

# FUNDAMENTALS OF GAS SWEETENING

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Natural gas has a wide range of acid gas concentrations, from parts per million to 50 volume percent and higher, depending on the nature of the rock formation from which it comes. Because of the corrosiveness of  $H_2S$  and  $CO_2$  in the presence of water and because of the toxicity of  $H_2S$  and the lack of heating value of  $CO_2$ , sales gas is required to be sweetened to contain no more than a quarter grain  $H_2S$  per 100 standard cubic feet (4 parts per million) and to have a heating value of no less than 920 to 980 Btu/SCF, depending on the contract. The most widely used processes to sweeten natural gas are those using the alkanolamines, and of the alkanolamines the two most common are monoethanolamine (MEA) and diethanolamine (DEA).

## THE AMINE SWEETENING PROCESS

The monoethanolamine and diethanolamine sweetening processes are similar in their flow schemes and operations. They are used as aqueous solvents to selectively absorb  $H_2S$  and  $CO_2$  from sour natural gas streams. The sour gas is introduced at the bottom of an absorber and flows up the tower countercurrent to an aqueous amine stream. Within the tower the acid gases are absorbed by the amine. The amine is described as being lean in acid gas as it enters the top of the absorber, and rich as it exits the bottom, loaded with acid gas. From the absorber the rich amine is directed to the top of a stripping tower where a drop in pressure and application of heat enables the solvent to be stripped of the acid gases. The amine, again lean, is circulated back to the absorber for sweetening, Figure 1.

Inlet Gas	Before entering the absorber, the gas is passed
Knockout	through an inlet separator where entrained droplets
	or slugs of liquid are removed from the gas stream
	by impaction devices, Figure 2. Baffles remove a
portion of	the liquids. Mist eliminator pads, located near the

gas outlet of the tank, trap the rest. Typical contaminants in natural gas streams may be liquid hydrocarbons, salt water, sands, well treating compounds, pipeline treating chemicals, and compressor oils. It is important that these contaminants be removed before the gas reaches the absorber. Once in the sweetening system, these contaminants can cause a number of operational problems including foaming, equipment fouling, and high corrosion rates, usually resulting in solvent loss and difficulty in meeting sweet gas specifications.

Absorber      The sour gas, freed of entrained liquids by the inlet separator, enters the bottom of the absorber. Usually the absorber is a tray column, although packed columns are also used. In either case, the objective is to provide intimate contact between the gas and the amine solvent so that the  $H_2S$  and  $CO_2$  molecules can transfer from the gas phase to the solvent liquid phase. In tray columns, a liquid level is maintained on each tray by a weir usually 2 or 3 inches high, Figure 3. The gas passes up from underneath the trays through openings in the trays such as perforations, bubble caps, or valves, and disperses into bubbles through the liquid, forming a froth. The gas disengages from the froth, travels through a vapor space, providing time for entrained amine solution to fall back down to the liquid on the tray, and passes through the next tray above. Nearly all absorption of  $H_2S$  and  $CO_2$  takes place on the trays, and not in the vapor between the trays. In packed columns the liquid solvent is dispersed in the gas stream, by forming a film over the packing, providing a large surface area for  $CO_2$  and  $H_2S$  transfer from the gas to the liquid solvent. The degree of sweetening achieved is largely dependent on the number of trays or the height of packing available in the absorber. Twenty trays or the equivalent height in packing are common, and are often a standard design.

A water wash consisting of 2 to 5 trays at the top of the absorber can be used to minimize vaporization losses of amine, and is often found in low pressure monoethanolamine systems (1). In most cases a mist eliminator pad is installed near the gas outlet of the absorber to trap entrained solvent, and a outlet knockout drum, similar to the inlet separator for the gas feed, is provided to collect solvent carryover.

Three Phase      In many units the rich amine solution is sent  
Flash Tank      from the absorber to a flash skimmer tank to  
                 recover hydrocarbons that may have dissolved or  
                 condensed in the amine solution in the absorber.  
The pressure of the solution is dropped as it enters the tank, allowing the lightest of the hydrocarbons to flash. The heavier hydrocarbons remain as a liquid, but separate from the aqueous amine, forming a separate liquid layer. Because the hydrocarbons have a lower density than the aqueous amine, they form the upper liquid layer, and can be skimmed off the top. The aqueous

amine, freed from the hydrocarbon, is drained from the bottom of the tank.

Not only is the flash tank valuable in recovering lost hydrocarbon product, it is also beneficial in maintaining the condition of the amine solution and the amine sweetening system. Hydrocarbon contamination in aqueous amine solutions often promotes foaming. Equipment fouling may be more severe and occur at a faster rate in the absence of a flash separator. Sulfur plant operations may be hindered if hydrocarbons are volatilized in the amine regenerator.

Lean/Rich Heat Exchanger      The rich solvent is preheated before entering the stripper. Because the lean amine exiting the reboiler must be cooled before entering the absorber, there is an opportunity to exchange heat from the lean to the rich stream, thereby reducing the heat load on the reboiler. This is usually done in a shell and tube lean/rich heat exchanger with the rich solvent passed through the tubes, which are usually made of stainless steel. A recommended maximum velocity to minimize corrosion in the tubes is 3 or 3.5 feet/sec (1,2,3).

Regenerator      Like the absorber, the stripper is either a tray or packed column with approximately 20 trays of the equivalent height in packing. To minimize amine vaporization loss, there may be a water wash section at the top of the column with an additional four to six trays (1). The preheated rich amine enters near the top of the column and flows down countercurrent to a gas stream of steam,  $H_2S$ , and  $CO_2$ . The steam is generated in the reboiler, lowering the partial pressure of  $H_2S$  and  $CO_2$  in the gas stream, enhancing the driving force of the acid gases from the amine solution. The overhead gas is passed through a condenser to recover water and the small amount of amine which is vaporized in the regenerator.

The overhead condenser, the reboiler tube bundle, and the upper third of the stripping column shell are all susceptible to high corrosion rates, and may need to be manufactured out of stainless steel (4). Thermal degradation, which can contribute to corrosion, can be minimized by designing the reboiler to use a low temperature heating medium such as low pressure steam.

The reboiler heat duty includes: 1) the sensible heat required to raise the temperatures of the rich amine feed, the reflux, and the makeup water to the temperature of the reboiler; 2) the heat of reaction to break the chemical bonds between the acid gas molecules and the amine; and 3) the heat of vaporization of water to produce a stripping vapor of steam. The ratio of moles of steam to moles of acid gas in the overhead gas upstream of the condenser, called the reflux ratio, commonly ranges from 1.5:1 to 4:1, depending upon the required degree of regeneration.

Filtration      A filtration scheme of mechanical and activated carbon filters is important in maintaining good solution control. Mechanical filters such as cartridge filters or precoat filters remove particulate material while carbon filters remove chemical contaminants such as entrained hydrocarbons and surface-active compounds.

Filters are located in the rich line in some plants, and in the lean line in others. One manufacturer recommends filters in both rich and lean lines (5). Locating the filters in the rich line upstream of the lean/rich heat exchanger will protect both the heat exchanger and the stripper from plugging, and reduce the erosion/corrosion rate from hydrocarbon contamination and reduce the tendency of the amine solution in the stripper to foam. However, because the amine solution is heavily loaded with acid gas, drops in pressure acid gas to flash from the solvent, causing gas pockets to form in the filter resulting in reduced or completely blocked flow (6). In terms of safety for workers to dismantle, inspect and clean out the filters, it is far more hazardous to locate the filters in the rich line than in the lean line. In many plants, it is specifically for this safety reason that the filters are placed in the lean line.

Regardless of the line in which the filters are located, the mechanical filter should be positioned upstream of the carbon filter. In the absence of a mechanical filter, the carbon filter will remove both particulate matter and chemical contaminants. This is, however, a costly way to operate because the carbon may plug up with solid material long before its chemical capacity is exhausted, requiring frequent changeouts of activated carbon.

A 10 to 20 micron mechanical filter should be adequate for particulate removal. If cotton filters are used, the cotton should be virgin cotton rather than recycled. Recycled cottons may contain fibers with coatings which may be the source of amine solution foaming problems. Circulation rates through mechanical filters range from 5 % of the circulating system to full flow, depending on the degree of contamination. Recommendations for flow through carbon filters range from less than 1 percent to 5 to 10 percent (7,8,6) and some units have been built with full flow (5).

The life of a carbon filter will vary depending on the level of contaminants and the flow rate of the amine through the bed. A typical life may be 4 to 6 months, although in some cases beds have lasted for many months longer than that. In determining when a carbon bed should be changed the following criteria can be used as a guide:

1. a high pressure drop across the bed, caused by solids plugging the voids

2. a color comparison between a sample taken from the outlet of the filter and a plant sample run through fresh carbon in the lab. Active carbon will remove color.

3. an increase in foaming tendency in the plant, or the start of a foaming problem.

