + 2.00 wt% DEA	44.6	55.4
w/ HSSs + 1.33 wt% DEA + 0.67 wt% MMEA	32.9	67.1

Enrichment of 34% H₂S Gas

The conditions for this case are the same as for the 8% H₂S gas already described except that the H₂S content of the acid gas feed to the AGE is now 34%, requiring solvent flow to increase from 1,250 USgpm to 3,500 USgpm. As can be seen in

Table 3, under all four sets of conditions without MMEA, the enriched gas is 75–76% CO₂. But when MMEA is present, H₂S 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.

Table 3 Enrichment from 34% H₂S Gas

Case	Enriched Gas	
	H ₂ S (mol%)	CO ₂ (mol%)
Virgin Solvent	75.3	24.7
w/ HSSs	76.1	23.9
1 wt% Secondary Amines		
w/ HSSs + 1 wt% DEA	76.6	23.4
w/ HSSs + 0.67 wt% DEA + 0.33 wt% MMEA	66.8	33.2
2 wt% Secondary Amines		
w/ HSSs + 2.00 wt% DEA	76.3	23.7
w/ HSSs + 1.33 wt% DEA + 0.67 wt% MMEA	61.4	38.6

An AGE unit design based on clean solvent may suggest satisfactory enrichment of acid gas. However, a small amount of MMEA can make the enriched gas unsuitable and a modified sulphur plant may be needed. 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

Critchfield, J. E., Jenkins, J. L., *Evidence of MDEA Degradation in Tail Gas Treating Plants*, PTQ, Spring, 1999.

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