

Selecting Amines for Sweetening Units

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ABSTRACT

The selection of an amine for gas sweetening is complex and must be based on several process considerations. These factors are analyzed based on experimental data and a process simulation program for gas sweetening called TSWEET.

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INTRODUCTION

The technology of using alkanolamines for removal of hydrogen sulfide and carbon dioxide from natural gases has been used for decades. Since the 1960's and 70's several amines have come into general use, however, limited information has been reported in the literature concerning the amine best suited to a particular service. Many amine units which are operating very inefficiently could be optimized by simply changing amines.

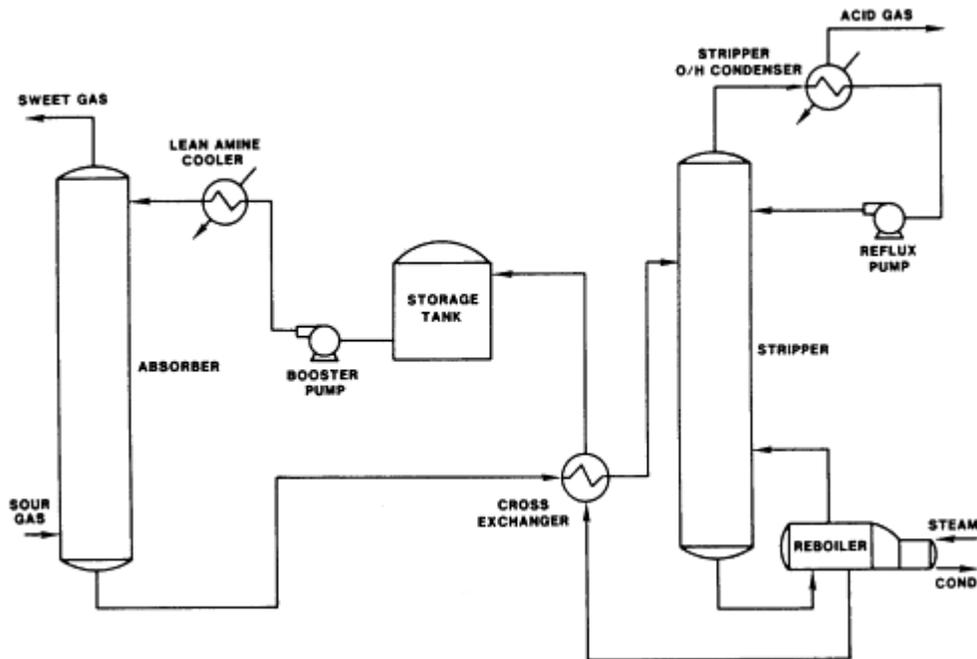


Figure 1. Process flow sheet for common sweetening plant.

The basic flow scheme for an amine sweetening unit is shown in Figure 1. In the design of the process, the primary concern is that the sweetened gas meet the required purity specifications with respect to H_2S and CO_2 . The secondary objective is to select the amine which optimizes equipment size and minimizes plant operating costs. Some of the factors to be considered in the selection of the proper amine for design or existing plant evaluation include:

1. Can the amine circulation rate be reduced by selecting an amine which may be used at a higher concentration and/or solution acid gas loading?
2. Could the reboiler/condenser size and duty be minimized by use of an amine which requires a lower circulation rate, and/or which has lower heats of reaction with H_2S and CO_2 ?
3. If the sales gas specifications allow, could H_2S be selectively absorbed from the sour gas while rejecting CO_2 ? Can the H_2S and CO_2 absorption from the sour gas be optimized by use of an amine mixture?
4. Do corrosion problems exist? If so, is there an amine or mixture of amines more resistant to degradation which can be used to minimize corrosion problems and reduce solution losses?
5. Could an alternate flow scheme increase the efficiency of the process (i.e. split flow, absorbers in series or parallel, use of a precontactor for bulk CO_2 removal, or bulk CO_2 removal using a pressure swing plant with no stripper)?