Amine Reclaimer Monoethanolamine solutions are purified by semi-continuous distillation in a reclaimer as part of the gas sweetening process, Figure 4. At the beginning of the reclaiming cycle, the reclaimer is filled with lean amine solution. During the filling, a strong base such as sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) or sodium hydroxide ( $\text{NaOH}$ ) is added to the reclaimer to neutralize the heat stable salts present in solution. Heat stable salts are reaction products of the amine with strong acids such as formic acid, acetic acid and sulfuric acid. The amine cannot be released from these strong acids under the conditions in the regenerator; however, with the addition of a stronger base than the amine, the amine is recovered. Heat is then added to the kettle and water vapor and MEA are distilled off the top, leaving the contaminants in the bottoms. A slipstream of 1 to 3 percent of the lean amine circulation is continuously fed to the reclaimer until the liquid temperature in the reclaimer, which rises as the contaminants accumulate, reaches 300 °F. The operation is then stopped and the reclaimer is drained, terminating the cycle. The 300 °F temperature limit is set to minimize thermal degradation of the amine. Typical contaminants which are removed from the MEA solution by the reclaimer are the degradation products, 1-(2-hydroxyethyl)imidazolidone-2 and N-(2-hydroxyethyl)ethylenediamine, and nonvolatiles such as inorganic ions, iron sulfide, high boiling hydrocarbons, and heat stable salts.

Diethanolamine has a higher boiling temperature than monoethanolamine, requiring other methods of reclaiming such as vacuum distillation in order to prevent thermal degradation of the amine. Moreover, diethanolamine has a slow degradation rate. Consequently, in most cases it is not practical, economical, or necessary to reclaim DEA solutions. Solution purification is maintained by mechanical and carbon filtration, and by caustic or soda ash addition to the system to neutralize the heat stable amine salts.

## OPERATING DIFFICULTIES

Amine gas sweetening plants can experience operating difficulties including foaming, failure to meet sweet gas specification, high solvent losses, corrosion, fouling of equipment, and contamination of the amine solution. Often one operating difficulty is the cause of another. Not all plants experience the same problems to the same degree, and what may be a continual problem

in one plant may occur only rarely in another.

Pure aqueous amine solutions do not foam. It is only in the presence of contaminants such as condensed hydrocarbons, small suspended particulate matter, or other surface-active agents such as some pipeline corrosion inhibitors or compressor oils, that a foaming problem may develop. Foaming usually occurs in the absorber or stripping tower, and is accompanied by a sudden noticeable increase in the differential pressure across the column. Other indications of a foaming condition may be a high solvent carryover, a drop in liquid levels, and the detection of off-specification gas.

An immediate method to control a foaming problem is the addition of an antifoam at a location just upstream of the foam. Effective foam inhibitors for amine sweetening systems are silicone antifoams and polyalkylene glycols. Also widely used are high-boiling alcohols such as oleyl alcohol and octylphenoxyethanol (1). It is advisable to test the antifoam on a plant sample in the laboratory before applying it in the field to verify that it will break the foam. In the event that one antifoam is ineffective, switching to another antifoam may solve the problem.

The silicone antifoams have proven to be quick and effective in controlling foaming problems in the gas treating industry. When using a silicone antifoam, the antifoam should be added downstream of the carbon filters because carbon filters will adsorb the silicone. Care should be exercised with respect to the amount of silicone antifoam added to a system. The silicone antifoams should be used only in small quantities, as recommended by the manufacturer. It is important to be aware that the silicone antifoams used in excessive quantities have the potential to promote the formation of foam.

The use of an antifoam may be only a temporary solution to a continuing problem. The objective in controlling foaming should be to minimize the level of contaminants in the amine solution. Of critical importance is the prevention of entrained contaminants in the feed gas from entering the amine system. The inlet separator, equipped with a demister pad and possibly filters, is instrumental in trapping most contaminants, and should be monitored to ensure that it is operating efficiently and not being overloaded. Mechanical and carbon filters are necessary in maintaining a clean solution. In order to prevent hydrocarbons from condensing in the absorber, the lean amine feed temperature should be held between 10 °F and 20 °F above the temperature of the feed gas.

Failure to Meet Gas Specification	Difficulty in meeting the sweet gas specification may be the result of poor contact between the gas and the amine solvent, which may in turn be caused by foaming or mechanical
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problems in the contacting equipment. In the case of foaming, the gas remains trapped in bubbles, unable to contact the rest of the solvent, resulting in poor mass transfer of acid gas from the gas to the amine solution. In terms of mechanical damage, if trays are broken or have fallen, there may not be enough contact zones (trays) for adequate sweetening. If the trays are plugged, there is less contact between the gas and liquid on each tray, resulting in poorer sweetening.

Other explanations for off-specification gas may be related to the amine solution: the circulation rate may be too low, the amine concentration too low, the lean solution temperature may be too high, or the acid gas loading in the lean solution may be too high. Monoethanolamine systems usually run with solution concentrations between 10 and 20 weight percent MEA, and a lean loading of 0.1 moles acid gas/mole of MEA. Diethanolamine systems are between 20 and 30 weight percent DEA, with lean loadings of 0.02 to 0.05 moles acid gas/mole DEA. In order to reach these lean loadings, regeneration resulting in a steam-to-acid gas ratio ranging from 1:1 to 3:1 (moles steam: moles acid gas) in the stripper overhead gas is usually required (1). In some cases, even higher ratios may be necessary to bring the loading down, as in low-pressure applications.

One way to estimate the overhead steam-to-acid gas ratio, knowing the stripper overhead temperature and pressure, is to use steam table data and Raoult's law:

$$pp_{H_2O} = x_{H_2O} p^{sat}$$

where:

$pp_{H_2O}$  = partial pressure of water in the overhead gas

$x_{H_2O}$  = mole fraction of water in the amine solvent

$p^{sat}$  = vapor pressure of pure water at the temperature of the overhead gas

Approximating the overhead gas as an ideal gas containing water,  $H_2S$  and  $CO_2$ , the partial pressure of the acid gases can be obtained by subtracting the partial pressure of water, calculated from Raoult's law, from the stripper overhead pressure:

$$pp_{acid\ gas} = P_{overhead} - pp_{H_2O}$$

The ratio of water partial pressure to acid gas partial pressure is equal to the mole ratio of steam to acid gas.

As an example calculation of the steam-to-acid gas ratio, a stripper with an overhead temperature and pressure of 200 °F and

20 psia, carrying a 27 weight percent (6 mole percent) DEA solvent, has a corresponding water vapor pressure of 11.5 psia as obtained from the steam tables. From Raoult's law, the partial pressure of water is 10.8 psia:

$$p_{\text{H}_2\text{O}} = (0.94) (11.5) = 10.8 \text{ psia}$$

The partial pressure of acid gas would be 20 psia less 10.8 psia or 9.19 psia, and the overhead steam-to-acid gas ratio would be 1.2 moles steam/mole acid gas (10.8 ÷ 9.19).

Monitoring the overhead pressure and temperature, and thereby monitoring the overhead steam-to-acid gas ratio, is one method that can be used to control heat to the reboiler to maintain specification gas.

Amine losses are largely through entrainment, Solvent Losses caused by foaming or excessive gas velocities, and by leakage due to spills or corrosion. In MEA units the reclaimer bottoms disposal significantly adds to the makeup requirement. On a much smaller scale are vaporization losses from the absorber, the overhead condenser, and the flash tank, and degradation losses by chemical and thermal degradation.

Corrosion is a problem experienced by many alkanol-amine gas sweetening plants. When loaded with CO<sub>2</sub> and H<sub>2</sub>S, aqueous amine solutions can become corrosive to carbon steel. Corrosion rates are increased by high amine concentration, high acid gas loading, high temperatures, degradation products, and foaming. Also corrosive are acid gases flashed from solution.

Monoethanolamine is more reactive than diethanolamine and similarly more corrosive. As a result, the concentration of MEA is restricted to 10 to 20 weight percent, while DEA strengths range from 20 to 30 weight percent. Rich solution loadings are normally limited to the range of 0.25 to 0.45 moles acid gas/mole MEA, while in DEA systems loadings may range from 0.5 to 0.6 moles acid gas/mole DEA. The corrosiveness of a loaded amine solution is strongly influenced by the relative proportion of CO<sub>2</sub> to H<sub>2</sub>S in the feed gas. CO<sub>2</sub> is more corrosive to carbon steel than is H<sub>2</sub>S in aqueous systems. Thus, for gases containing a higher ratio of CO<sub>2</sub> to H<sub>2</sub>S, the rich acid gas loading should be maintained at the lower end of the recommended loading range. In cases where the feed gas is predominantly H<sub>2</sub>S, loadings at the higher end of the loading range may be acceptable.

In terms of design, a number of measures can be taken to minimize corrosion. Solution velocities should not exceed 3 or 3.5 ft/sec (1,2,3). The rich solution should be on the tube side of the lean/rich heat exchanger, and pressure should be maintained



on the exchanger to prevent acid gases from flashing, creating an erosion/corrosion cycle. A low temperature heating medium should be used in the reboiler, thereby preventing accelerated corrosion rates and thermal degradation of the amine. All equipment should be stress relieved.

There are certain areas of amine sweetening plants which are more susceptible to corrosion than others, and, as a result, are constructed of corrosion-resistant materials such as Type 304 stainless steel. These areas include: 1) the lean/rich heat exchanger tube bundle, 2) the reboiler tube bundle, 3) the stripping column, particularly the upper section and overhead gas line, 4) the reflux condenser, and 5) the rich solvent let-down valve and subsequent piping to the stripper.

