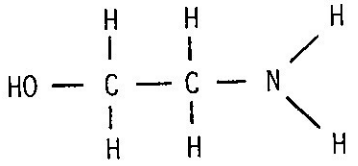
3

AMINE PROCESSES

The *alkanolamines* are the most generally accepted and widely used of the many available solvents for removal of H_2S and CO_2 from natural gas streams. Credit for use of the alkanolamines must go to Bottoms *(3.1)* who was granted a 1930 patent covering their use for sweetening natural gas. Because of their reactivity and availability at low cost, notably monoethanolamine and diethanolamine, have achieved a position of prominence in the gas sweetening industry.

The alkanolamines to be considered in the natural gas sweetening include monoethanolamine, diethanolamine, triethanolamine, diglycolamine (ββ' hydroxiaminoethyl ether), diisopropanolamine, and methyldiethanolamine. All of these materials may be classed as "chemically reactive." This is what accounts for their popularity for use in sweetening natural gas. There are differences in the chemical reactions that the various ethanoloamines undergo with certain acid gas constituents. These reaction similarities and differences will be covered in detail in Chapter 4.

The prefixes "mono", "di" and "tri" refer to degree of radical substitution on the amino nitrogen. Monoethanolamine, for example, has the structure:

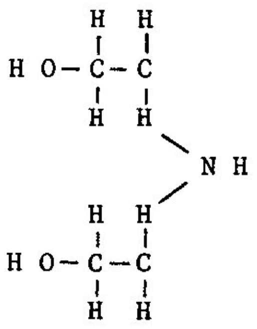


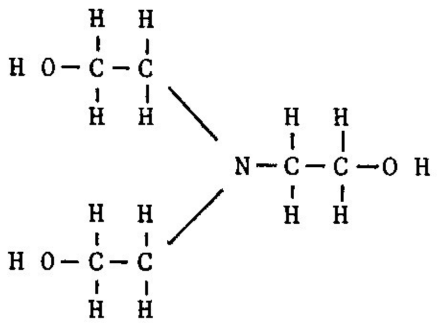
The OH group is the part of the structure that causes the compounds to be "olamines" rather than simple amines. The nitrogen is the so called "amino" nitrogen. Study of the structure shows that the first member of the amine homologous series would be ammonia (NH3). Ammonia can be used for acid gas removal from a natural gas stream but its volatility and other problems cause operating diffculties. The chemical structure of the remaining amines are shown in Figure 3.1.

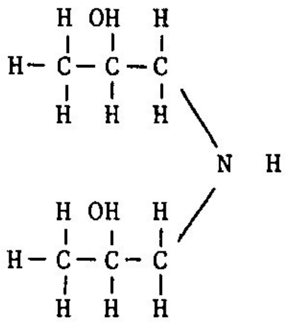
Physical properties for the ethanolamines are shown in Table 3.1. The ethanolamines are clear, colorless liquids that have a slightly pungent order. All except triethanolamine are considered to be chemically stable materials because they can be heated to their boiling point without decomposition. Triethanolamine decomposes below its normal boiling point of 680° F.

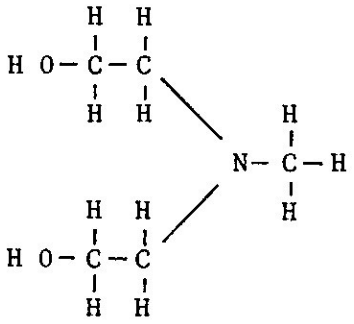
FIGURE 3.1

CHEMICAL STRUCTURAL FORMULAS FOR ALKANOLAMINES
OF INTEREST IN GAS SWEETENING


Diethanolamine


Triethanolamine


Diisopropanolamine


Methyldiethanolamine

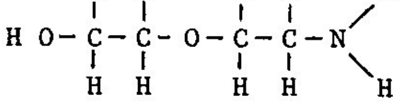

Diglycolamine ®

TABLE 3.1

	Monoethanolamine	Diethanolamine	Triethanolamine	Diglycolamine	Diisopropanolamine	Methyldiethanolamine
Formula	$HOC_2H_4NH_2$	$(HOC_2H_4)_2NH$	$(HOC_2H_4)_3N$	$H(OC_2H_4)_2NH_2$	$(HOC_3H_6)_2NH$	$(HOC_2H_4)_2NCH_3$
Molecular Wt.	61.08	105.14	148.19	105.14	133.19	119.17
Boiling point @ 760 mm Hg.,°F	338.9	516.2	680(Decomposes)	430	479.7	477
Freezing point, °F	50.9	82.4	72.3	9.5	107.6	-5.8
Critical constants						
Pressure, psia	868	474.7	355	547.11	546.8	5623[5]
Temperature, °F	662	827.8	957.7	756.6	750[5]	611.6[5]
Density @ 20°C., gm/cc	1.018	1.095	1.124	1.058 @ 60°F	0.999 @ 30°C	1.0426
Weight, lb/gal.	8.48 @ 60°F	9.09 @ 60°F	9.37 @ 68°F	8.82 @ 60°F	-	8.69
Specific gravity, 20°C/20°C	1.0179	1.0919(30°C/20°C)	1.1258	1.0572	0.989 @ 45°C/20°C	1.0418
Specific heat @ 60°F, BTU/lb/°F	0.608 @ 68°F	0.600	0.70	0.571	0.69 @ 30°C	-
Thermal conductivity @ 68°F BTU/hr FT' °F./ft.	0.148	0.127	-	0.121	-	-
Heat of vaporization, BTU/lb	355 @ 760 mm Hg	288 @ 73 mm Hg	230 @ 760 mmHg	219.14 @760 mmHg	185 @ (?)mm Hg	223
Heat of reaction, BTU/lb of Acid Gas						
H_2S	-	-	-400	-674	-	-
CO_2	-	-	-630	-850	-	-
Viscosity, cp	24.1 @ 68°F	350 @ 68°F (at 90% wt. solution)	1013 @ 68°F (at 95% wt. solution)	40 @ 60°F	870 @ 86°F 198 @ 113°F 86 @ 129°F	101 @ 20°C
Refractive index, n_D @ 68°F	1.4539	1.4776	1.4852	1.4598	1.4542 @ 113°F	-
Flash point, COC, °F	200	280	365	260	255	-
Constants for Antoine Equation						
A	8.02401	8.12303	9.6586	8.6211	9.8698	16.23
B	1921.6	2315.46	4055.05	2721.1	3600.3	7456.8
C	203.3	173.3	237.67	249.54	265.54	311.71

Footnotes for Table 3.1

1. Data for MEA, DEA, TEA, DGA and DIPA (except for Antoine constants) from GPA Engineering Data Book (3.3).
2. Data for MDEA (except for Antoine constants) from Kohl and Riesenfeld (3.4).
3. Antoine constants for MEA and DEA from Dow (3.5).
4. Antoine constants for TEA, DGA, DIPA and MDEA fitted by author.
5. Calculated by method of Lydersen (3.2).

The Antoine constants for estimating the vapor pressure for the various ethanolamines are shown in Table 3.1. The Antoine equation is:

$$\log P = A - \frac{B}{T + C} \tag{3.1}$$

where: P = vapor pressure, mmHg

T = temperature, $^{\circ}C$.

A, B, and C = constants, obtained from Table 3.1

The vapor pressures of ethanolamine-water mixtures can be satisfactorily estimated using ideal solution behavior, ethanolamine vapor pressures from Table 3.1 and the vapor pressure of water. The Antoine equation constants for water are:

$A = 7.96681$
$B = 1668.210$
$C = 228.000$

Table 3.2 shows some of the key properties of the alkanolamines. The vapor pressure values, which are at typical contactor conditions, show that vaporization losses of monoethanolamine (MEA) will be much greater than for any of the other ethanolamines. Also on the basis of relative acid gas capacity MEA shows two distinct advantages. However, as will be shown in Chapter 4, there are many other considerations than must be taken into account when selecting a sweetening agent.

Monoethanolamine (MEA)

MEA is the strongest base of the different amines and so reacts most rapidly with the acid gases. MEA will remove both hydrogen sulfide and carbon dioxide and generally is considered to be non-selective between these two acid gases. With the lowest molecular weight of the common amines, it has the largest carrying capacity for acid gases on a unit weight or volume basis. This generally means less solution circulation to remove a given amount of acid gases. In addition, MEA is chemically stable, which minimizes solution degradation; it can be separated easily from the acid gas constituents by steam stripping.

MEA reacts irreversibly with carbonyl sulfide and carbon disulfide. This results in solution loss and in the buildup of reacted solids in the MEA solution. MEA has a higher vapor pressure than the other amines. This can result in significant solution losses through vaporization. The problem usually can be overcome by a simple water wash of the sweetened gas stream.

The rate of reaction of CO_2 in MEA is slower than that of H_2S. The process is not considered selective, however, because carbon dioxide is readily absorbed and essentially will be removed completely when treating natural gas for H_2S removal to pipeline specifications.

MEA will easily reduce acid gas concentrations to pipeline specifications (generally less than 0.25 grains per 100 cu ft). By proper design and operation, the acid gas content can be reduced as low as 0.05 grains per 100 cu ft.

TABLE 3.2

SOME CHARACTERISTICS OF ETHANOLAMINES

	MEA	DEA	TEA	DGA	DIPA	MDEA
Mol. Wt.	61.08	105.14	148.19	105.14	133.19	119.17
VP @ 100°F mm Hg.	1.05	0.058	0.0063	0.160	0.010	0.0061
Rel. Capacity, %	100	58	41	58	46	51

Diethanolamine (DEA)

The aqueous DEA process is similar in principle and operation to the MEA process. One primary difference is the reaction of DEA with carbonyl sulfide and carbon disulfide. The reactions of DEA with carbonyl sulfide and carbon disulfide are slower than those of MEA, and result in different products. Consequently there is minimum DEA loss caused by reactions with these sulfur compounds.

As a result, it is especially favored for sweetening refinery and manufactured gas streams where these contaminants are prevalent. DEA is non-selective and will remove both H_2S and CO_2. Difficulty is sometimes encountered with the DEA process in reducing hydrogen sulfide concentrations to pipeline specifications. Wendt and Dailey *(3.2)*, however, describe the SNPA modification of the DEA process and report its capability for removing H_2S to the level of approximately 0.1 grains per 100 std cu ft. DEA is much less volatile than MEA, resulting in significantly lower losses of amine solution by vaporization.