According to Astarita, et al. (1983) 50 to 70% of the initial investment for an amine sweetening unit is directly associated with the magnitude of the solvent circulation rate, and another 10 to 20% of the initial investment is dependent on the regeneration energy requirement. In addition, about 70% of operating costs, excluding labor, result from regeneration. Since selection of the proper amine can greatly reduce both the regeneration energy requirement and solution circulation rate, choice of the amine or combination of amines best suited to the conditions can have a dramatic impact on the overall costs associated with a sweetening unit. Alternative flow schemes for amine sweetening plants have been previously discussed in detail by Polasek, Donnelly and Bullin (1983) and will not be investigated in the present work.

GENERAL CONSIDERATIONS FOR SELECTING AMINES

The general criteria for amine selection in sweetening plants have changed over the years. Until the 1970's monoethanolamine (MEA) was the amine first considered for any sweetening application. Then in the 1970's, as

exemplified in papers by Beck (1975) and Butwell and Perry (1975), switching from MEA to diethanolamine (DEA) yielded favorable results. In the past ten years, MDEA, DGA, and mixed amines have steadily gained popularity.

As different operating conditions are tested and proven with a particular amine, they become accepted on an industry-wide basis. Thus each amine has a currently "accepted" range of process conditions and parameters associated with it. These "accepted" conditions and parameters are discussed below. Some of the typical operating conditions for common amines are summarized in Table 1.

Table 1. Typical Operating Conditions and Data for Amines

Amine:	MEA	DEA	DGA	MDEA
Solution strength, wt. %	15-20	25-35	50-70	20-50
Acid gas loading, mole/mole (carbon steel)	0.3-0.35	0.3-0.35	0.3-0.35	Unlimited
Ability to selectively absorb H_2S	No	Under Limited Conditions	No	Under Most Conditions

Monoethanolamine:

MEA is generally used as a 10 to 20 weight % solution in water. Due to corrosion problems, the acid gas loading is usually limited to 0.3 to 0.35 moles acid gas per mole of amine for carbon steel equipment. Loadings as high as 0.7 to 0.9 mole/mole have been used in stainless steel equipment with no corrosion problems. Although MEA itself is not considered to be particularly corrosive, its degradation products are extremely corrosive. MEA reacts with oxidizing agents such as COS, CS₂, SO₂, SO₃, and oxygen to form the soluble products which must be removed from the circulating system to avoid serious corrosion problems. Degradation or deactivation of MEA also lowers the effective amine concentration but fortunately a reclaimer can recover most of the deactivated amine. Since MEA is a primary amine, it has a high pH which enables MEA solutions to produce a sweetened gas product containing less than 1/4 grain H₂S per 100 SCF at very low H₂S partial pressures. When MEA is used, essentially all of the CO₂ must be absorbed to produce gas which meets the quarter grain H₂S specification. Since the heat of reaction for MEA is about 825 BTU/lb CO₂, a feed gas containing high concentrations of CO₂ will cause either extremely high reboiler duty or poor acid gas stripping. The heat of reaction for MEA with H₂S is 550 BTU/lb. Note that the heat of reaction for all amines is a function of loading and other conditions and usually varies by only 50 to 60 BTU/lb up to about 0.5 mole/mole total acid gas loadings. Above this loading, the heat of reaction varies considerably and should be calculated as a function of loading.

Diethanolamine:

DEA is most commonly used in the 25 to 35 weight % range. The total acid gas loading for DEA is also limited to 0.3 to 0.35 mole/mole for carbon steel equipment. DEA can safely be loaded to equilibrium (~1 mole/mole) when using stainless steel equipment or when using inhibitors as in the SNPA process (Kohl and Reisenfeld, 1979). The degradation products of DEA are much less corrosive than those of MEA. Exposure to oxygen forms corrosive acids and COS and CS₂ may react irreversibly with DEA to some extent. DEA is not reclaimable in most units because at atmospheric pressure it decomposes below its boiling point and vacuum reclaimers have proved operationally unreliable. Since DEA is a secondary alkanolamine, it has a reduced affinity for H₂S and CO₂ and may not be able to produce pipeline specification gas for some low pressure gas streams. In general, as the gas pressure is lowered, the stripping steam must be increased or a split flow design must be used. In some cases, even these measures will not suffice and another solvent must be used.