## AMINE PLANT DESIGN CALCULATIONS

A preliminary design of an amine gas treating plant includes calculation of the amine solvent circulation rate, reboiler heat duty, and tower diameters. Assumptions used in the design include an estimation of the approach to equilibrium of the acid gas in the rich solvent at the bottom of the absorber and of the exiting sweet gas stream at the top. As an illustration of design calculations for a sweetening unit, an 80 MMSCFD gas with 7 percent CO<sub>2</sub> and 3 percent H<sub>2</sub>S at 100 °F and 1000 psia is treated with a 27 weight percent diethanolamine solution to meet a 4 ppm H<sub>2</sub>S specification.

Amine Circulation Rate      The amine circulation rate is determined by an iterative calculation of material and energy balances around the absorber based on an initial estimate of the exiting rich solvent temperature. The remaining three temperatures - the product gas temperature, the lean solvent temperature, and the feed gas temperature - are set by design considerations. In order to minimize hydrocarbon condensation in the absorber, the lean solvent temperature is set 20 °F above the feed gas temperature. Because the acid gas concentration in the feed gas is high, the product gas temperature is assumed to be the same as the temperature of the lean solvent at the top of the absorber (120 °F).

The calculation procedure for determining the amine solvent circulation rate is as follows:

1. Estimate the rich solvent temperature
2. Determine the acid gas loadings at the estimated rich solvent temperature and at the acid gas partial pressures of the feed gas.
3. Calculate the quantity of acid gas absorbed
4. Calculate the circulation rate

5. Do a heat balance around the absorber and solve for the temperature rise of the solvent.
6. Compare the temperature rise of the solvent as calculated in Step 5 with the temperature rise assumed in Step 1. The circulation rate is obtained when the temperature rises obtained in Steps 5 and 1 are the same.
7. If the two temperature rises are different, estimate a new rich solvent temperature and recalculate a new circulation rate until the two temperature rises are the same. If the assumed  $\Delta T$  (from Step 1) is smaller than the calculated  $\Delta T$  (from Step 5), choose a higher temperature for the new estimate; if it is larger, choose a lower temperature for the new estimate.

Equilibria data on the solubility of  $H_2S$ ,  $CO_2$  and  $H_2S$ - $CO_2$  mixtures in monoethanolamine and diethanolamine solutions are available in the literature. Literature reviews appear in several papers including three by Lee, Otto and Mather (9,10,11) and one by Lawson and Garst (12). In this example, the solubility data of Lee, Otto and Mather (10) for  $CO_2$ - $H_2S$  mixtures in diethanolamine have been used. The data were reported for two temperatures, 50 °C and 100 °C, and two DEA concentrations, 20 and 35 weight percent. Figures 5 through 8 are graphical representations of the data for 35 weight percent DEA at both 50°C and 100°C. These data and the data for 20 weight percent DEA are reproduced in graphical form in the *Engineering Data Book* (13). Linear interpolation of acid gas loadings obtained at 20 and 35 weight percent DEA has been used to obtain the acid gas loadings at 27 weight percent. Linear interpolation of acid gas loadings obtained at 50 °C and 100 °C has been used to obtain acid gas loadings at intermediate temperatures.

Using the equilibria data presented in Figures 5 and 6 or Figures 7 and 8 requires an iterative method to determine the acid gas loadings for a specific combination of  $H_2S$  and  $CO_2$  partial pressures. In this example, the partial pressure of  $H_2S$  in the feed gas is 30 psia (3 % x 1000 psia), and the partial pressure of  $CO_2$  is 70 psia (7 % x 1000 psia). To obtain the acid gas loadings in 35 weight percent DEA at 50 °C, Figures 5 and 6 can be used:

Make an initial estimate of the  $CO_2$  loading and find the corresponding  $H_2S$  loading for the  $H_2S$  partial pressure of the feed gas (30 psia) from Figure 5. Then, using the  $H_2S$  loading obtained from Figure 5, find the  $CO_2$  loading corresponding to the  $CO_2$  partial pressure of the feed gas (70 psia) in Figure 6. Compare the  $CO_2$  loading used in Figure 5 with that obtained in Figure 6. If they are the same, the initial estimate of  $CO_2$  loading and the corresponding  $H_2S$  loading are the equilibrium acid gas loadings at 50 °C. If they are different, use the  $CO_2$  loading obtained from Figure 6 to obtain a new  $H_2S$  loading from Figure 5 to obtain a new  $CO_2$  loading from Figure 6. The equilibrium loadings are obtained when the values do not change from one

iteration to the next.

As an example, start with an initial CO<sub>2</sub> loading estimate of 0.3 mole CO<sub>2</sub>/mole DEA. With an H<sub>2</sub>S partial pressure of 30 psia, Figure 5 gives an H<sub>2</sub>S loading of 0.46 mole H<sub>2</sub>S/mole DEA. Using Figure 6 with 0.46 mole H<sub>2</sub>S/mole DEA and the CO<sub>2</sub> partial pressure of 70 psia, the CO<sub>2</sub> loading obtained is 0.43 mole CO<sub>2</sub>/mole DEA. The initial CO<sub>2</sub> loading and the CO<sub>2</sub> loading obtained from Figure 6 are different; thus, a second iteration is required. Figure 5 gives an H<sub>2</sub>S loading of 0.35 mole H<sub>2</sub>S/ mole DEA and Figure 6 gives a CO<sub>2</sub> loading of 0.51 mole CO<sub>2</sub>/mole DEA. After 6 iterations the solution converges, giving acid gas equilibrium loadings of 0.58 moles CO<sub>2</sub>/mole DEA and 0.23 moles H<sub>2</sub>S/mole DEA. The iterations are as follows:

<u>Iteration</u>	<u>moles CO<sub>2</sub>/mole DEA</u>	<u>moles H<sub>2</sub>S/mole DEA</u>
1	0.30	0.46
2	0.43	0.35
3	0.51	0.27
4	0.56	0.24
5	0.58	0.23
6	0.58	0.23

When the initial CO<sub>2</sub> loading estimate is 0.8 moles CO<sub>2</sub>/mole DEA, the iterations are as follows:

1	0.80	0.11
2	0.67	0.17
3	0.62	0.20
4	0.61	0.20

The equilibrium loading values obtained from these graphs will be slightly different, depending on whether the initial CO<sub>2</sub> loading estimate is higher or lower than the equilibrium value. This is a consequence of the accuracy of the graphical technique and the equilibria data. In this case the values obtained differ by 5 and 15 percent. The averages of the loadings based on the high and low initial estimates were used in the design calculations. Thus at 50 °C, the acid gas loadings obtained are 0.60 moles CO<sub>2</sub> mole/DEA and 0.22 moles H<sub>2</sub>S/mole DEA.

At 100 °C and 35 weight percent DEA, the acid gas loadings obtained are 0.35 moles CO<sub>2</sub>/mole DEA and 0.24 moles H<sub>2</sub>S/mole DEA, based on a high initial estimate of 0.5 moles CO<sub>2</sub>/mole DEA and a low initial estimate of 0.2 moles CO<sub>2</sub>/mole DEA.

The acid gas loadings obtained for 20 weight percent DEA at 50 °C are 0.58 moles CO<sub>2</sub>/mole DEA and 0.32 moles H<sub>2</sub>S/mole DEA, and at 100 °C are 0.4 moles CO<sub>2</sub>/mole DEA and 0.29 moles H<sub>2</sub>S/mole DEA.

By linear interpolation of the equilibrium acid gas loadings at 20 and 35 weight percent, the acid gas loadings of 27 weight percent DEA at 50 °C are 0.59 moles CO<sub>2</sub>/mole DEA and 0.273 moles/mole DEA, and at 100 °C are 0.38 moles CO<sub>2</sub>/mole DEA and 0.267 moles H<sub>2</sub>S/mole DEA.

In order to determine the amine solvent circulation rate, an estimate of the rich solvent temperature is made. Using 65 °C as a first estimate, the equilibrium acid gas loadings in 27 weight DEA are 0.53 moles CO<sub>2</sub>/mole DEA and 0.27 moles H<sub>2</sub>S/mole DEA, by linear interpolation of the acid gas loadings at 50 °C and 100 °C. The total acid gas loading is 0.8 moles acid gas/mole DEA.

A 75 percent approach to equilibrium was selected for the bottom of the absorber, resulting in a rich loading of 0.60 moles acid gas/mole DEA. To meet the sweet gas specification, a lean loading of 0.02 moles CO<sub>2</sub>/mole DEA is assumed sufficient. Thus, the quantity of acid gas absorbed is 0.60 less 0.02 or 0.58 moles of acid gas/mole DEA, and the first estimate of the amine circulation rate is now calculated:

1. Gas flow = 80 MMSCFD = 55 556 SCFM = 146.35 moles/min
2. H<sub>2</sub>S flow = (0.03) x (146.35) = 4.39 lb moles H<sub>2</sub>S/min
3. CO<sub>2</sub> flow = (0.07) x (146.35) = 10.24 lb moles CO<sub>2</sub>/min
4. Acid gas flow = 14.63 lb moles acid gas/min
5. Circulation rate =  $\frac{14.63 \text{ lb moles acid gas/min}}{0.58 \text{ lb moles acid gas/lb mole DEA}}$   
= 25.2 lb moles DEA/min

Using a 27 percent DEA solution at 120 °F, the density is 8.49 lb/gal (Figure 9); molecular weight of DEA is 105.