After regeneration, DEA solutions typically have much lower concentrations of residual acid gas constituents than do MEA solutions. As will be seen in Chapter 4, this stems from the basic equilbrium relationships between diethanolamine and the acid gases. It does provide a basis for the advantages DEA demonstrate over MEA solution.

Triethanolamine (TEA)

Although aqueous triethanolamine (TEA) was the first commercially applied amine sweetening process, it has been largely displaced by either MEA, DEA or DGA. The tertiary amines appear to be less reactive with H_2S and CO_2. Because of traditional problems in treating natural gas to pipe line specification very little TEA is used commercially for natural gas sweetening.

Diglycolamine (DGA)

$\beta\beta'$ Hydroxietholamine [2-(2-amino-ethoxy)ethanol] is a more recent addition to the list of ethanolamines used for natural gas sweetening. The process is proprietary and the material has been trade named "Diglycolamine." It is a primary amine and has all of the potential advantages of high reactivity, low equilibrium partial pressures, etc., that are characteristic of the primary ethanolamines. Table 3.3 from the paper by Huval and Van De Venne (3.6) shows that DGA can satisfactorily meet pipe line H_2S specifications at rather low pressures.

Even though DGA is primary ethanolamine it maintains the same advantage of low residual acid gas concentrations in the regenerated solution as does DEA.

TABLE 3.3

ARAMCO DGA PLANTS

	FEED	PRODUCT	
RAS TANURA	130 MMSCFD		
	15-20 PSIG		
	125°F		
	9-13% H_2S	400-500 PPM H_2S	
	1.5-2.5% CO_2	1000-2500 PPM CO_2	
UDHAILIYAH	75 MMSCFD		
	220 PSIG		
	125°F		
	1-2% H_2S	< 2 PPM H_2S	
	10-11% CO_2	< 150 PPM CO_2	
MASTER GAS SYSTEM	> 4000 MMSCFD		
(BERRI, SHEDGUM,	115-170 PSIG		
UTHMANIYAH)	120-140°F	RESIDUE GAS	ETHANE
	8-3% H_2S	1-2 PPM H_2S	< 2 PPM H_2S
	8-14% CO_2	< 100 PPM CO_2	20-80 PPM CO_2

Diisopropanolamine (DIPA)

Diisopropanolamine is the reactive ingredient in the sulfinol process patented by Shell. It is also used in the ADIP process which is designed for removal of carbonyl sulfide. Diisopropanolamine will treat to pipeline specifications for sweet gas. Because data for the sulfinol process are proprietary to Shell its use is normally restricted to plants where the process/design calculations have been carried out by Shell engineers.

Methyldiethanolamine (MDEA)

MDEA is another newcomer to the group of ethanolamines used for natural gas sweetening. It has received a great deal of attention recently because of its capability for "selective" reaction with H_2S in the presence of CO_2. It was first mentioned as a sweetening agent in the early 50's (3.7, 3.8) but has had recent attention because of potential energy saving. According to Pearce and Brownlie (3.9) MDEA is capable of treating new gas to sweet gas specifications for H_2S.

Solution Concentrations

The primary differences in process schemes for MEA and DEA sweetening are in solution concentrations. MEA is ordinarily used in a 10 to 20 per cent by weight aqueous solution. By far the most common concentration would be approximately 15 per cent by weight MEA. DEA is also used in the 10 to 20 per cent by weight concentration. The SNPA (Societe Nationale des Petroles d'Aquitaine) modification of the DEA process uses a higher concentration of DEA. The process unit flow scheme is conventional, but the DEA solution concentration will range upward to 30 or more weight per cent DEA. This higher concentration of DEA (because of the higher molecular weight of DEA) gives about the same molar ratio of amine and water as does a 15 to 20 weight per cent MEA solution.

DIPA, DGA, and MDEA are also used in higher concentrations. Typical concentration ranges for DIPA and MDEA are 30% to 50% by weight in the aqueous solution. DGA concentrations range from approximately 40% to 70% by weight.

Use of amines in aqueous solution, of course, saturates the sweet gas with water vapor, regardless of whether the entering sour gas is wet or dry. For most amine processes, this means that a dehydration step necessarily follows sweetening. One process which overcomes this shortcoming is the use of MEA or DEA in combination with *ethylene or diethylene glycol.* Combination of amine and glycol will usually do an excellent job in removing acid gas constituents, but generally does not dehydrate as well as a conventional glycol installation. Severe corrosion problems are frequently encountered when using the glycol-amine combination so that this process is not currently in widespread use.

The general process flow for an amine sweetening plant is shown in Fig. 3.2 (3.10). The process flow scheme varies little, regardless of the aqueous amine solution used as the sweetening agent. The primary pieces of equipment of concern are the absorber column and stripper column, together with the associated piping, heat exchange, and separation equipment.

The sour gas containing H_2S and/or CO_2 should always enter the plant through a scrubber to remove any free liquids and/or entrained solids. The sour gas then enters the bottom of the contactor and flows upward through the column in intimate counter-current contact with the aqueous amine solution. Sweetened gas leaves the top of the contactor and flows to a dehydration unit before being considered ready for sale.

Lean amine solution from the bottom of the stripper column still is pumped through an amine-amine heat exchanger and then through a water or air-cooled exchanger before being introduced to the top tray of the contactor. The amine moves downward through the contactor counter-current to the sour gas, and removes acid gas constituents from the gas stream. Rich amine solution flows from the bottom of the contactor through the amine-amine heat exchanger and then to the top of the stripper column.

The amine-amine heat exchanger serves as a heat conservation device and lowers total heat requirements for the process. A part of the acid gases will be flashed from the heated rich solution on the top tray of the stripper. The remainder of the rich solution flows downward through the stripper in counter-current contact with vapor generated in the reboiler. The reboiler vapor (primarily steam) strips the acid gases from the rich solution. The acid gases and the steam leave the top of the stripper and pass overhead through a condenser, where the major portion of the steam is condensed and cooled. The acid gases are separated in a separator and sent to the flare or to processing. The condensed steam is returned to the top of the stripper as reflux.

Rich amine solution leaves the bottom of the contactor at an elevated temperature due to the heat of reaction released when acid gases react with the amine. For this reason heat exchange on the lean amine solution in the amine-amine exchanger does not cool it sufficiently for many processes. The amine cooler serves to lower the lean amine temperature to the 100° F. range. Higher temperatures for the lean amine solution will result in excessive amine losses through vaporization and also lower acid gas carrying capacity in the solution because of temperature effects.

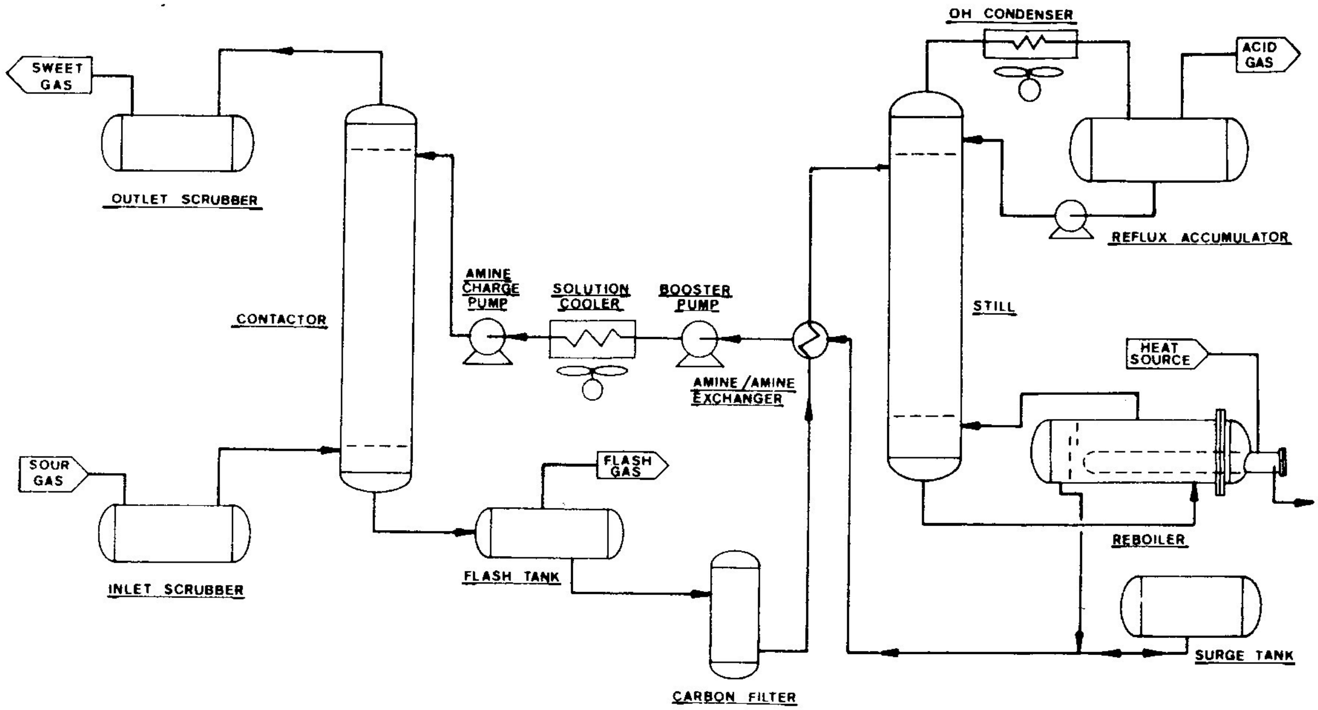


Figure 3.2 Process flow for typical ethanolamine sweetening unit

A process modification attributed to Shoeld (3.11) and described by Kohl and Riesenfeld (3.12) is shown in Fig. 3.3 This modification uses two amine solutions fed at different points to the contactor — a semi-lean solution introduced at a mid-way point and a lean solution introduced in the conventional manner on the top tray. This process is particularly advantageous for treating sour gases with a high acid gas content — above approximately 30 per cent. The liquid withdrawn from the mid-point of the stripper is not completely stripped and is circulated to the middle part of the contactor, where the acid gas concentration is highest. The lean solution introduced at the top contacts the gas with the lowest acid gas concentration and reduces it to the specified level.