Under some conditions, such as low pressure and a liquid residence time on the tray of about 2 seconds, DEA is selective toward H₂S and will permit a significant fraction of the CO₂ to remain in the sales gas. At least one case of selective absorption of H₂S with DEA has been documented by Donnelly and Henderson (1974). In this particular case, selective absorption was not desired but was encountered due to a low contactor pressure of 11 psig and a short liquid residence time on the trays. An H₂S/CO₂ feed gas ratio >1 would probably rule out any chance of significant CO₂ slippage while producing 1/4 grain H₂S/100 SCF sales gas. The heat of reaction for

DEA with CO₂ is 653 BTU/lb, which is about 25% less than for MEA. The heat of reaction of DEA with H₂S is 511 BTU/lb.

Diglycolamine:

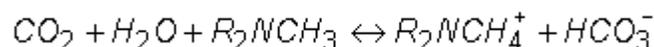
DGA is generally used as a 50 to 70 weight % solution in water. As with MEA, the corrosion problems with DGA prevent solution loadings above about .35 mole/mole. Sweetening of gas streams containing high acid gas partial pressures can result in absorber bottoms temperatures in excess of 200°F. DGA has a tendency to preferentially react with CO₂ over H₂S. It also has a higher pH than MEA and thus can easily achieve quarter grain H₂S specification except in some cases where large amounts of CO₂ are present relative to H₂S. DGA has some definite advantages over the other amines in that higher DGA concentrations in the solution result in lower circulation rates and also in lower freezing points. In addition, DGA is not as likely to react irreversibly with COS, CS₂, SO₂ and SO₃. In fact, DGA has a known but unquantified ability to absorb COS as well as methyl- and ethyl-mercaptans. One of the primary disadvantages of DGA is the high heat of reaction for both CO₂ (850 BTU/lb) and H₂S (674 BTU/lb).

Methyldiethanolamine:

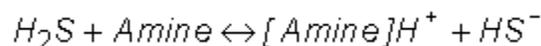
An accepted set of operating conditions has not been as firmly established for MDEA as for the previously mentioned amines. This has been due to the flexibility and versatility of MDEA and the resulting wide range of applications. Although the range of operating conditions for MDEA is expanding, the present range of successful applications will be discussed below.

MDEA is commonly used in the 20 to 50 wt % range. Lower weight % solutions are typically used in very low pressure, high selectivity applications such as a SCOT tail gas cleanup unit. Due to considerably reduced corrosion problems, acid gas loadings as high as 0.7 to 0.8 mole/mole are practical in carbon steel equipment. Higher loadings may be possible with few problems. Exposure of MDEA to oxygen forms corrosive acids which, if not removed from the system, can result in the buildup of iron sulfide in the system. MDEA has several distinct advantages over primary and secondary amines which include lower vapor pressure, lower heats of reaction (600 BTU/lb CO₂ and 522 BTU/lb H₂S), higher resistance to degradation, fewer corrosion problems and selectivity toward H₂S in the presence of CO₂. Most of these advantages have also been reported by Blanc et al. (1982). Depending on the application, some of the advantages have special significance. For example, due to its lower heat of reaction, MDEA can be employed in pressure swing plants for bulk CO₂ removal. In a pressure swing plant, the rich amine is merely flashed at or near atmospheric pressure and little or no heat is added for stripping.

At the present time, the overwhelming advantage that MDEA possesses over the other amines is that it is readily selective toward H₂S in the presence of CO₂. At high CO₂/H₂S ratios, a major portion of the CO₂ can be slipped through the absorber and into the sales gas while removing most of the H₂S. The enhanced selectivity of MDEA for H₂S results from the inability of tertiary amines to form a carbamate with CO₂. MDEA does not have a hydrogen attached to the nitrogen and cannot react directly with CO₂ to form carbamate. The CO₂ reaction can only occur after the CO₂ dissolves in water to form a bicarbonate ion which then undergoes an acid-base reaction with the amine:



At least six different mechanisms for the CO₂-MDEA reaction have been proposed by Cornelissen (1982), Barth, et al. (1981), and Danckwerts (1979). MDEA can, however, react with H₂S by the same proton transfer mechanism of primary and secondary amines (Jou, et al., 1982):



Selective absorption of H₂S can be enhanced by optimizing absorber design to obtain a liquid tray residence time between 1.5-3.0 seconds and by increasing the temperature in the absorber. Both of these conditions favor H₂S absorption with CO₂ rejection.