6. Circulation rate = 1161 gpm

The circulation rate is based on the assumption that the rich solution exits the absorber at 65 °C. To check this assumption, an energy balance calculation is required. As the acid gas is absorbed, heat is produced by the chemical reaction between the acid gases and the amine. Some of the heat is transferred to the gas, while the remainder causes the temperature of the solvent to rise.

Approximate heats of reaction for the acid gases with DEA are 511 Btu/lb H<sub>2</sub>S and 653 Btu/lb CO<sub>2</sub> (1). The heat generated by

reaction in this example design is:

1.  $\text{H}_2\text{S}$  reaction heat =  $(4.39 \text{ moles H}_2\text{S/min}) \times (34 \text{ lb/lb mole}) \times (511 \text{ Btu/lb H}_2\text{S})$   
= 76 272 Btu/min
2.  $\text{CO}_2$  reaction heat =  $(10.24 \text{ lb moles CO}_2\text{/min}) \times (44 \text{ lb/lb mole}) \times (653 \text{ Btu/lb CO}_2)$   
= 294 216 Btu/min
3. Total reaction  
heat = 370 488 Btu/min

The heat absorbed by the gas raising its temperature from 100 °F (37.8 °C) to 120 °F (48.9 °C) is evaluated using the following correlation (14):

$$\Delta H_{\text{gas}} = a(T_2 - T_1) + \frac{b}{2}(T_2 - T_1)^2 + \frac{c}{3}(T_2 - T_1)^3 + \frac{d}{4}(T_2 - T_1)^4$$

where:

$a = 8.200$	$\Delta H_{\text{gas}}$ = heat absorbed by the gas, cal/g mole
$b = 1.307 \times 10^{-2}$	$T_1$ = feed gas temperature in centigrade (37.8 °C)
$c = 0.0875 \times 10^{-5}$	$T_2$ = product gas temperature in centigrade (48.9 °C)
$d = -2.63 \times 10^{-9}$	

Solving the above equation gives 97.33 cal/g mole which is equivalent to 175.2 Btu/lb mole, or 23 038 Btu/min:

$$(175.2 \text{ Btu/lb mole}) \times (131.5 \text{ lb mole CH}_4\text{/min}) = 23 038 \text{ Btu/min}$$

The heat absorbed by the solvent is the heat generated by reaction less the heat absorbed by the gas or:

$$370 488 - 23 038 = 347 450 \text{ Btu/min}$$

The heat change of the solvent is described by the equation:

$$\Delta H_{\text{solv}} = m C_p \Delta T = 347 450 \text{ Btu/min}$$

where:

$m$ = solvent circulation rate, lb/min
$C_p$ = specific heat of the solvent, Btu/lb °F, (Figure 10)
$\Delta T$ = temperature rise of the solvent, °F

The circulation rate was calculated previously as 1161 gpm. Using a density of 8.49 lb/gal gives a circulation rate of 9853 lb/min. By interpolation from Figure 10, the specific heat of a 27 weight percent DEA solution at an average temperature of 135 °F,  $(1/2 \times [149 + 120])$ , is 0.91 Btu/lb °F. Solving for the

temperature rise,  $\Delta T$ , gives:

$$\Delta T = \frac{(347\ 450)}{(9853)(0.91)} = 38.8\ ^\circ\text{F}$$

The initial estimate for the rich solvent temperature of 149 °F (65 °C) gives a temperature rise of 29 °F, (149 °F - 120 °F). The energy balance result of  $\Delta T = 38.8\ ^\circ\text{F}$  indicates that the initial rich solution temperature estimate was too low. A second estimate of 70 °C (158 °F) is selected.

Again the partial pressures of the acid gases are 70 psia CO<sub>2</sub> and 30 psia H<sub>2</sub>S. Interpolation of the equilibrium loadings at 50 °C and 100 °C, obtained earlier, give acid gas loadings of 0.50 moles CO<sub>2</sub>/mole DEA and 0.27 moles H<sub>2</sub>S/mole DEA for 70 °C. The total equilibrium acid gas loading is 0.77 moles acid gas/mole DEA. With a 75 percent approach to equilibrium the rich solvent loading is 0.58 moles acid gas/mole DEA. The calculated circulation rate is:

$$\frac{14.63\ \text{lb moles acid gas/min}}{0.58\ \text{lb mole acid gas/mole DEA}} \times \frac{105\ \text{lb DEA}}{1\ \text{lb mole DEA}} \times \frac{1\ \text{lb soln}}{0.35\ \text{lb DEA}} \times \frac{\text{gal}}{8.49\ \text{lb soln}}$$
$$= 1194\ \text{gpm}$$

In the energy balance, the heat of reaction, the heat absorbed by the gas, and the heat absorbed by the solvent are the same values as calculated in the first iteration; however, because the circulation rate is different, the temperature rise in the solvent will change:

$$\Delta H_{\text{soln}} = m C_p \Delta T = 347\ 450\ \text{Btu/min}$$

where:

$$m = (1194\ \text{gpm}) \times (8.49\ \text{lb soln/gal}) = 10\ 137\ \text{lb/min}$$

$$C_p = 0.91\ \text{Btu/lb } ^\circ\text{F}$$

$$\Delta T = \frac{347\ 450}{(10\ 137)(0.91)} = 37.7\ ^\circ\text{F}$$

This calculated  $\Delta T$  compares well with the temperature difference based on the rich solvent temperature estimate of 70 °C (158 °F), where 158 °F less 120 °F gives 38 °F. Thus, the design circulation rate is 1194 gpm, with corresponding rich solution loadings of 0.38 mole CO<sub>2</sub>/mole DEA and 0.20 moles H<sub>2</sub>S/mole DEA. The temperature of the rich DEA solution exiting the absorber is estimated to be 158 °F (70 °C).

The heat requirements in the regenerator include:

Reboiler      1) the sensible heat needed to heat the rich solvent from the feed temperature to the temperature

Heat Duty

of the reboiler, 2) the heat of reaction to break the acid gas-amine chemical bonds, 3) the heat of vaporization of water and 4) the sensible heat of reflux and makeup water to the stripper (Figure 11).

The temperature in the reboiler is fixed by the amine concentration and the pressure, and is approximated as the saturation temperature of steam corresponding to the saturation pressure calculated from Raoult's law. It is assumed that the partial pressure of water in the reboiler is closely approximated by the total pressure in the reboiler. As an example, if the reboiler pressure is 12 psig, and the amine concentration is 27 weight percent DEA (6 mole percent), the water saturation pressure will be 28 psia:

$$\frac{p_{H_2O}}{x_{H_2O}} = p^{sat} = \frac{(12 + 14.7)}{(0.94)} = 28 \text{ psia}$$

The temperature corresponding to 28 psia from the steam tables is 247 °F.

Assuming a solvent temperature rise of 20 °F, and a reboiler temperature of 247 °F, the sensible heat requirement is  $1.89 \times 10^5$  Btu/min:

$$Q_{\text{sensible}} = m C_p \Delta T = (10 \text{ 137 lb/min}) \times (0.93 \text{ Btu/lb } ^\circ\text{F}) \times (20 ^\circ\text{F})$$

The heat of reaction to break the chemical bonds between the acid gas and the amine is the same energy as that generated in the absorber and is 370 484 Btu/min.

The heat required to vaporize water and provide the sensible heat of reflux and makeup water is given by:

$$\Delta H = [(hg)_{T_{\text{ovh}}} \times M_{\text{ovh}}] - [(hf)_{T_{\text{rfl}}} \times (M_{\text{loss}} + M_{\text{rfl}})]$$

where:

$(hg)_{T_{\text{ovh}}}$  = enthalpy of water vapor at the overhead temperature

$(hf)_{T_{\text{rfl}}}$  = enthalpy of liquid water at the reflux temperature

$M_{\text{ovh}}$  = mass flow rate of water vapor overhead

$M_{\text{loss}}$  = mass flow of water lost by evaporation

$M_{\text{rfl}}$  = mass flow of water vapor condensed and returned to the tower

NOTE: in this case,  $M_{\text{ovh}} = M_{\text{loss}} + M_{\text{rfl}}$

With an overhead ratio of 1.5 moles of steam per mole of acid gas selected to strip the solvent of acid gas, the overhead water vapor rate is:

$$\frac{1.5 \text{ moles H}_2\text{O}}{\text{moles acid gas}} \times \frac{14.63 \text{ moles acid gas}}{\text{min}} \times \frac{18 \text{ lb H}_2\text{O}}{1 \text{ lb mole}} = 395 \frac{\text{lb steam}}{\text{min}}$$

The overhead temperature estimated using the steam tables is 208 °F. The reflux temperature is 110 °F. With an (hg)<sub>208 °F</sub> of 1149 Btu/lb and an (hf)<sub>110 °F</sub> of 77.98 Btu/lb, the heat requirement of water is  $4.23 \times 10^5$  Btu/min:

$$\Delta H_{\text{vap}} = (1149 - 77.98) \text{ Btu/lb H}_2\text{O} \times (395 \text{ lb H}_2\text{O/min})$$

The total heat requirement is the sum of the sensible heat, heat of reaction, and heat of vaporization of water, and is equal to  $9.82 \times 10^5$  Btu/min or 58.9 MMBtu/hr.