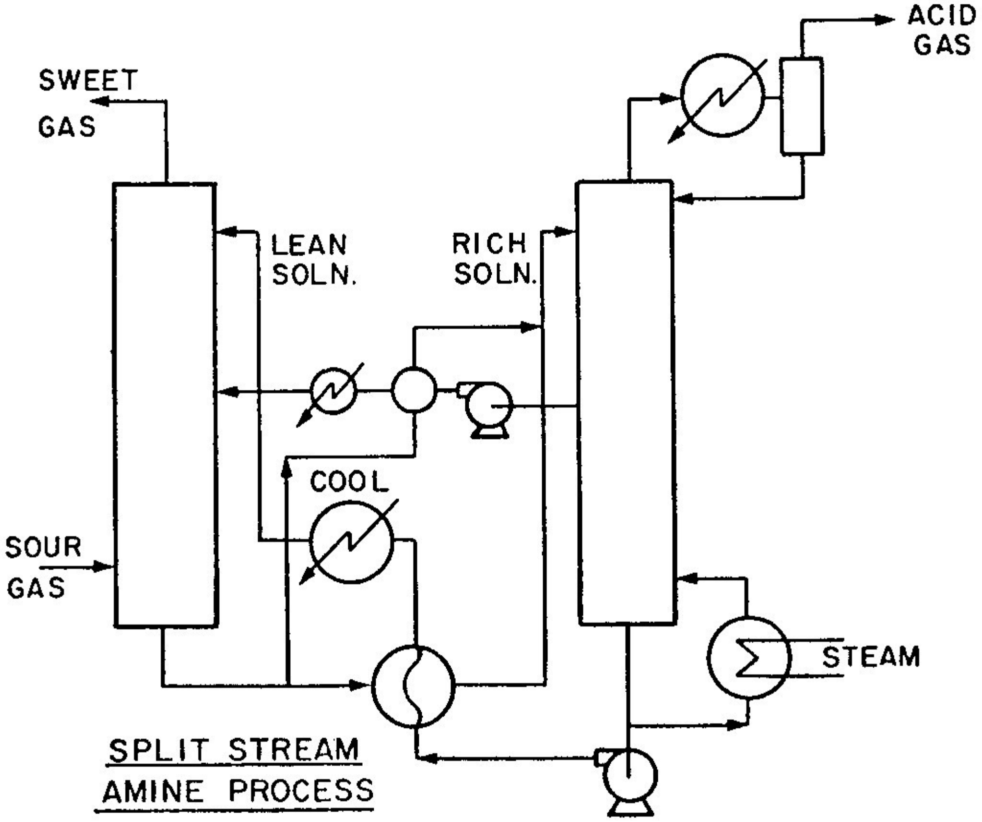


Figure 3.3 Flow sheet of split-stream amine process

This process modification offers the possibility of significant savings in steam costs, particularly for high acid gas content streams. It has the disadvantage that the stripper column needs to contain more trays and both the contactor and the stripper are more complex. The two lean amine streams require separate pumps and heat exchangers together with a more complicated control system. However, in many cases the overall plant investment will be less than would a conventional process like Figure 3.2 utilizing all of the amines with complete regeneration.

Figure 3.4 shows an MEA flow sheet with typical temperatures and solution concentrations. The MEA solution used is 20% by weight. It enters the contactor at 90° F and leaves at 136° F. The sour gas being treated contains slightly more than 11% H_2S. By heat exchange the rich MEA is heated to 200° F before being introduced to the regenerator. The lean amine leaving the regenerator is at 240° F and by amine heat exchange combined with water cooling it is cooled to 90° F for introduction to the contactor. Though the temperatures shown in Figure 3.4 are for MEA they would change little for DEA because the vapor pressure of water is the controlling parameter in determining regenerator reboiler temperatures.

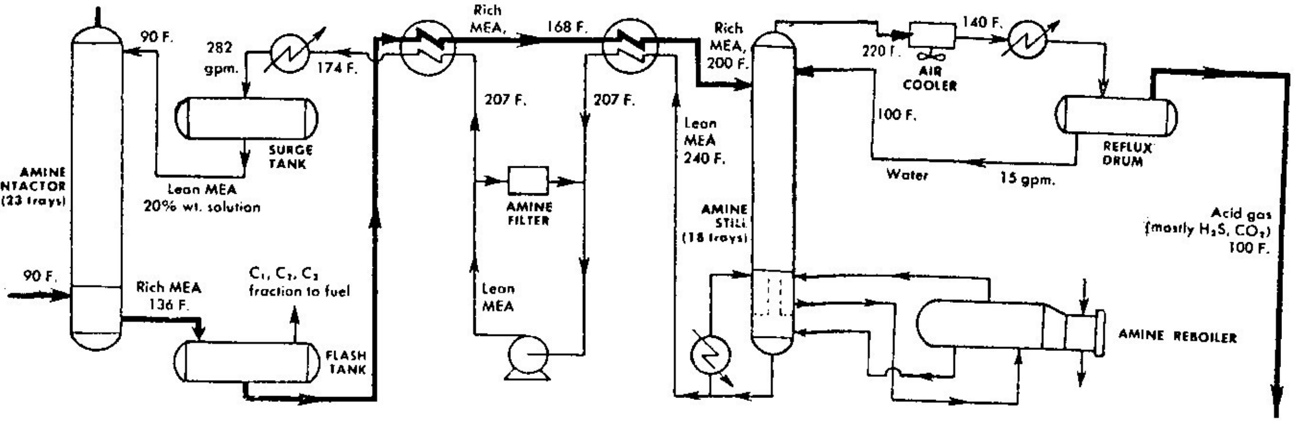


Figure 3.4 MEA process flow sheet showing typical temperatures

The flow sheet for diglycolamine, though basically similar to the MEA and DEA process flow sheet, differs considerably in some details. A typical DGA flow sheet is shown in Figure 3.5 (3.6). Because of the higher concentration of DGA a flash drum on the rich DGA stream leaving the bottom of the contactor is generally considered to be essential in order to prevent excessive hydrocarbons in the acid gas going to the sulfur plant. In the DGA system this flash drum normally contains a small contacting section where a portion of the DGA circulation is used to retain H_2S/CO_2 in the amine. Regenerator temperatures tend to run considerably higher being in the range of 260° to 280° F as opposed to the 230° to 240° typical of MEA and DEA. In addition the reclaimer runs almost 100° hotter because of the higher boiling temperature of DGA. High solution loadings lead to a high discharge temperature of the rich solution from the bottom of the contactor. The process shown in Figure 3.6 uses a side cooler on the contactor. This side cooler will typically lower bottom tray temperatures by 10° to 15° F. Regardless of the amine used a contactor intercooler should be considered in high loading ethanolamine units.

Fig. 3.6 is a convenient correlation for converting the weight percent of amine in water solution to the equivalent normality. Many solubility test results are reported in terms of the normality of the amine solution. *Diglycolamine* and *diethanolamine* fall on the same line because they have essentially the same molecular weights.

SUMMARY OF AMINE PROCESSES

There actually are five different types of basic amine sweetening processes to be considered for use:

— *The aqueous monoethanolamine process, which has been widely used for sweetening of natural gas streams.*