Mixed Amines:

Mixtures of amines are generally mixtures of MDEA and DEA or MEA and are used to enhance CO₂ removal by MDEA, as described by Polasek, Bullin, and Iglesias-Silva (1992). Such mixtures are referred to as MDEA-based amines with DEA or MEA as the secondary amine. The secondary amine generally comprises less than 20% of the total amine on a molar basis. At lower concentrations of MEA and DEA, the overall amine concentration can be as high as 55 wt % without the implementation of exotic metal equipment.

MDEA-based mixtures are normally used to increase the CO₂ pickup in cases where the MDEA is allowing too much CO₂ to slip overhead in the absorber. Spiking the MDEA with MEA or DEA to achieve the desired CO₂ pickup is often advantageous over a complete amine switch out to a DEA or MEA system because the MDEA regenerator reboiler may be undersized for the DEA or MEA system. Amine mixtures are particularly useful for lower pressure applications since the MDEA becomes less capable of picking up sufficient CO₂ to meet pipeline specifications at lower pressures. At higher pressures, amine mixtures appear to have little or no advantage over MDEA (Polasek et. al, 1992). Mixed amines are also useful for cases where the CO₂ content of the feed gas is increasing over time due to field aging.

Operating problems associated with mixed amines are determining and maintaining amine mixture concentration.

PROCESS DESIGN AND EVALUATION CAPABILITY

Most of the above general considerations for selecting amines have been common knowledge for some time. However, since design procedures have historically been very approximate, engineers have had no means by which to accurately and systematically investigate the potential of each amine. The design and evaluation capability was greatly improved with the development of a process simulation program called TSWEET for gas/liquid amine sweetening units. TSWEET was initially developed in 1979 and has undergone constant improvement and expansion in the ensuing years.

TSWEET is an advanced process simulation program using the flexible flowsheet concept. Beginning with the process flowsheet and operating parameters, complete material and energy balances for steady state operating conditions can be performed. Rigorous tray-by-tray calculations using the Ishii-Otto (1973) or Boston & Sullivan (1974) method are used as an aid in the design of the stripper and absorber columns or in the evaluation of existing units. The common amines MEA, DEA, DGA, and MDEA are included in TSWEET's component base as well as water, H₂S, CO₂, ammonia, and compounds present in natural and synthetic gases and NGL streams. Mixed amine systems may also be modeled. Vapor pressures of H₂S and CO₂ over the amine solutions are calculated by a modified Kent and Eisenberg (1976) equilibrium model or by the NRTL (Non-Random Two-Liquid) model. A kinetic model predicts the effect of residence time, temperature, solution concentration, pressure and type of amine on the rate of CO₂ absorption. The program has been demonstrated to be very reliable in calculating the performance of amine gas sweetening plants and will accommodate multiple absorbers in LPG and/or gas service which feed a common stripper. The capabilities of TSWEET have been previously described by Polasek et al. (1983), Holmes and Bullin (1983), and Polasek et al. (1982).

DISCUSSION OF SPECIFIC CASES

The general considerations for selecting amines were applied to several specific cases. In these cases, an operating plant was used as a base and the sweetening simulation program TSWEET was used to explore the potential of different amines in each plant.

The first two cases are taken from a text published in the early 1960's by Estep, McBride, and West (1962). This text discussed the performance and problems of a pair of sweetening and sulfur production facilities. One of the facilities, a split-flow unit, was located at Okotoks, Alberta in Western Canada. The other, a unit with both a high and a low pressure absorber, was located in the United States at Worland, Wyoming. Both of these facilities used MEA in their amine sweetening plants and both facilities were reported to operate effectively. The primary problem in these sweetening units was corrosion due primarily to the fact that the 15 weight % MEA was being loaded to above 0.6 mole acid gas per mole of amine.