The diameter in tray towers can be determined by empirical correlations of superficial velocity (15,16). The superficial flooding gas velocity is given by:

$$U_f = C_{sb} \left[ \frac{\sigma}{20} \right]^{0.2} \left[ \frac{\rho_L - \rho_G}{\rho_G} \right]^{0.5}$$

where:

$U_f$  = superficial gas velocity, based on net area for vapor flow, ft/sec

$\sigma$  = liquid surface tension, dynes/cm

$\rho_L$  = liquid density, lb/ft<sup>3</sup>

$\rho_G$  = gas density, lb/ft<sup>3</sup>

$C_{sb}$  = empirical constant which varies with liquid and gas flows, liquid and gas densities, and tray spacing, ft/sec

Values of the empirical constant  $C_{sb}$  are plotted in the *Chemical Engineers' Handbook* (15) as a function of tray spacing and a parameter  $F_v$ :

$$F_v = \left( \frac{L}{G} \right) \left( \frac{\rho_G}{\rho_L} \right)^{0.5}$$

where:

$L$  = liquid flow rate, lb/ft<sup>3</sup>

$G$  = gas flow rate, lb/ft<sup>3</sup>

Equations for  $C_{sb}$  for bubble cap trays and for sieve trays are presented by Treybal (16), and some typical values of  $C_{sb}$  are



given in Table 1 - 6 in *Gas Purification* (1).

The largest volume of gas passing through the absorber is at the bottom of the tower. The density of the solvent at the bottom is 62.8 lb/ft<sup>3</sup>, Figure 9. The density of the gas is calculated for 100 °F and 1000 psia by determining the density of each pure component and then the average density of the gas mixture:

Gas	Molecular weight	Specific gravity	$\rho$ Density lb/ft	Mole fraction	$Y_w$ Weight fraction	$Y_{w0}$
CH <sub>4</sub>	16.04	0.554	2.67	0.9	0.78	2.08
CO <sub>2</sub>	44.01	1.53	7.38	0.07	0.17	1.25
H <sub>2</sub> S	34.08	1.19	5.74	0.03	0.06	0.34

$$\text{Density of the gas} = 3.67 \text{ lb/ft}^3 = (2.08 + 1.25 + 0.34)$$

With a gas flow rate of 2716 lb/min and a liquid flow rate of 10 137 lb/min,  $F_v$  is calculated to be 0.9. For a 24 inch spacing, the corresponding  $C_{sb}$  value is 0.13 (15). At the exiting rich solvent temperature, the surface tension of the solvent is 56 dynes/cm, Figure 12. The superficial flooding gas velocity, based on net area for vapor flow, can be calculated:

$$U_f = 0.64 \text{ ft/sec} = 0.13 \left( \frac{56}{20} \right)^{0.2} \left( \frac{62.8 - 3.67}{3.67} \right)^{0.5}$$

It is recommended that velocities be designed to not exceed 60 percent of flooding velocity (1). In this case the design velocity would be 23.1 ft/min. The volumetric flow rate of the gas feed is 879.5 ACF/min, thus the area required for the gas to flow at a velocity no greater than 23.1 ft/min is:

$$\frac{Q}{U} = \frac{879.5 \text{ ACF/min}}{23.1 \text{ ft/min}} = 38.1 \text{ ft}^2$$

Assuming that the segmental area of one downspout is 9 percent of the tower cross section in a single-pass cross-flow column, then the total area of the column is 42 ft<sup>2</sup>, and the column diameter is 7.3 ft.

The largest volume of gas in the stripper is at the bottom of the tower where the gas is all water vapor. In the reboiler, the heat supplied by the reboiler generates steam at 943 700 Btu/min. Water saturated in the reboiler at 247 °F has a heat of vaporization of 947.5 Btu/lb. Thus the rate of water vapor generated is 1036 lb/min, and the volumetric flow rate is 16 360 ft<sup>3</sup>/min:

$$V = \frac{NRT}{P} = \frac{(57.6 \text{ lb moles})(10.73)(247^\circ\text{F} + 460)}{26.7 \text{ psia}}$$

The flooding velocity is calculated to be 551 ft/min using the following data:

$$\rho_G = 0.69 \text{ lb/ft}^3 \text{ (steam tables)}$$

$$\rho_L = 61 \text{ lb/ft}^3 \text{ (Figure 9)}$$

$$F_v = \left(\frac{10\,137}{1036}\right)\left(\frac{0.069}{61}\right)^{0.5} = 0.33$$

$$C_{sf} = 0.26 \text{ (15)}$$

$$\sigma = 47.5 \text{ dynes/min (Figure 12)}$$

$$U_f = (0.26)\left(\frac{47.5}{20}\right)^{0.2} \left(\frac{61 - 0.069}{0.069}\right)^{0.5} = 9.2 \text{ fps} = 551 \text{ fpm}$$

A tower diameter of 8.3 feet is obtained, based on a superficial gas velocity of 60 percent of the flooding velocity and a net area vapor flow of 91 percent of the tower cross section.

Results of Circulation rate, heat requirements, equipment size and plant cost depend on a number of factors including:  
Amine Plant  
Design Cases

- gas volume being processed
- gas pressure
- acid gas concentrations
- type of amine solvent
- concentration of amine solvent

Design calculations were done for five different feed gas conditions using a 30 weight percent DEA solution and, in two cases, a 15 weight percent MEA solution to illustrate these effects. All calculations were based on a 75 percent approach to equilibrium in the rich solvent, and a stripper reflux ratio of 1.5 moles steam per mole acid gas. Figure 15 summarizes the results.

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## NATURAL GAS SWEETENING PLANT