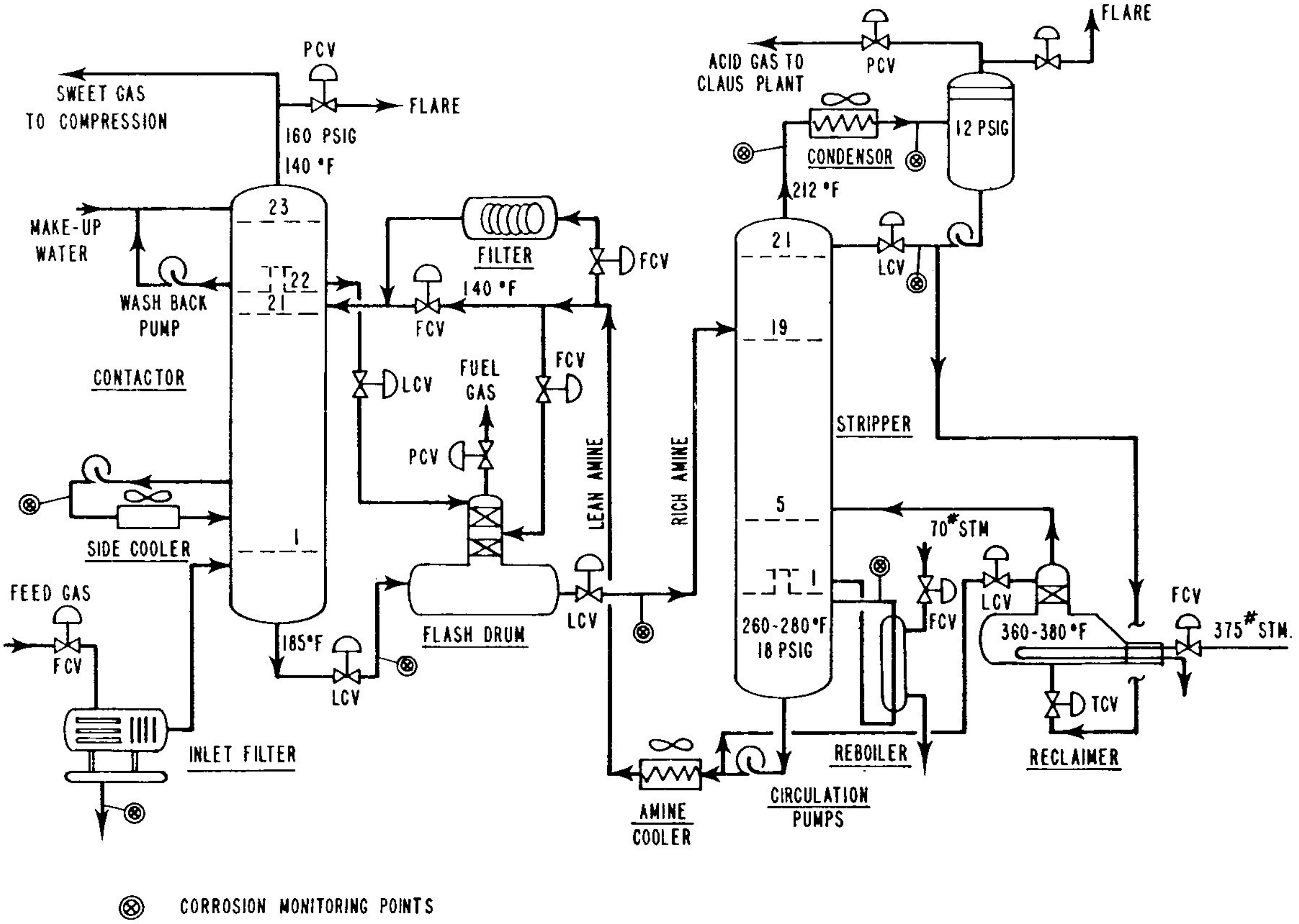


Figure 3.5 DGA process flow sheet showing typical temperatures

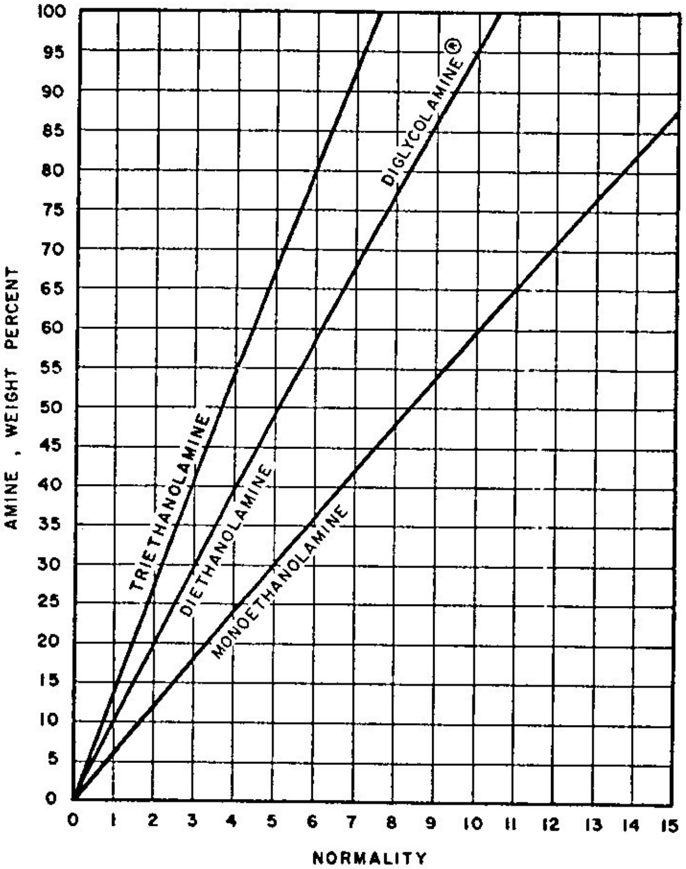


Figure 3.6
Normality of aqueous amine solutions
(Courtesy Jefferson Chemical Co.)

- *The aqueous diethanolamine process, which traditionally has been used primarily for refinery or manufactured gas sweetening, but is now finding applications in natural gas sweetening.*

- *Glycol-amine processes which use either monoethanolamine or diethanolamine in combination with a glycol to simultaneously sweeten and dehydrate the gas stream.*

- *Aqueous triethanolamine systems, which in general have been displaced by mono or diethanolamine systems.*

- *The methyldiethanolamine system (a tertiary amine like triethanolamine) which, in reality, is not commercially competitive with the other alkanolamine processes.*

Of the systems listed above, MEA and DEA have found the most general application in the sweetening of natural gas streams.

GENERAL OPERATING PROBLEMS

Amine treating processes tend to be troubled with the same operating difficulties regardless of the type amine used. These operating problems can be categorized broadly as *corrosion, solution degradation and foaming.*

These are not necessarily independent problems. The same basic condition may cause difficulty in all three areas. For this reason separating them for discussion is difficult, and is only done as a matter of convenience.

Corrosion

Looking at characteristics of the ethanolamine solutions gives the impression that corrosion would not be a problem. As a matter of fact many amines are used as corrosion inhibitors. The amines in water solution are basic as shown in Fig. 3.7 for MEA (3.5), Fig. 3.8 for DEA (3.5), and Fig. 3.9 for DGA (3.14). Extrapolation of the lines in Fig. 3.7 and 3.8 would indicate a basic solution for both MEA and DEA even at conditions in the regenerator reboiler. However, as shown in Fig. 3.10 (3.15), the situation changes drastically when the acid gases enter the picture. Though the individual effects of H_2S and CO_2 appear to differ, the common ingredient is a sharp lowering of the pH with the possibility at high loading that an acidic solution can be reached at reboiler temperatures.

Polderman et al. (3.16) report tests showing that a 20 per cent MEA solution in the absence of acid gases is less corrosive toward steel than is water. They also report that it can be converted (through its carbonate salt) to corrosive products at temperatures expected to be encountered in gas treating plants.

As pointed out by Polderman et al. and also by Ballard (3.17) the presence of acid gas constituents causes corrosion directly. This type of corrosion is all but impossible to eliminate as removal of acid gases is the name of the game. It can be minimized or controlled, or at least limited, by proper design and operation. Corrosion will be most severe at places where the highest concentrations of acid gases encounter the highest temperatures. These points will include the *amine-amine heat exchanger, the stripping column* and the *reboiler.*

Stress corrosion is prevalent in amine systems. This generally is associated with residual stresses which result from localized heating during vessel construction such as welds in absorbers, strippers and piping. Stress relieving all major equipment and piping will help to alleviate stress corrosion.

Solution Degradation

Amine solutions will slowly oxidize when exposed to air or oxygen. The products of these oxidation reactions are generally considered to cause corrosion problems. The oxidation can be minimized by use of an inert gas blanket on amine storage containers and surge drums.

MEA of course reacts with carbonyl sulfide (COS) to form an insoluble salt. This will result in a mol-for-mol loss of MEA unless the solution is reclaimed. The reaction can be reversed by placing the MEA in a basic solution and heating. DGA also reacts with COS and the reaction can be reversed by heating.

There is a large body of literature available on degradation of ethanolamine solutions. While some of the degradation products do have structures that will remove H_2S and/or CO_2 they generally are not so effective as the original ethanolamine and, for this reason, represent a loss in solution activity. MEA and CO_2 can react under reboiler conditions to form an oxazolidone which in turn can react to form N-(2-Hydroxyethyl)-ethylenediamine which is more basic than MEA but whose sulfide salts are very difficult to regenerate. As reported by Polderman and Steele (3.18) DEA forms N,N'-bis(2-Hydroxyethyl)-piperazine (HEP). Hakka et al., (3.19) showed that degraded DEA contains N,N',N'-tris(2-Hydroxyethyl)-ethylenediamine] (THEED) or 3,6-diaza-1, 8-dihydroxy-3-(2-Hydroxyethyl)-octane. Both HEP and THEED are basic and will react with H_2S and/or CO_2 but they are not so reactive as DEA and result in a loss of solution activity.