The operating data and corresponding TSWEET simulation results for the Okotoks and the Worland Plants are shown in Tables 2 and 3, respectively. The results from TSWEET simulations using DEA are also shown in each table. As can be seen from Tables 2 and 3, the calculated outlet gas composition and reboiler duty matched the operating data very closely for both plants.

Table 2. Comparison of Okotoks Plant Performance with Different Amines

	MEA Operating Data	TSWEET for MEA Operating Data	TSWEET for DEA Alternative
Lean Amine Conc. wt %	21.5	21.8	51.9
Semi-Lean Conc. wt %	15.0	15.7	34.7
Rich Amine Conc wt %	15.7	16.1	36.3
Circulation rate, gpm	lean 390 semi-lean 1620	389 1611	387 1613
Gas Flow, MMSCFD	29.46	same	same
H2S inlet, %	33.4	same	same
CO2 inlet, %	10.4	same	same
H2S out, gr/100scf	0.01	0.009	0.016
CO2 out, ppm	--	155	40
Total rich loading, mole/mole	0.65	0.62	0.40
Approach to Equilibrium at absorber bottom	--	49	35
Steam Rate, lb/gal	0.9	0.9	0.9
Reboiler Duty, MMBTU/lb	109	109	78
Total Steam to Reboilers, lb/hr	113,600	113,200	113,400

Table 3. Comparison of Worland Plant Performance with Different Amines

	MEA Operating Data	TSWEET for MEA Operating Data	TSWEET for DEA Alternative
Lean Amine Conc,wt %	14.7	14.7	36
Circulation rate, gpm	High P Absr 980 Low P Absr 120	980 120	980 120
Gas Flow, MMSCFD	High P Absr 26.33 Low P Absr 0.513	same same	same same
H2S inlet, %	High P Absr 23.7 Low P Absr 58.0	same same	same same
CO2 inlet, %	High P Absr 2.3 Low P Absr 1.2	same same	same same
H2S out, gr/100scf	High P Absr 0.25 Low P Absr 0.50	0.29 0.82	0.18 0.50
CO2 out, ppm	High P Absr N/A Low P Absr N/A	138 175	81 106
Total rich loading, mole/mole	0.66	0.68	0.42
Approach to Equilibrium at absorber bottom	High P Absr N/A Low P Absr N/A	67 26	50 19
Steam Rate, lb/gal	1.12	1.12	1.12
Reboiler Duty, MMBTU/lb	N/A	66	66
Total Steam to Reboilers, lb/hr	74,200	73,000	73,100

After demonstrating that TSWEET accurately predicted the performance of the existing operations, TSWEET was then used to explore the use of DEA as an alternative. The results of a simulation with 36 weight % DEA are shown in the last column in Tables 2 and 3. For the Okotoks unit, a 36.3 weight % rich DEA solution was simulated. Using the MEA solution circulation rate and reboiler duty, the rich loading for the DEA case decreased to 0.4 mole acid gas/mole amine. This lower rich amine acid gas loading, in addition to the lower corrosion associated with DEA, would result in greatly reduced corrosion problems. The sweetened gas would also still easily meet the pipeline specifications. Very similar results are observed for the Worland Plant. If corrosion inhibitors or stainless steel were used with the DEA solution, and the loading was increased to the MEA level of 0.66, the DEA circulation rate and thus the reboiler duty could be reduced by more than 30%. Since the feed to the stripper must be heated by 40°F and since the amine solutions have a heat capacity of 0.7 to 0.9 BTU/lb, about 25 to 30 BTU's are saved for each one pound reduction in circulation rate. Another factor responsible for the reduced reboiler duty is the lower heat of reaction for DEA. This results in a savings of about 170 BTU per pound of acid gas recovered in the still.