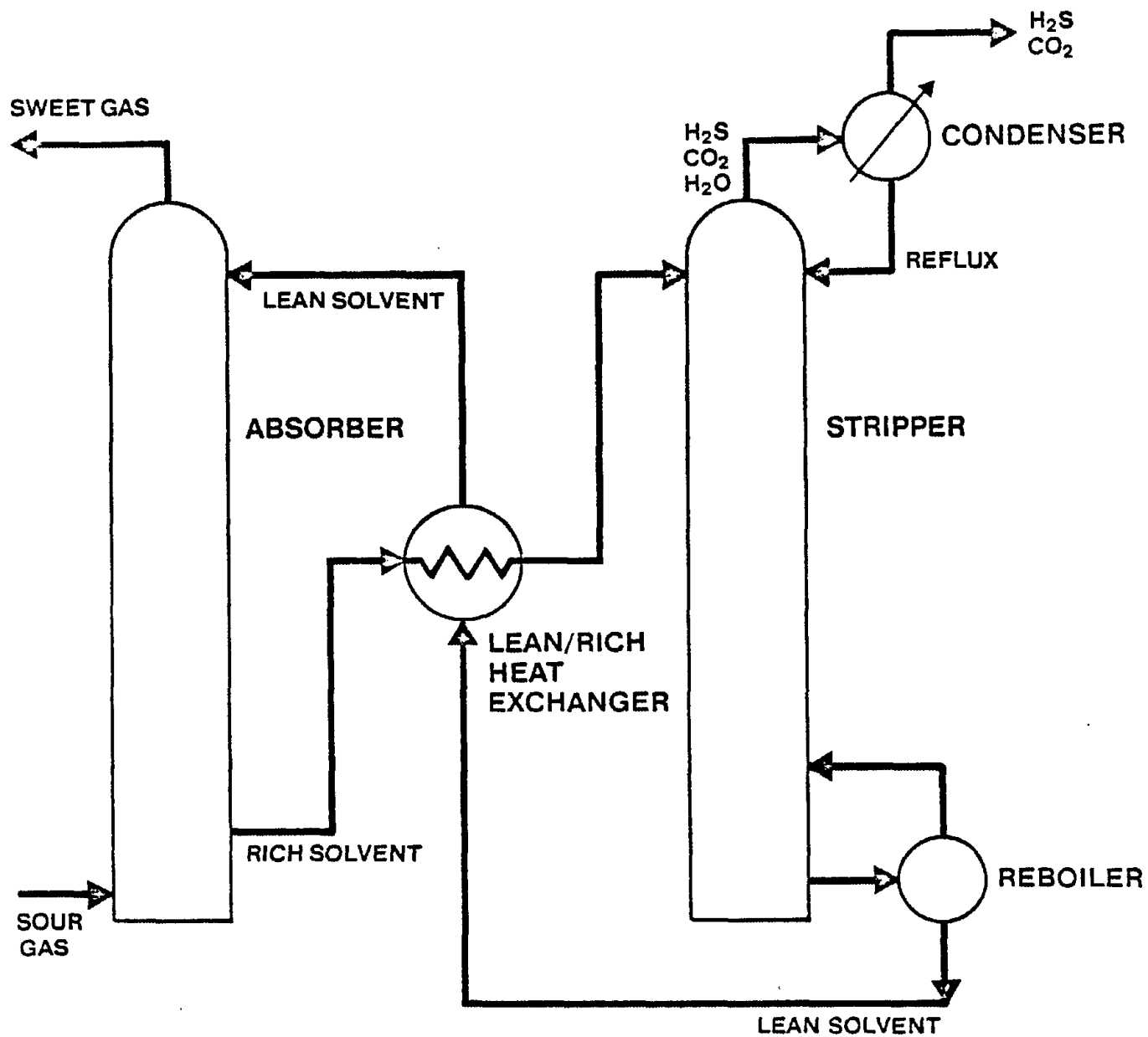


Figure 1. Simplified amine gas sweetening process flow diagram

# NATURAL GAS SWEETENING PLANT

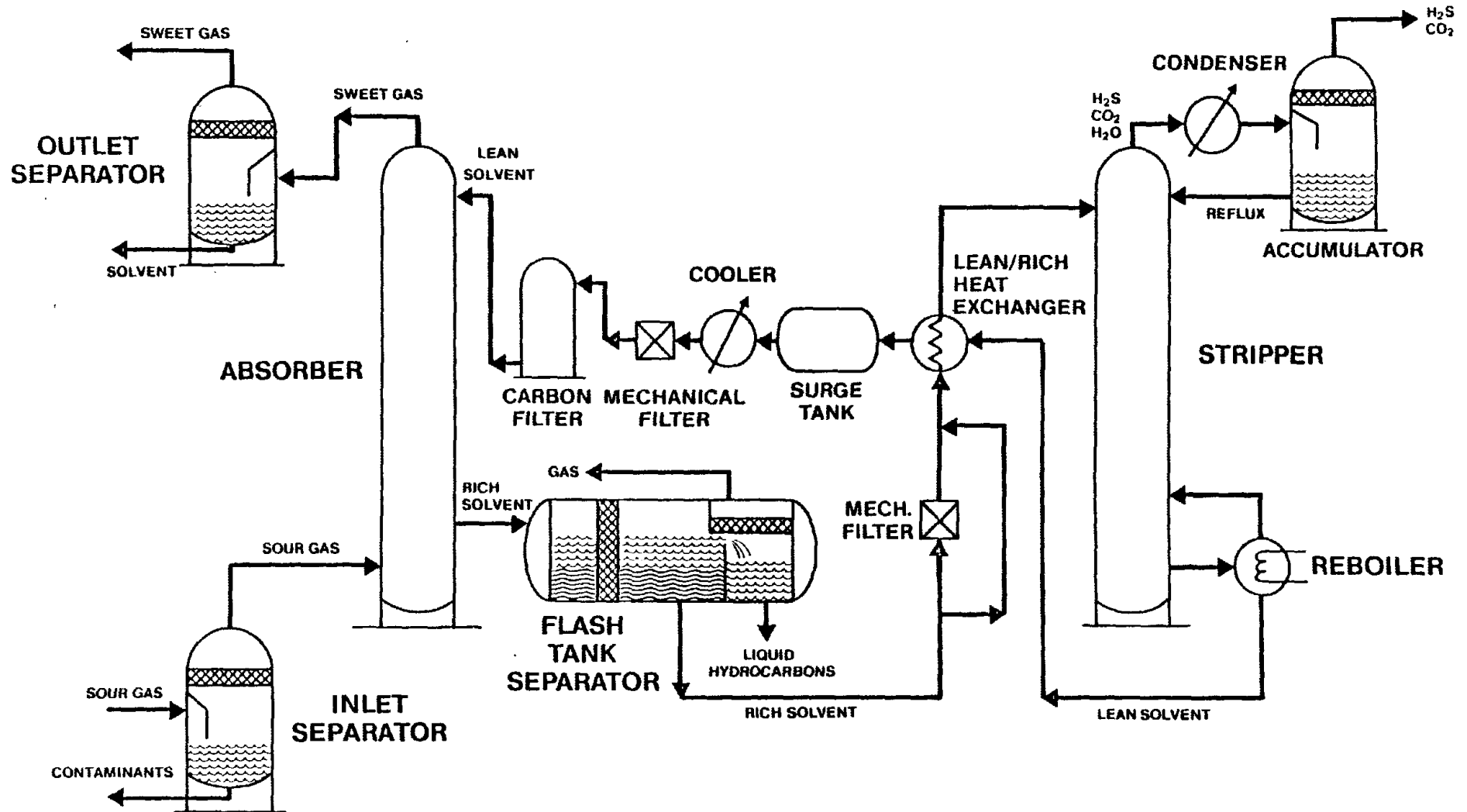


Figure 2.

## TRAY TOWER ABSORBER

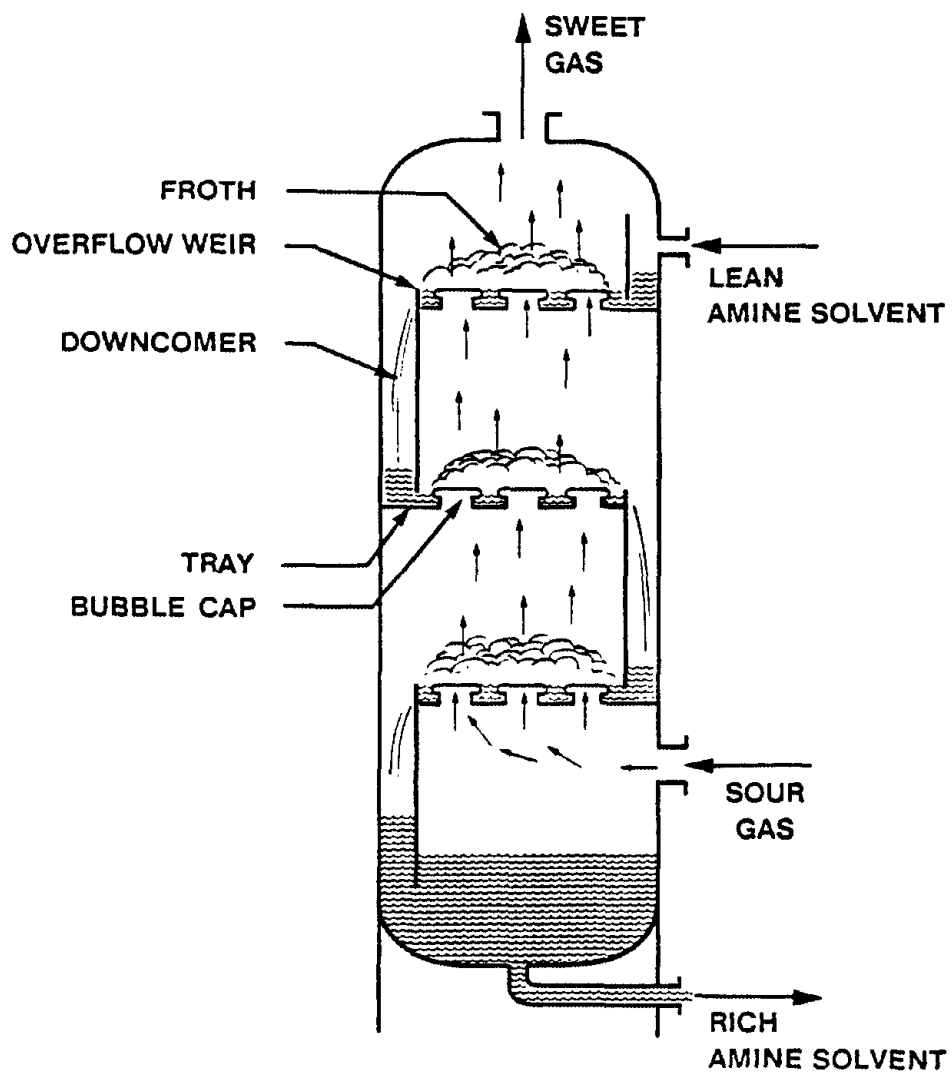
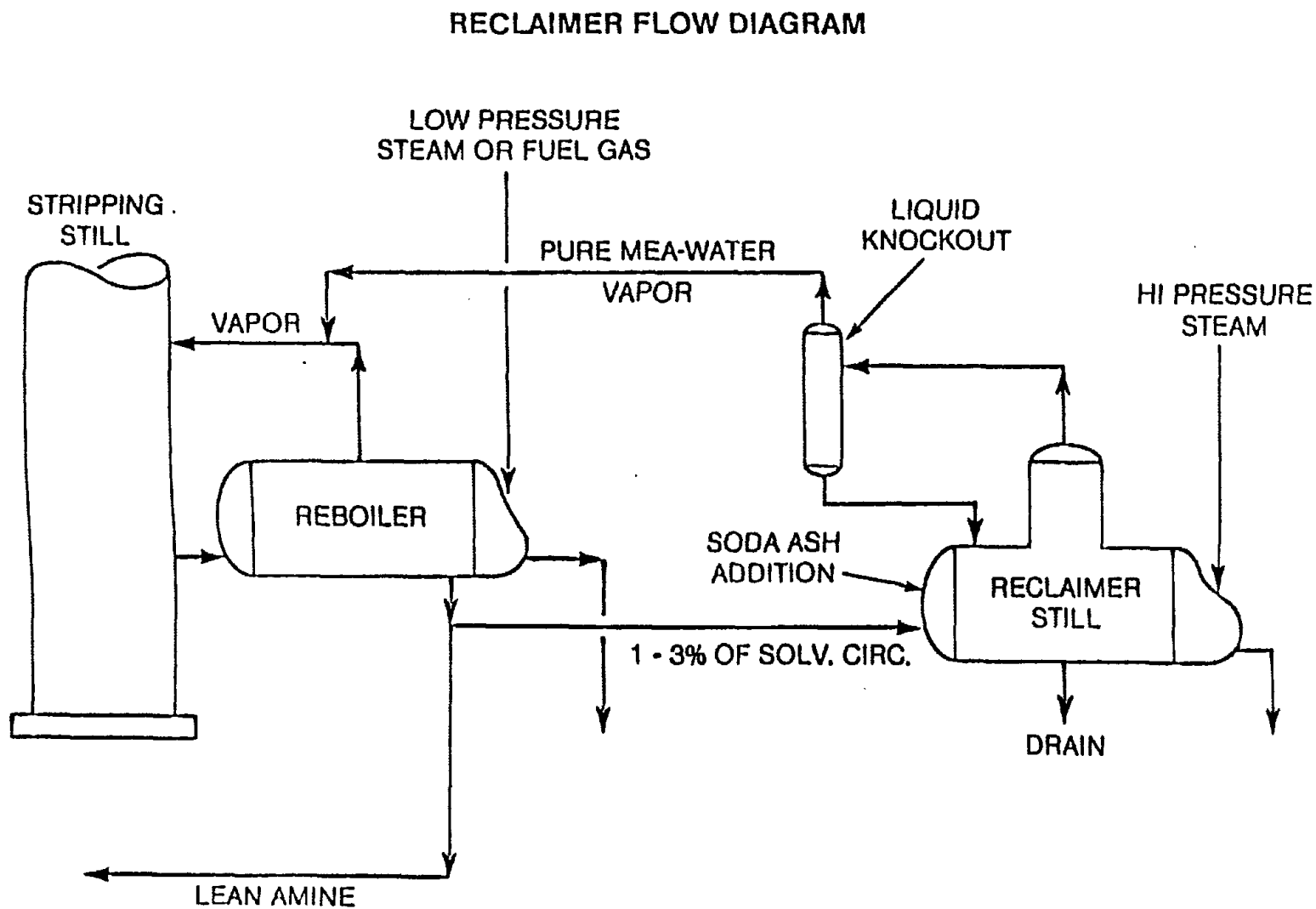