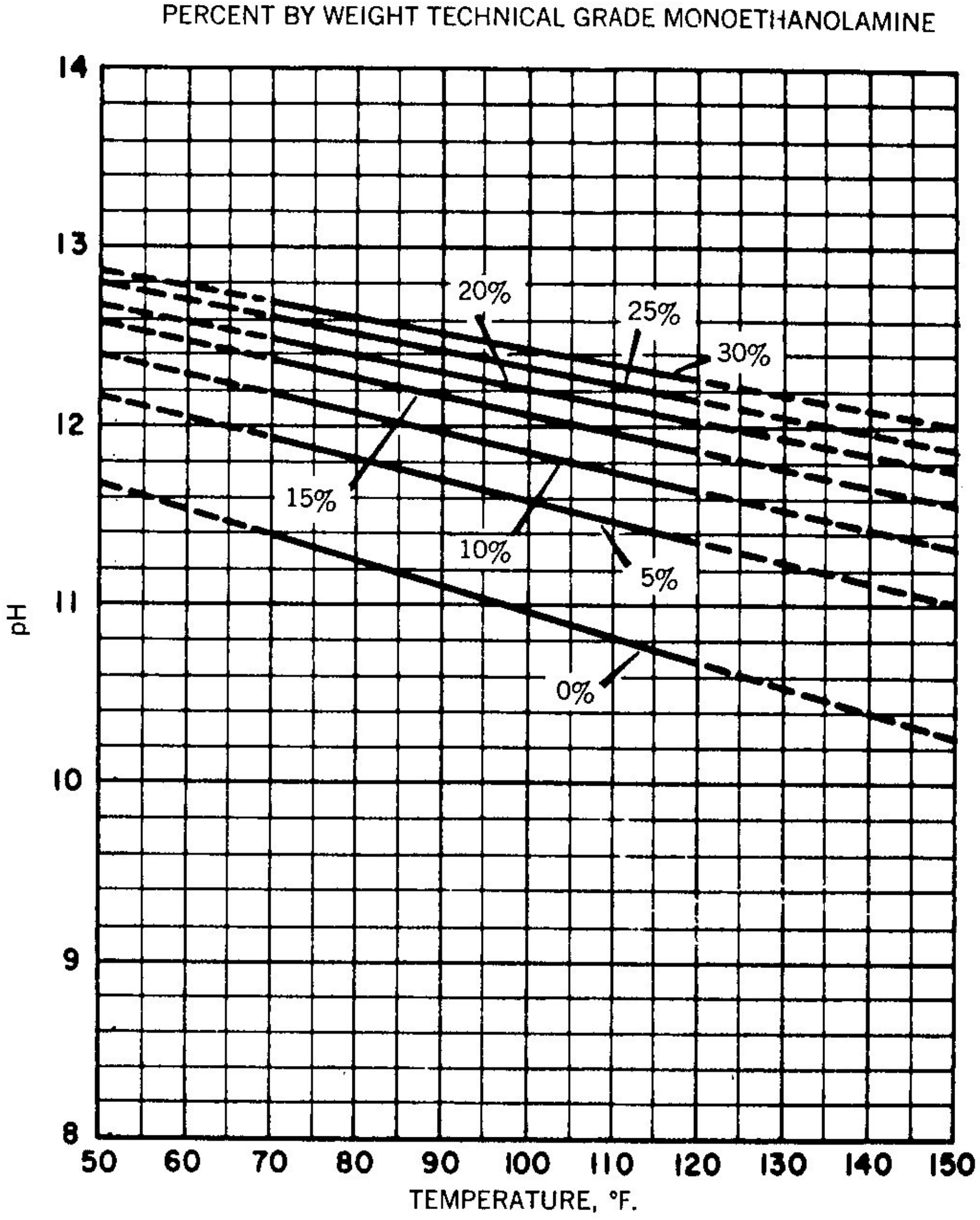


Figure 3.7 pH of MEA solutions at various temperatures

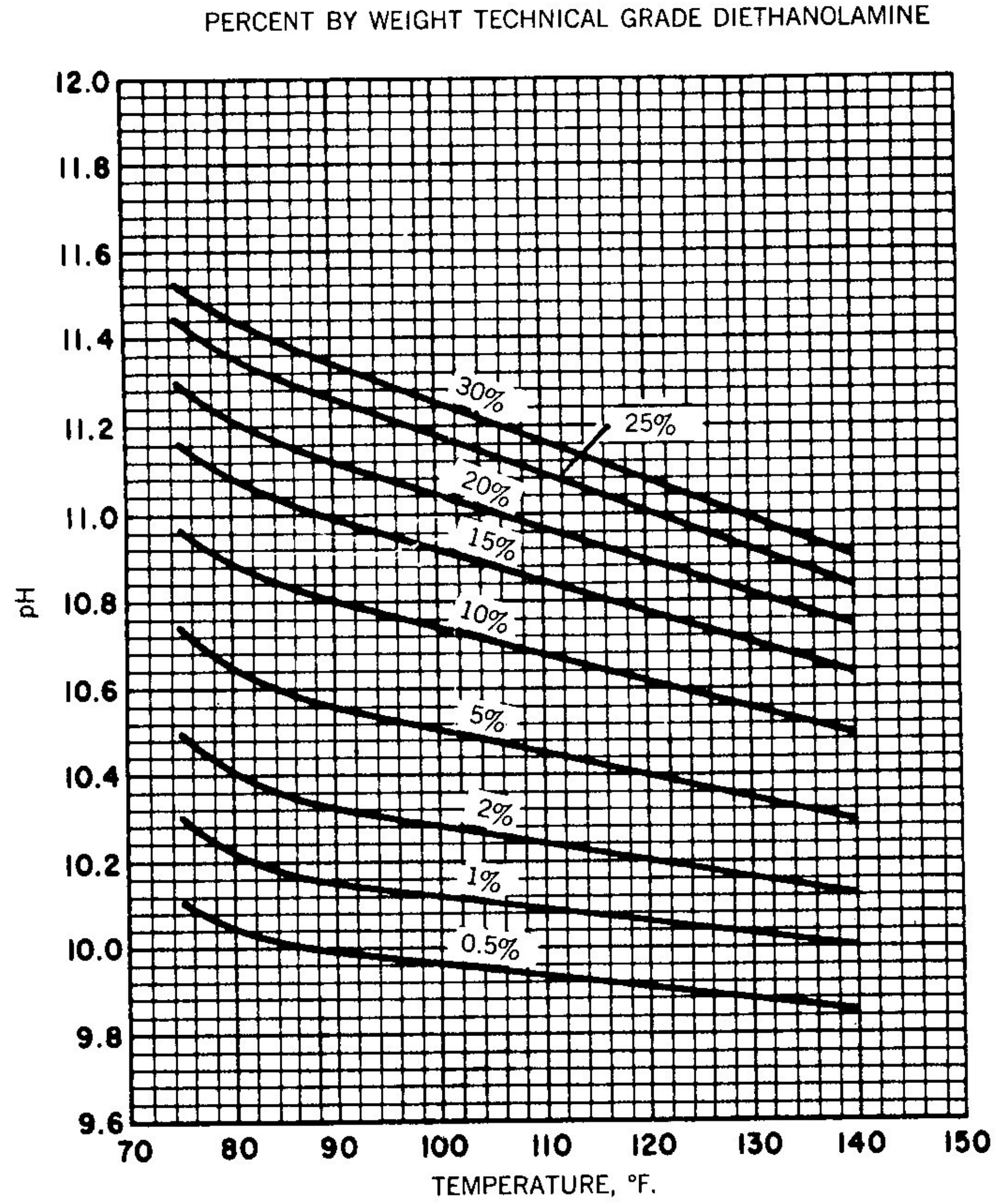


Figure 3.8 pH of DEA solutions at various temperatures

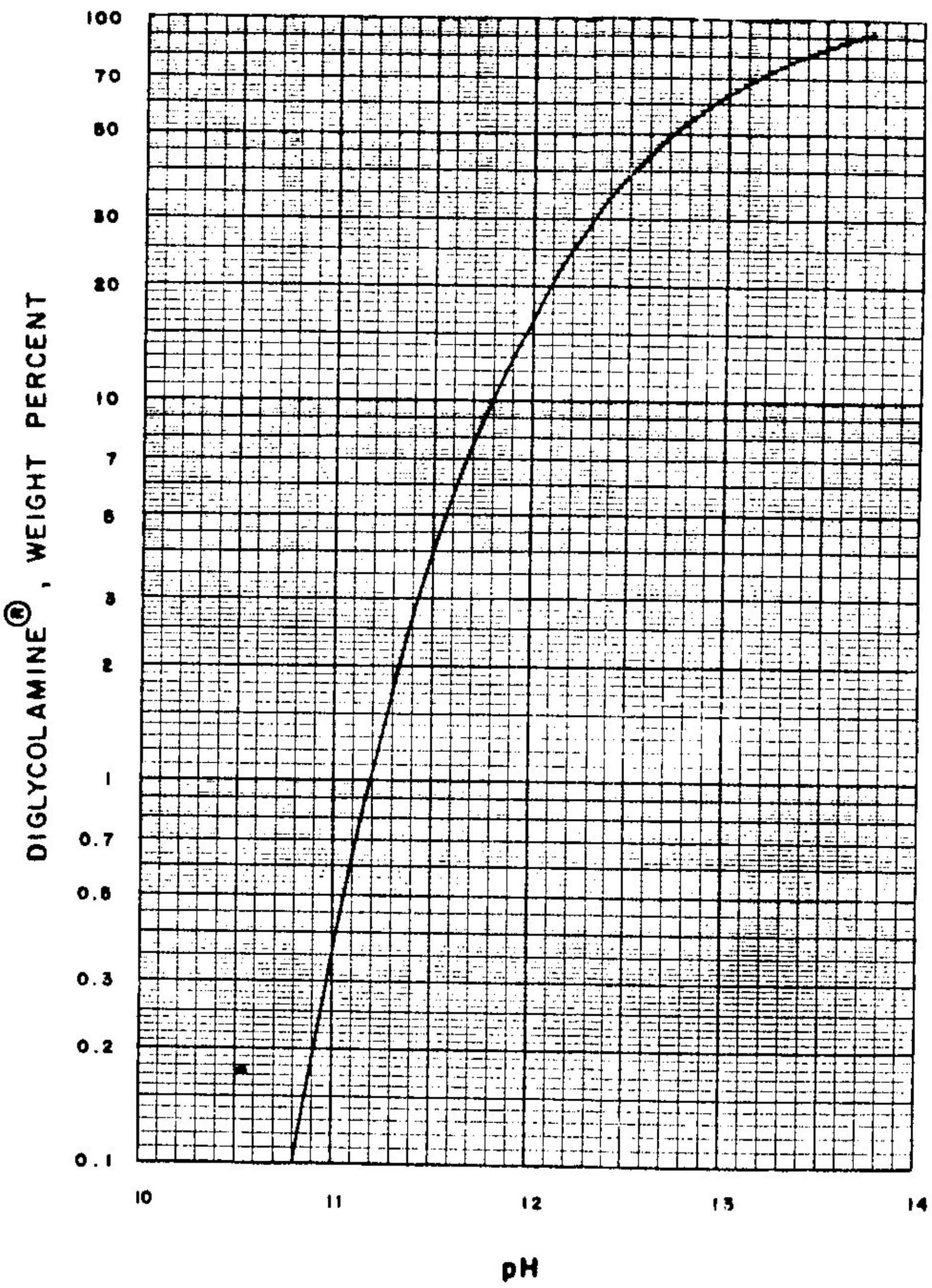


Figure 3.9 pH of DGA solutions at various temperatures

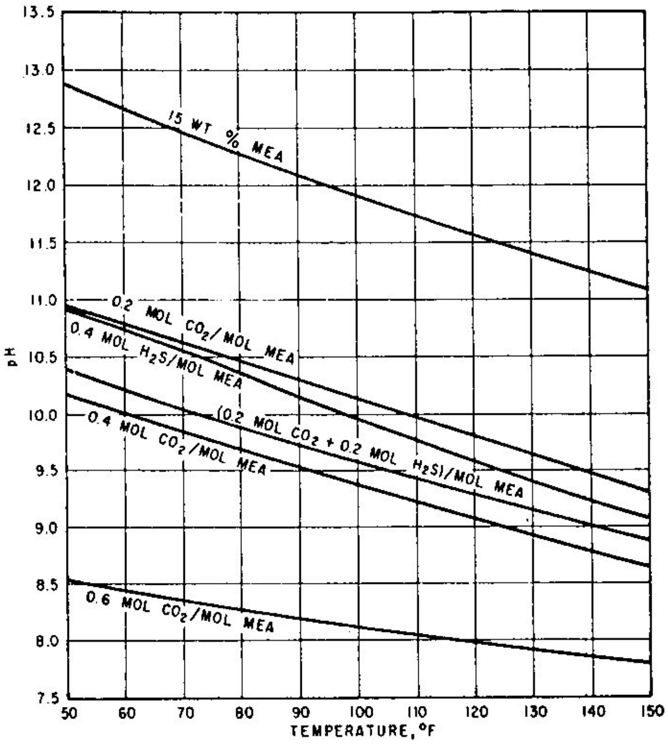


Figure 3.10

Effect of acid gas loading on pH of MEA solutions

Foaming

Foaming in an amine sweetening process can result in a number of different problems. Plant gas through-put may be severely reduced; sweetening efficiency may be decreased to the point that pipeline specifications cannot be met; amine losses may be significantly increased. Some of the materials that can cause foam problems in amine units include:

- *suspended solids*
- *condensed hydrocarbons*
- *amine degradation products*
- *almost any foreign material such as corrosion inhibitors, valve grease, or even impurities in makeup water*

The use of an amine reclaimer in combination with proper solution filtration will help to solve many foaming problems.

Amine Reclaiming

The amine reclaimer is usually a batch distillation system, which is operated semi-continuously. Its purpose is to distill the water and amine from the fouled solution, leaving behind the entrained solids; dissolved salts and degradation products that cause foaming and corrosion problems. Except in unusual cases the reclaimer will operate on 3 per cent or less of the solution circulation rate. Ballard (*op. cit.*) presents an excellent detailed discussion of the proper operation of an amine reclaimer. He lists the following specific operating suggestions for a reclaimer:

"1. An easy-to-open manway should be located on the reclaimer shell so the solids can be simply washed out at the end of the cycle. The drain line should be large enough to pass solids.