The North Carolina Plant of Dome Petroleum was selected for the third case since this unit was switched from DEA to MDEA. The performance and operating data for the plant were reported by Daviet, et al. (1984). The acid gas contaminants in the feed consisted of about 3.5% CO₂ and 50 ppm H₂S. When using DEA, the amine plant was operating at its maximum capacity due primarily to reboiler limitations in the stripper. The amine unit operation was also unstable. Since the plant produced gas only marginally below the 1/4 grain H₂S/100 SCF specification, any upset would bring the plant down. The H₂S came primarily from one well which usually contained around 300 ppm H₂S. However, each time this well was shut in for a few hours, the H₂S concentration in the gas from the well increased to about 1200 ppm for a short period after startup. Since the amine unit could not accommodate any additional H₂S, the sales gas exceeded pipeline specification and was automatically flared. Dome was understandably not satisfied with this state of affairs and explored a number of alternatives to alleviate the problem. After running TSWEET for a variety of conditions, Dome's engineering group determined that the unit could be converted to MDEA with no equipment modifications. The calculations showed that selective absorption would occur in the absorber thus increasing its H₂S scrubbing capability.

In May of 1983, the North Carolina plant was shut down, washed, charged with 33 wt % MDEA, and started up. No operating problems were encountered during and the unit has performed very smoothly since startup. The operating conditions and outlet gas concentrations for the absorber are shown in Table 4, along with the TSWEET simulation results. As evidenced by the H₂S level of less than 0.1 ppm in the sales gas, the conversion from DEA to MDEA greatly improved the performance of the plant at a very low cost. The operation with MDEA is also very stable.

Table 4. Performance of North Carolina Plant with MDEA

	MDEA <u>Operating Data</u>	TSWEET for MDEA <u>Operating Data</u>
Amine Conc, wt%	33	33
Circulation Rate, gpm	123	123
Gas Flow, MMSCFD	30.24	same
H ₂ S inlet, ppm	55	same
CO ₂ inlet, %	3.5	same
H ₂ S out, gr/100scf	<0.06	0.009
CO ₂ out, %	1.13	1.26
Rich Loading, mole/mole	.45	.45
Reboiler Duty, MMBTU/hr	N/A	57

SUMMARY AND CONCLUSION

Many factors must be considered when selecting an amine for a sweetening application. The initial selection is based on the pressure and acid gas content of the sour gas as well as the purity specification of the sales gas. As different process conditions have been tested and proven with each amine, they have become widely accepted in the gas processing industry.

Based on the currently "accepted" operating conditions, MEA is usually not the first amine considered due to its high heat of reaction and lower acid gas carrying capacity per gallon of solution. However, MEA is still used for plants where the inlet gas pressure is low and pipeline specification gas or total removal of the acid gases is desired.

As operating experience was broadened during the late 1960's and early 1970's for DEA, it became the "workhorse" of the industry due to its lower heats of reaction, higher acid gas carrying capacity and resultant lower energy requirements. DEA could also have potential for selective H₂S removal from streams containing CO₂ under certain conditions.

Although DGA has high heats of reaction, its very high acid gas carrying capacity usually produces very reasonable net energy requirements. DGA also has a good potential for absorbing COS and some mercaptans. Sweetening with DGA is limited to total removal of small (<5-10%) amounts of acid gas.

Depending on the application, MDEA has some outstanding capabilities. Due to its low heat of reaction, it can be used in pressure swing plants for bulk acid gas removal. MDEA is currently best known for its ability to preferentially absorb H₂S and is used in SCOT tail gas cleanup units since it is desirable to slip as much CO₂ as possible while absorbing the maximum amount of H₂S to be recycled back to the Claus unit.

Mixed amines are typically mixtures of MDEA and DEA or MEA which enhance CO₂ removal while retaining desirable characteristics of MDEA such as reduced corrosion problems and low heats of reaction.

The considerations for selecting amines were applied to several specific cases involving existing plants. Using the TSWEET process simulation program, the reported operating conditions for several plants were matched. TSWEET was then used to examine the performance of other amines in these plants. This analysis demonstrated that the proper selection of the amine can have a major impact on the performance and cost of a sweetening unit.

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