Figure 3.

Figure 4.



**SOLUBILITY OF MIXTURES OF H<sub>2</sub>S AND CO<sub>2</sub>  
IN 35% DEA AT 50°C**

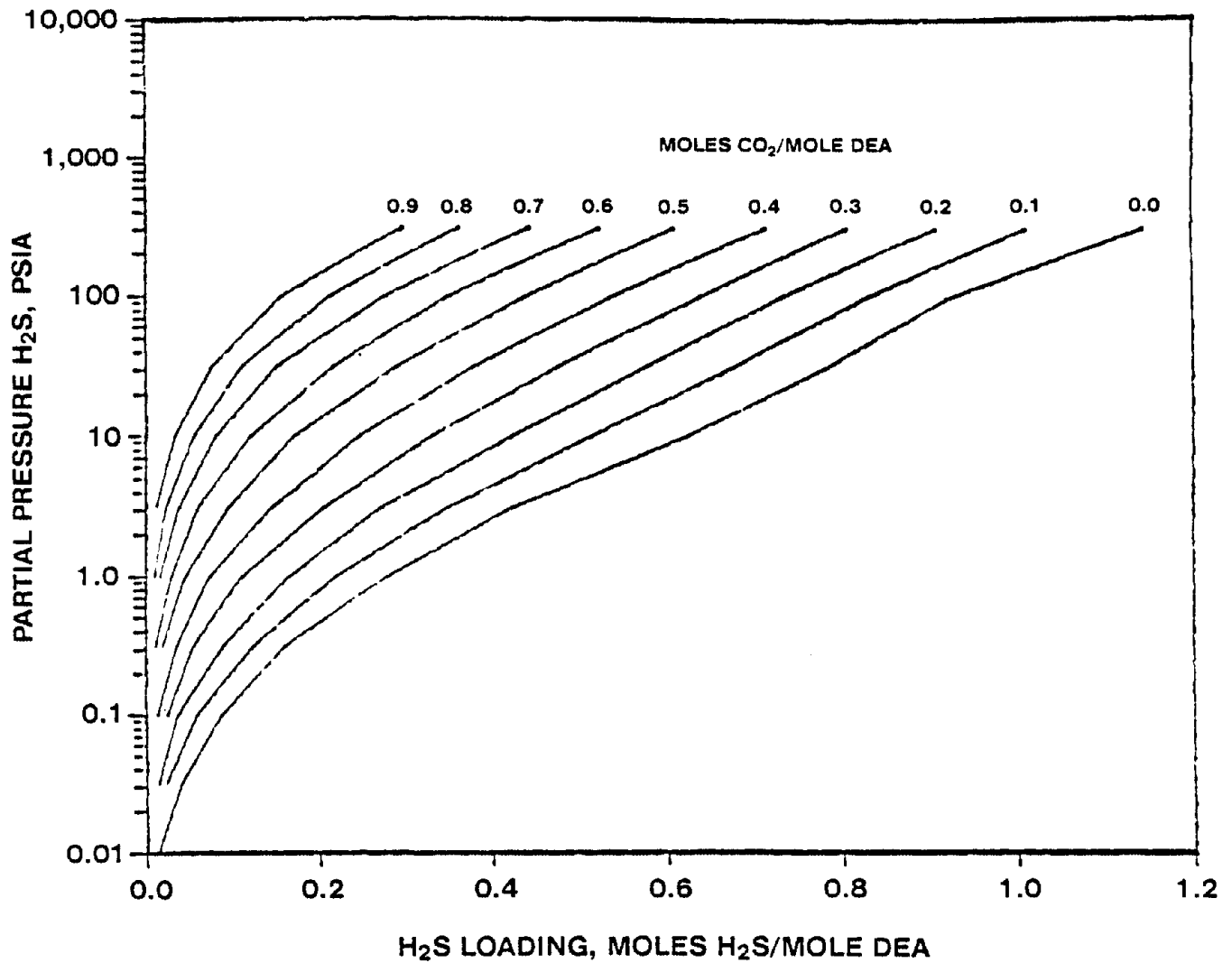


Figure 5.

Source: Lee, Otto, Mather (10)



**SOLUBILITY OF MIXTURES OF H<sub>2</sub>S AND CO<sub>2</sub>  
IN 35% DEA AT 50°C**

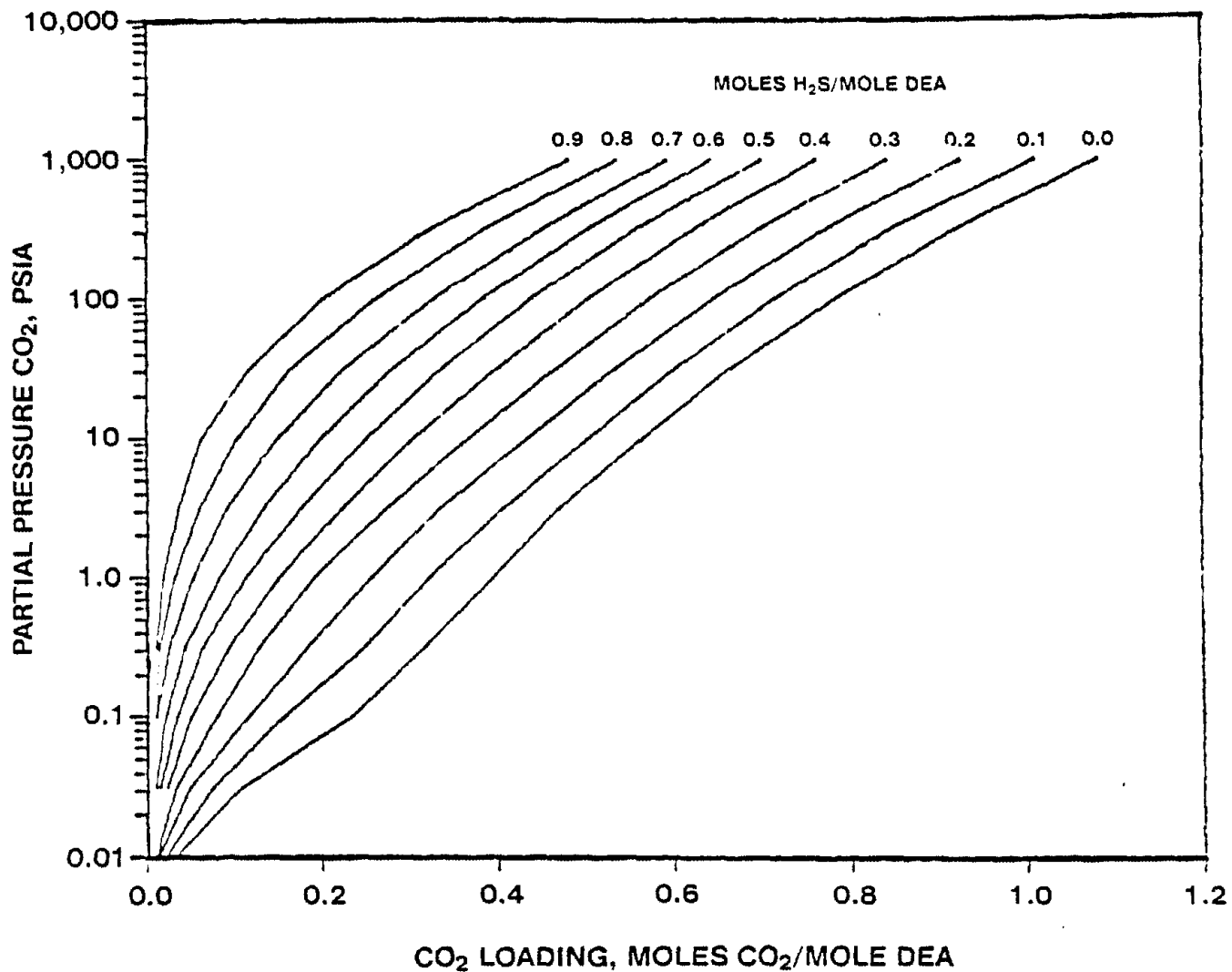


Figure 6.