2. *The tube bundles should be raised 6 inches or more from the bottom of the reclaimer shell to provide space for sludge accumulation below the tubes, and to give better solution flow around the tubes.*

3. *A packed column should be placed on top of the reclaimer to eliminate foam and entrainment from the overhead vapor stream. The installation of a glass site port in the vapor line will help keep a check on this carry over. An analytical evaluation will help pinpoint suspected entrainment.*

4. *The tubes should be widely spaced for easy cleaning.*

5. *Make certain the steam supply is not superheated.*

6. *Use a chart recorder to monitor the reclaimer temperature throughout the cycle. Inspect the recorder routinely to make sure it is indicating true temperature readings.*

7. *Control the amine feed to the reclaimer by a level controller on the kettle to maintain a liquid level at least 6 inches above the tube. Install a rotameter in the feed line to indicate when the feed falls off and steam stripping should be started.*

8. *Allow sufficient vapor space above the liquid layer in the reclaimer to prevent liquid carryover in the overhead vapor line.*

9. *A chemical analysis of the reclaimer bottoms and the amine solution identifies the solution contaminants and determines the degree and rate of solution contamination."*

The reclaimer is an integral part of a successful amine sweetening process. It normally operates on a sidestream of the lean amine solution leaving the bottom of the stripping column.

Reclaimers are not ordinarily used on DEA systems. The DEA and its degradation products tend to boil at very nearly the same temperature. For this reason they are difficult to separate in a simple flash distillation in the way that most reclaimers operate. In addition, the boiling point of DEA is higher than normally available process steam temperatures.

Filtration

Proper solution filtration is extremely important. Some solids, particularly iron sulfide, are very difficult to remove in separators and surge vessels. Any entrained iron sulfide particles entering with the sour gas will be picked up by the amine solution in the absorber. Recommendations that filtration remove particles in the one micron range are frequent. Attempting this with a full stream filter is difficult, and expensive. As a result, a combination of filters is frequently used. A full stream filter on the outlet from the absorber will remove particles down to the 10-25 micron range. A sidestream activated charcoal filter will then be used on 10 or 20 per cent of the amine solution circulation to remove smaller particles. In addition, the activated charcoal will remove the hydrocarbons, some of the degradation products, and reaction products to improve amine solution quality.

Scheirman (3.20) has given an excellent review of solution filtration practices in DEA plants. According to Hakka et al. (3.19) the primary decomposition products in a DEA plant are N,N' - bis (2-hydroxy ethyl) piperazine (HEP) and N,N,N' - tris (2-hydroxy ethyl) ethylenediamine (THEED). Scheirman indicates that the addition of soda ash or caustic soda can aid in regeneration of some of the compounds by adjusting the pH of the solution. He recommends a cartridge-type filter followed by a fixed bed carbon filter for DEA service. The fixed bed carbon filter will have a design flow rate of 2 gpm per sq ft of vessel cross section to 15 gpm per sq ft. The recommended minimum bed depth is 10 ft. If a precoat filter is used, either diatomaceous earth or a mixture of powdered asbestos and powdered carbon may be used as a filter. However, precoat filters can provide a nuisance factor in operations.

* Note: gpm as used herein is an abbreviation for U.S. gallons per minute.

Perry (3.21) has given a very valuable discussion of the benefits of activated carbon filtration for maintaining clear, clean amine solution. He discusses graded bed carbon filters as shown in Fig. 3.11 and deep bed filters as shown in Fig. 3.12. The graded bed filter has a minimum life and requires frequent backwashing and steam regeneration. In deep bed filtration there is a much greater depth of activated carbon giving longer bed life between regenerations.

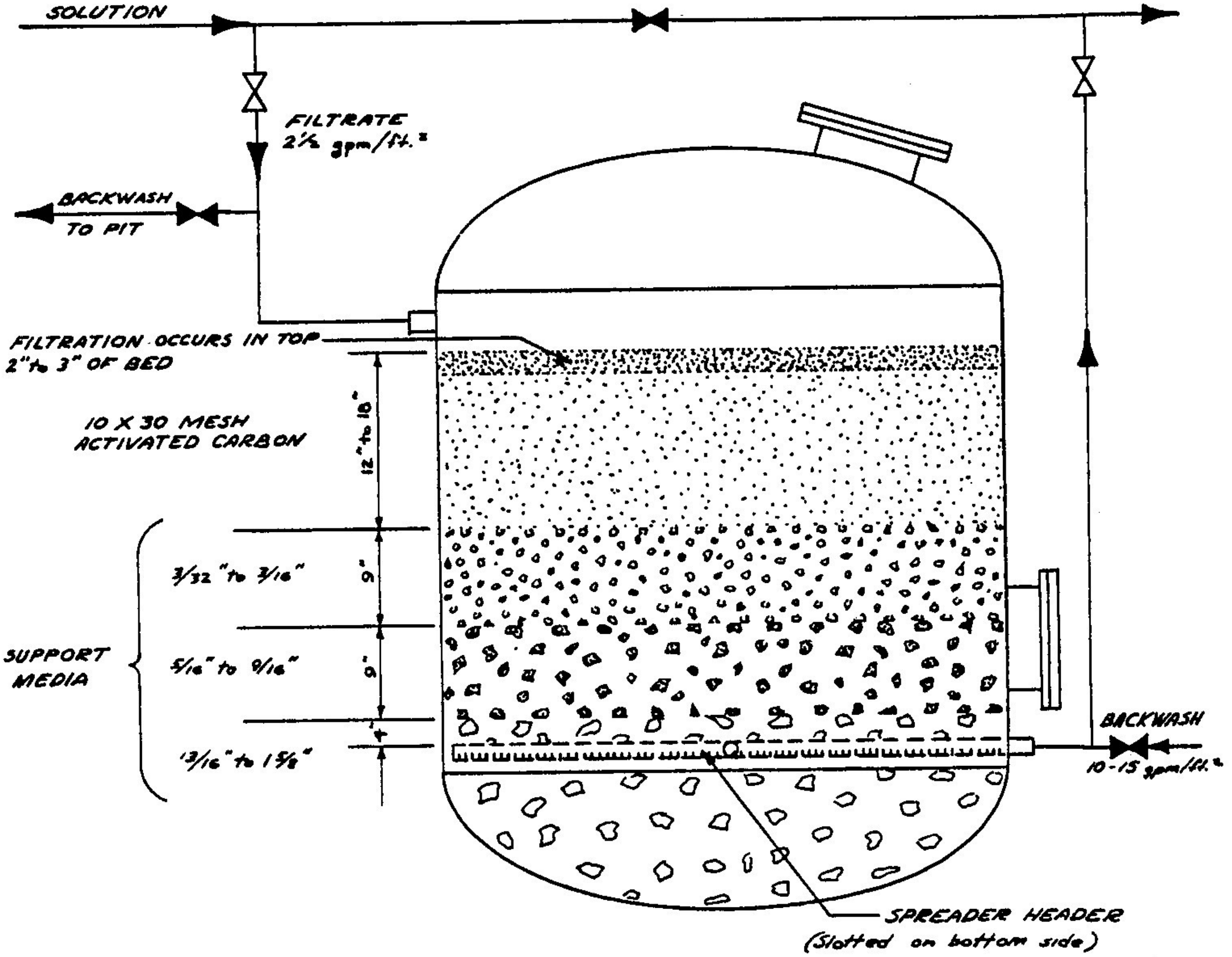


Figure 3.11 Graded bed activated carbon filter

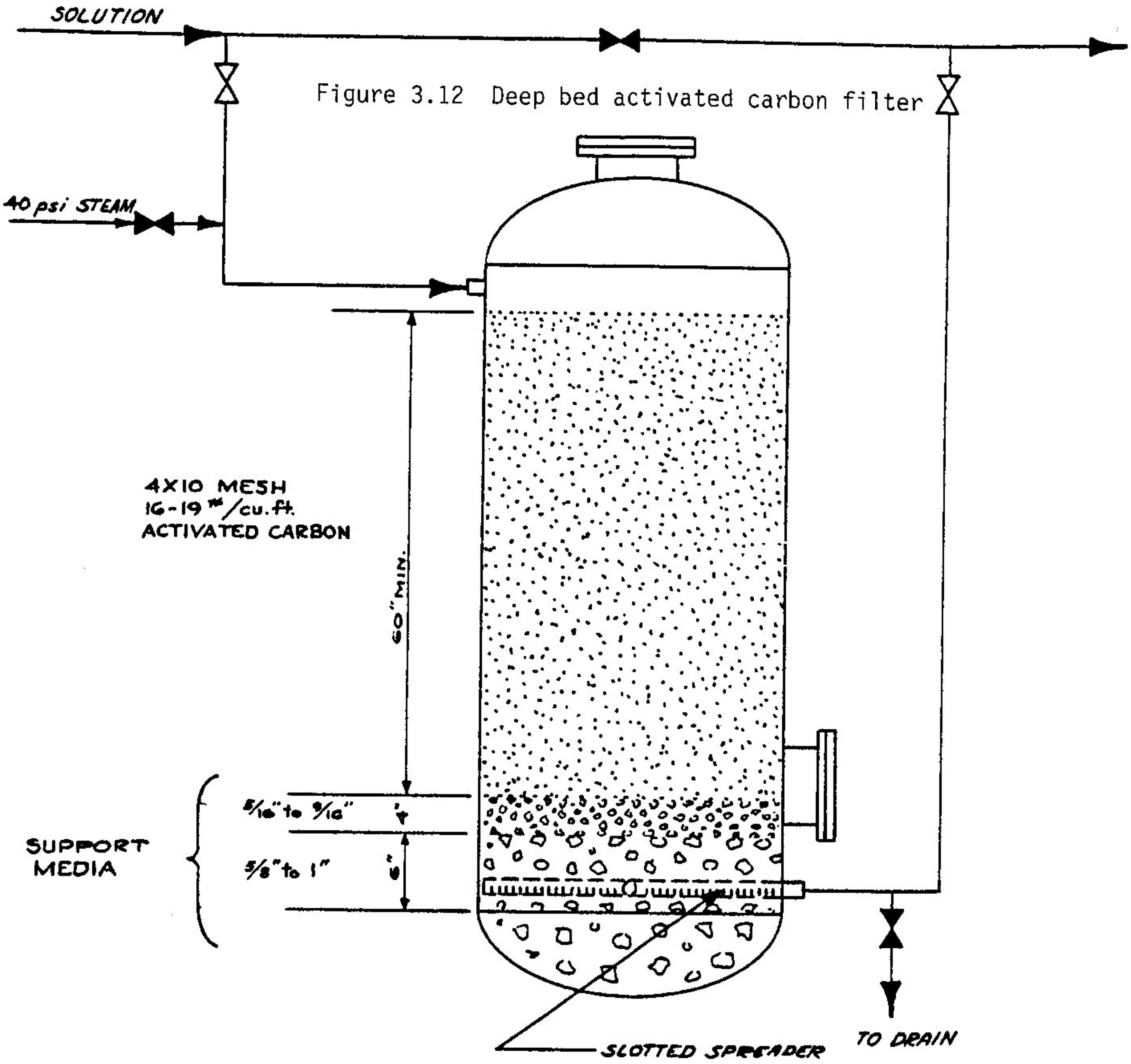


Figure 3.12 Deep bed activated carbon filter

Foam Inhibitors

In some cases, reclaiming and filtration of the amine solution will not cure the foaming problem. In these cases, use of a foam inhibitor may be necessary. If so, an inhibitor should never be used in the plant without first being tested on a laboratory scale; one that works in one situation may not in another. Important to remember, also, is that the foam inhibitor does not solve the basic problem. It merely provides a means for controlling foam. Search for the cause of the foaming should be continued until the cause is located and eliminated.

If a foam inhibitor is used, it is necessary to control its concentration very carefully. Too much foam inhibitor can promote foam.

Corrosion Inhibitors

Corrosion inhibition systems have been developed for ethanolamine units, particularly those for MEA where corrosion appears to be most severe. Kelley (3.22) and Butwell et al. (3.23) have described the UCAR amine guard system developed by Union Carbide Corporation. It is intended for systems removing CO_2 only. Solutions in concentrations as high as 50% by weight and acid gas loadings as high as 0.5 moles per mole have been used successfully without excessive corrosion. Dow Chemical Company also has a CO_2 corrosion system. Dow also has a corrosion inhibitor that can be used on systems with both H_2S and CO_2.

GENERAL CONSIDERATIONS

Over the years of operation of amine sweetening units a substantial amount of information has been collected and reported for improvement of operation and design (3.6, 3.14, 3.15). These studies have led to guidelines which, even though empirical, if followed and properly implemented in the design stages of a sweetening unit, will serve to greatly reduce, if not eliminate, most operating problems.

Inlet Scrubbing

The importance of proper and efficient inlet scrubbing of the sour gas is difficult to over-emphasize. Many problems in amine plant operations such as foaming, corrosion and reboiler tube burn-out can be traced to the presence of excessive amounts of foreign material in the amine solution. Liquid hydrocarbons and entrained solids frequently can enter the plant with the sour gas stream. In addition, such foreign materials as corrosion inhibitors, drilling muds and well acidizers can also enter with the sour gas stream, particularly on lease-type sweetening units. The inlet separation equipment should be sized and designed with these factors in mind. The fact that these materials do not enter at a steady rate but slug or surge into the plant should also be kept in mind. Instantaneous flow rates may be extremely high and the inlet separating system must be designed to handle that.

Most problems in the contactor section of the plant can be traced to foaming or entrainment. The most frequent sources of these troubles are entrained solids or entrained hydrocarbons.

Amine Losses

Amine losses can be very expensive. For this reason a separator on the sweet gas stream leaving the contactor is usually advisable. A reduction of MEA losses by only 0.1 pounds of MEA per MMSCF will give a savings of about $7500 per year in a 100 MMSCFD treating unit. In addition, the sweet gas scrubber will help eliminate amine losses from unexpected foaming or surges. The savings in down time and loss of production may be many times the savings in amine solution lost.

Filtration

Proper solution filtration is important for the maintenance of a clean, efficient amine solution, as noted previously. In general, a two-stage filtration is recommended often for this service. Any secondary filtration may be activated charcoal and will remove degradation products, should they exist, along with some of the smaller particles of entrained solids. The filter system would be capable of handling at least 10 to 20% of the amine circulation rate. Doing this will permit quick clean up of the amine solution after an upset. During normal usage the time between filter clean ups would be extended. When used in combination with a sock type or pre-coated filter, the activated charcoal sometimes can be regenerated. Figure 3.13 (3.21) illustrates a series installation of a "Sock" type and activated charcoal filters.

One can make a good case for full-flow filtration even though it requires higher capital cost. *Positive removal* of all solids from the system minimizes corrosion and associated problems.

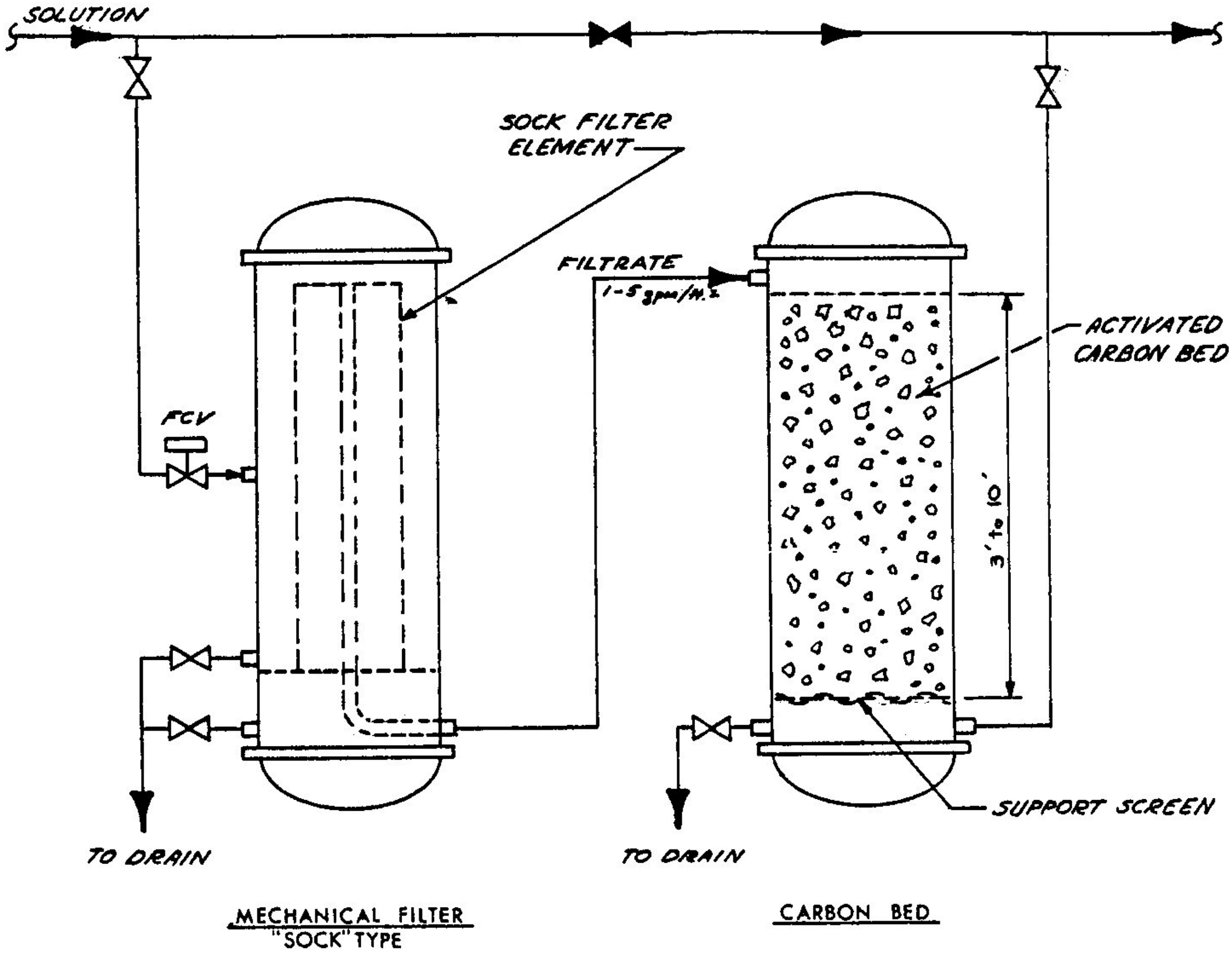


Figure 3.13 Series installation of filters

With full-flow filtration, parallel filters with no by-pass might be recommended. If a by-pass is present, it will frequently be found open to "prevent plugging the filter."

There are differing opinions about the best place for the filter location. The two favored positions seem to be on the rich amine solution at the outlet of the contactor, and on the lean amine solution just before the solution enters the contactor. There are some arguments which seem to favor the former as the better location. However, the location is not nearly so important as is having a properly designed and sized filtration system for the amine solution.

The importance of reclaiming — and some points to consider in the proper design of reclaiming equipment — have already been mentioned. A reclaimer is essential to maintenance of a proper amine solution. The unit should be designed for low vapor velocities to minimize entrainment of what otherwise would be residual material. Frequently soda ash or caustic soda will be used as an additional agent to the reclaimer. When this is done, the soda ash is usually added at the beginning of the batch cycle and remains in the reclaimer as sludge or waste. Each time the reclaimer sediment is dumped the soda ash or caustic will have to be renewed as it is not recovered.

If the filtration system, the separation system and the reclaiming system maintain a water-white circulating amine solution, foaming and entrainment problems will be minimized. When treating a hydrocarbon saturated sour gas stream the amine solution will frequently absorb significant amounts of hydrocarbons — particularly those in the butane and heavier range. In these instances a flash tank or separator downstream from the absorber and before the amine-amine heat exchanger is advisable. This flash will remove from the solution a large portion of the condensed or absorbed hydrocarbons. The limitations on operating pressure for this intermediate separator are imposed by heat exchanger operations. In order to prevent breakout of excess acid gases in the amine-to-amine heat exchanger, it must operate in the range of 100 to 200 psia. This means that the intermediate flash tank must operate slightly above this pressure in order for solution to flow from the separator to the exchanger.

Amine-Amine HEX

If an intermediate flash separator is not used, contactor pressure should be maintained through the amine-to-amine heat exchanger. Doing this minimizes breakout of acid gases from the rich amine solution, thereby minimizing excessive corrosion of control valves, heat exchanger and downstream piping. Operation at high pressure increases the cost of the exchangers, but this generally will be more than offset by the increased life due to lessened corrosion. The rich amine solution should be on the tube side of the exchanger, which again tends to minimize investment in the exchanger.

Linear velocities in the amine-to-amine heat exchanger should be low — in the range of 2 to 3 feet per second. This reduces the heat transfer coefficient and increases the surface area requirement. However, again the return on the reduced maintenance costs for the exchanger will more than offset the increased investment. Flowing amine solutions should not impinge directly on vessel surfaces; impingement baffles should be utilized in the exchangers.

Amine Regeneration

The regeneration section of an amine unit is the place where troubles in corrosion are most likely to start. It is here where acid gases are broken out of solution and also where temperatures are the highest. The combination of these two elements can lead to severe corrosion problems.

The best regeneration will be obtained at higher pressures. Higher operating pressures on the stripper increase the bottom temperature which, in turn, causes more complete stripping of the acid gases from the amine solution. However, increased temperatures lead to excess corrosion and to chemical degradation of the amine. Lean amine solution temperatures leaving the stripper are generally kept in the 230 to 240° F. range with a valid absolute maximum temperature of not more than 260° F. This leads to a stripper bottom pressure in the range of 25 psia as a maximum.

Various heating media are used in the reboiler of the regenerator. Low pressure saturated steam, heating oil and direct firing have all been used successfully. The real key to successful reboiler operation from a corrosion standpoint is the temperature of the metal which is in contact with the amine solution. This temperature is controlled by heat transfer resistances and only an analysis of the individual resistances can tell exactly the maximum temperature that can be used. Steam temperatures above 285° F. should never be used. Also avoiding super-heat in the steam is critical, again because of the balance of heat transfer resistances which is automatically made by the system.

Fig. 3.14 and 3.15 (3.25) depict the temperature distributions that can be expected in a properly designed direct fired amine reboiler. In the case illustrated the combustion gases are from the first stage of a Claus sulphur unit. At the hottest point in the pipe, where the temperature of the fired gases is 2500° F. and the boiling amine temperature on the outside of the fire tube is 240° F., the metal skin temperature in contact with the amine is only 260° F. The extremely high temperature drop across the gas film on the inside of the fire tube wall is caused by the relatively low heat conductance of that film in comparison with the other film coefficient and the conduction through the tube wall. These two figures graphically illustrate the necessity for careful and accurate design of the reboiler system in amine regeneration units.

Ballard (3.17) lists thirteen steps which, if carefully followed, will provide for proper care and maintenance of amine reboilers:

1. *Low pressure saturated steam at approximately 45-55 psia (274-287° F.) is commonly used to strip the amine solution. Steam temperatures above 285° F. should be avoided to prevent excessive skin temperatures on the tubes. It is advisable to monitor the temperatures of the steam to make sure superheat has been eliminated. Superheat can be removed by injecting steam condensate into the low pressure line to the reboiler.*

2. *Amine plants should be designed for "pressure operation." Higher operating pressures increase the bottom temperature of the regenerator and are believed to provided more complete stripping of the acid gases, especially the* CO_2. *However, some people have experienced increased corrosion in the reboiler, exchangers and stripper with the higher reactivator operating pressures. Therefore, it may be necessary to operate at a minimum reactivator pressure, with the lower limit set usually either by the pressure required to supply the acid gas to a sulfur plant or by the pressure required to force the amine out of the regenerator through the heat exchangers to a surge tank or pump suction.*

3. *The maximum allowable kettle temperature recommended for regeneration of the solution is 260° F. to prevent amine degradation.*

4. *The temperature controller valve should be on the steam inlet, not on the condensate outlet, to keep excessive condensate out of the tubes. When condensate partially floods the reboiler tube, the heat load concentrates in the top section of the bundle which can cause tube failure.*

5. *Stripping steam requirements will vary depending on the degree of sweetening required for the process stream being treated. Normally, the steam consumption should be at least one pound of excess steam per gallon of solution circulated.*

6. *To provide good circulation of the amine solution around the tubes and to reduce fouling caused by a sludge accumulation, the tube bundle should be placed on a slide about 6 inches above the bottom of the reboiler shell.*

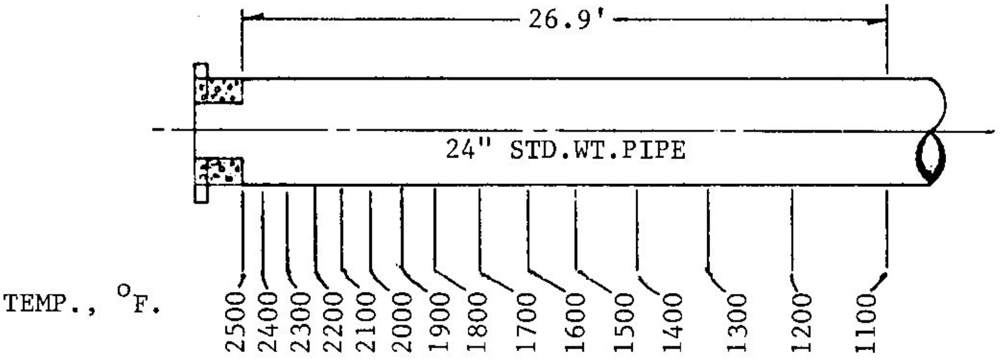
7. *The amine solution should enter the reboiler at several locations to help improve the natural circulation of liquid in the reboiler shell. Several vapor exit locations will reduce the stagnant pockets of acid gases in the reboiler.*

8. *The tube bundle should be supported to prevent tube vibration. Teflon or other protective inserts will prevent tube cutting.*

9. *The length of the tubes should be limited to prevent condensate "logging" and water hammer. The water hammer effect can produce severe tube vibration and grooving of the tubes at the support baffles.*

COMP	MOLS/HR	#/Hr
H_2S	17.1	581
CO_2	2.6	114
H_2O	28.3	509
N_2	100.8	2822
SO_2	17.1	1094
S_2	12.8	819
TOTAL	178.7	5939

OUTSIDE TEMP. = 240°F.



FIRETUBE DESIGN

Figure 3.14
Typical temperature distribution in an amine reboiler (Ref. 3.25)

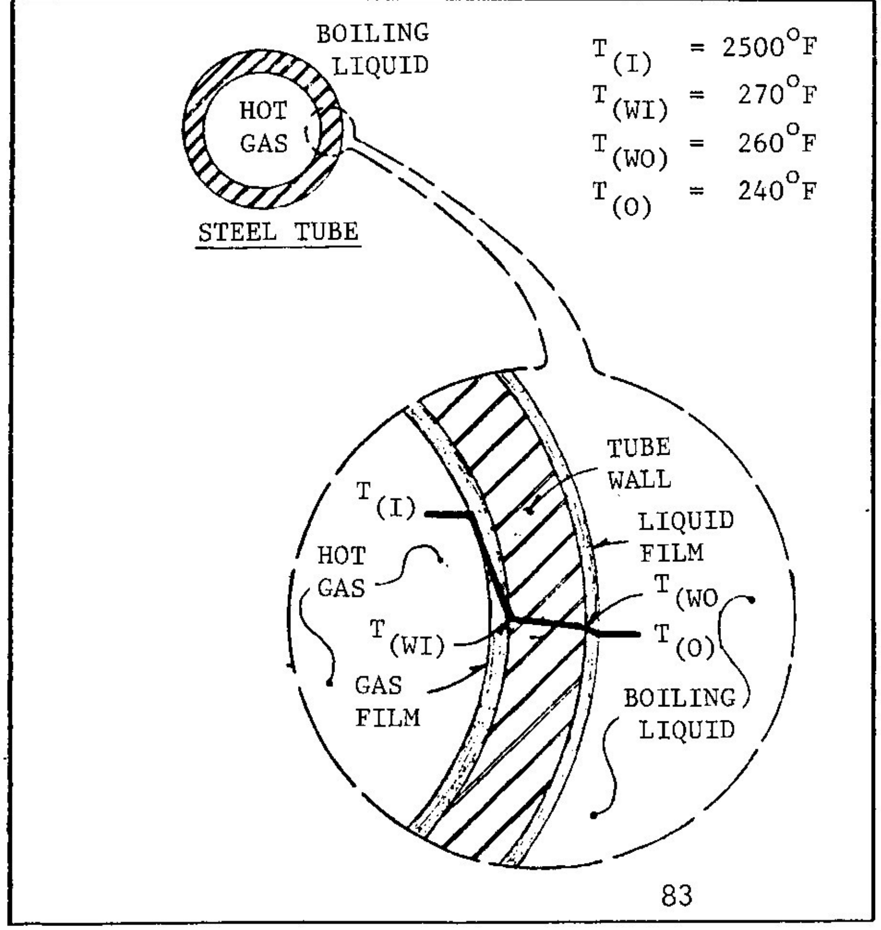


Figure 3.15
Temperature profile across the wall of an amine firetube (Ref. 3.25)

10. *A square pitch tube pattern is recommended for both reboiler and heat exchange bundles to provide easy cleaning. The tubes should be widely spaced to permit a rapid escape of liberated gases and to reduce the high velocity scrubbing action associated with two phase flow. This scrubbing action will remove the protective film and increase corrosion.*

11. *The reboiler should be designed to provide a liberal amount of vapor disengaging space between tubes, and with sufficient surface to produce a "simmering" action rather than violent boiling. In existing installations where vapor binding is a problem, some tubes can be removed to form an "X" or "V" in the center of the bundle to provide a path of low resistance to escaping vapors.*

12. *The reboiler bundle should always be kept covered with 6-8 inches of liquid to prevent localized drying and overheating. Severe corrosion will occur if the liquid level is lowered until some of the tubes are exposed.*

13. *An analysis of the amine solution entering and leaving the reboiler will determine the efficiency of the stripping operation. A high acid gas loading in the reboiler causes tube corrosion.*

With proper design and operation, trouble free reliable service can be expected from an amine sweetening unit. In considering alternatives, every effort should be made to avoid purchasing an undersized unit. First cost investment for adequate capacity in the amine processing unit is seldom money poorly spent.

Piping Design

If the velocity is too high in the piping the corrosion layer is eroded away causing a higher net loss in the metal wall. High velocity also makes it difficult (if not impossible) to maintain a filming type corrosion inhibitor on the metal surfaces. In addition, direct erosion can occur. For all these reasons it is advisable to:

1. Maintain liquid velocity below 3 ft/sec in all piping.

2. Avoid the use of screwed fittings whenever practical.

3. Use welded fittings with long radius ells; avoid tees when possible.

4. When making up pipe with valves, instruments, etc., avoid the use of dissimilar metals to avoid bimetallic corrosion.

CONCLUSION

Amine Sweetening units have a history of severe corrosion and solution degradation problems. Present day technology allows for design that will eliminate problems of the past and assure efficient trouble free operation. In order to obtain such a design the operator must forget the axiom "all bids are equal." A well designed ethanolamine sweetening system is expensive but will pay for the additional costs many times over by decreasing down time and lost production due to operating problems.

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