Source: Lee, Otto, Mather (10)

**SOLUBILITY OF MIXTURES OF  $H_2S$  AND  $CO_2$   
IN 35% DEA AT 100°C**

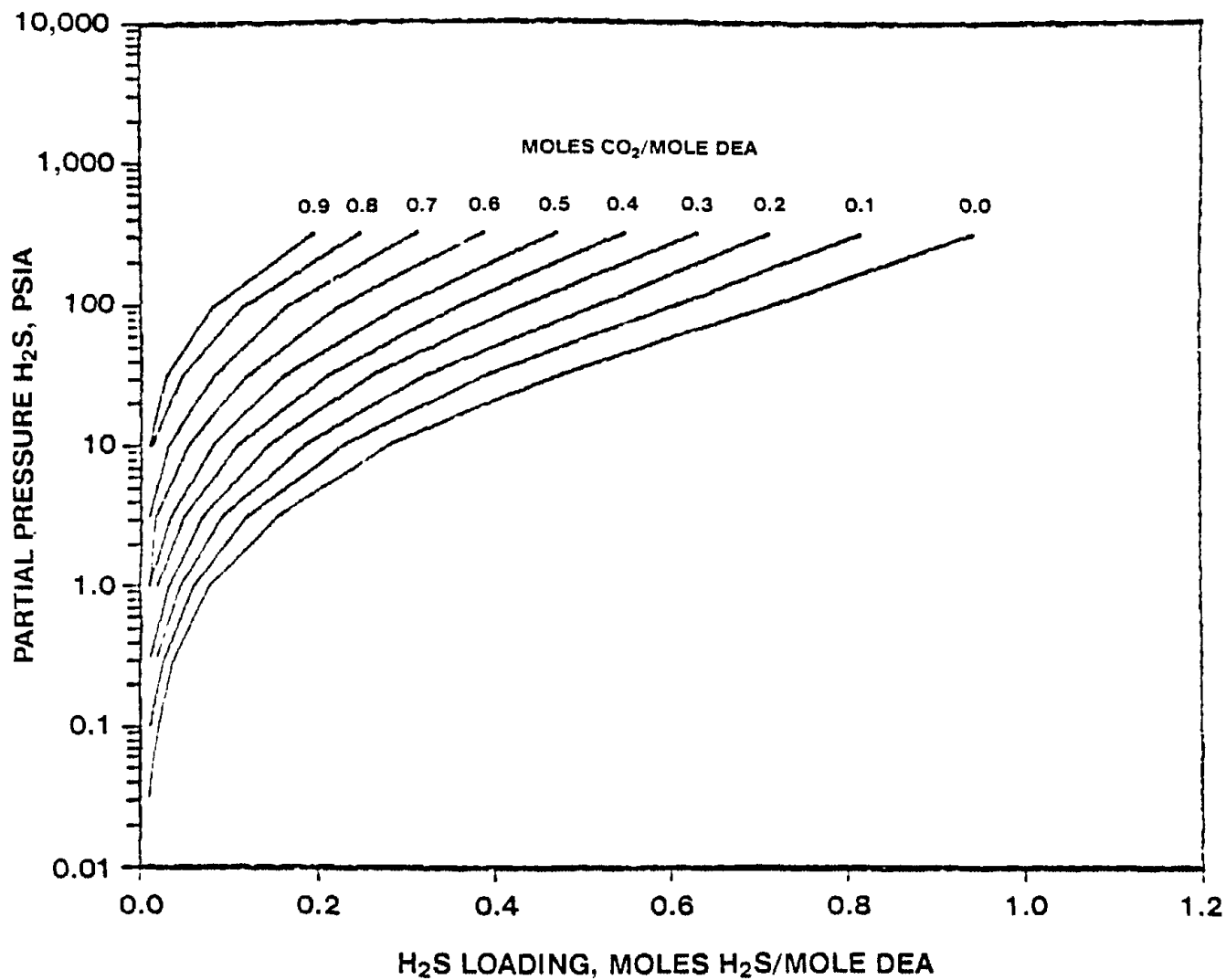


Figure 7.

Source: Lee, Otto, Mather (10)

**SOLUBILITY OF MIXTURES OF H<sub>2</sub>S AND CO<sub>2</sub>  
IN 35% DEA AT 100°C**

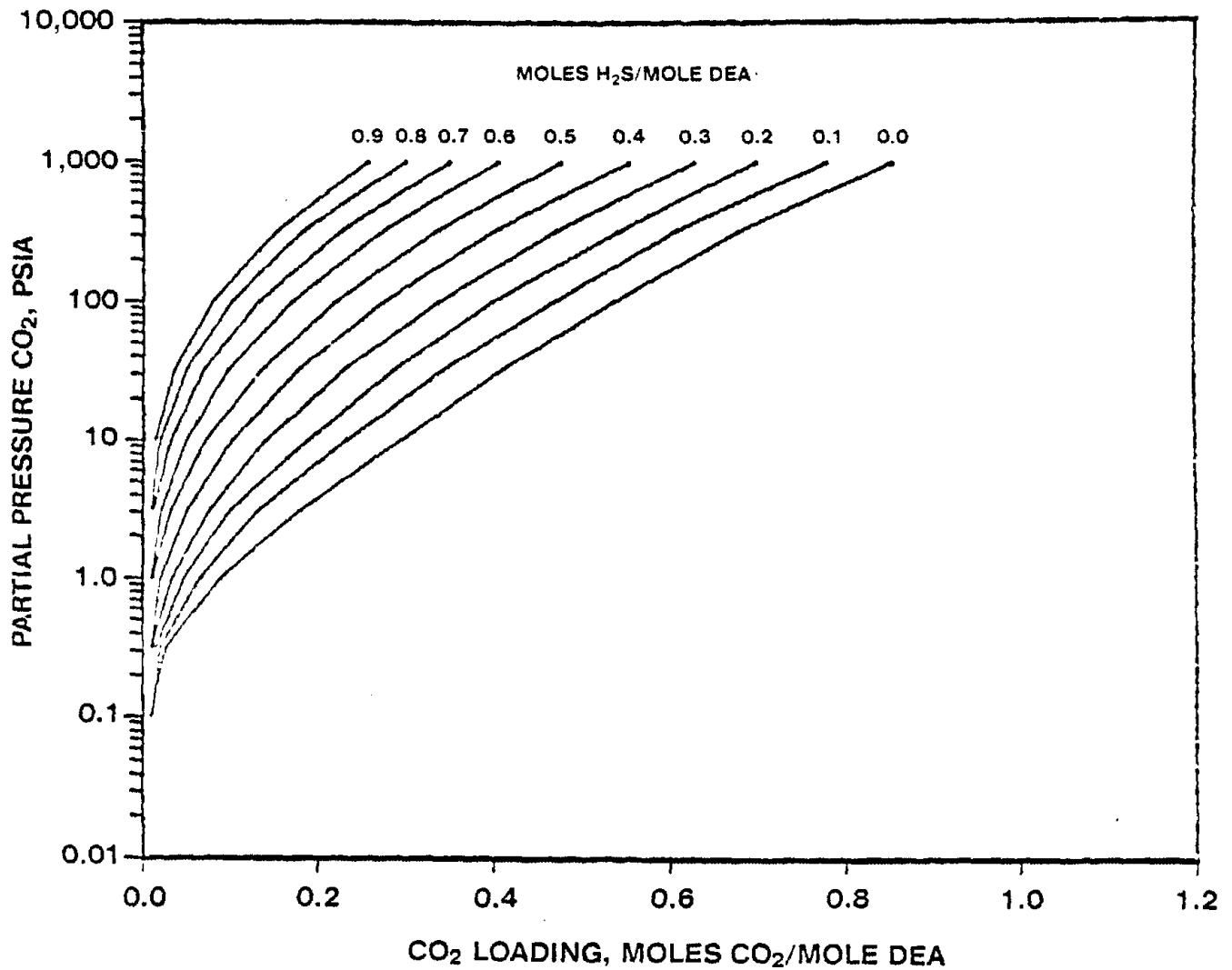


Figure 8.

Source: Lee, Otto, Mather (10)

# Weight Per Gallon of Aqueous Diethanolamine Solutions at Various Temperatures

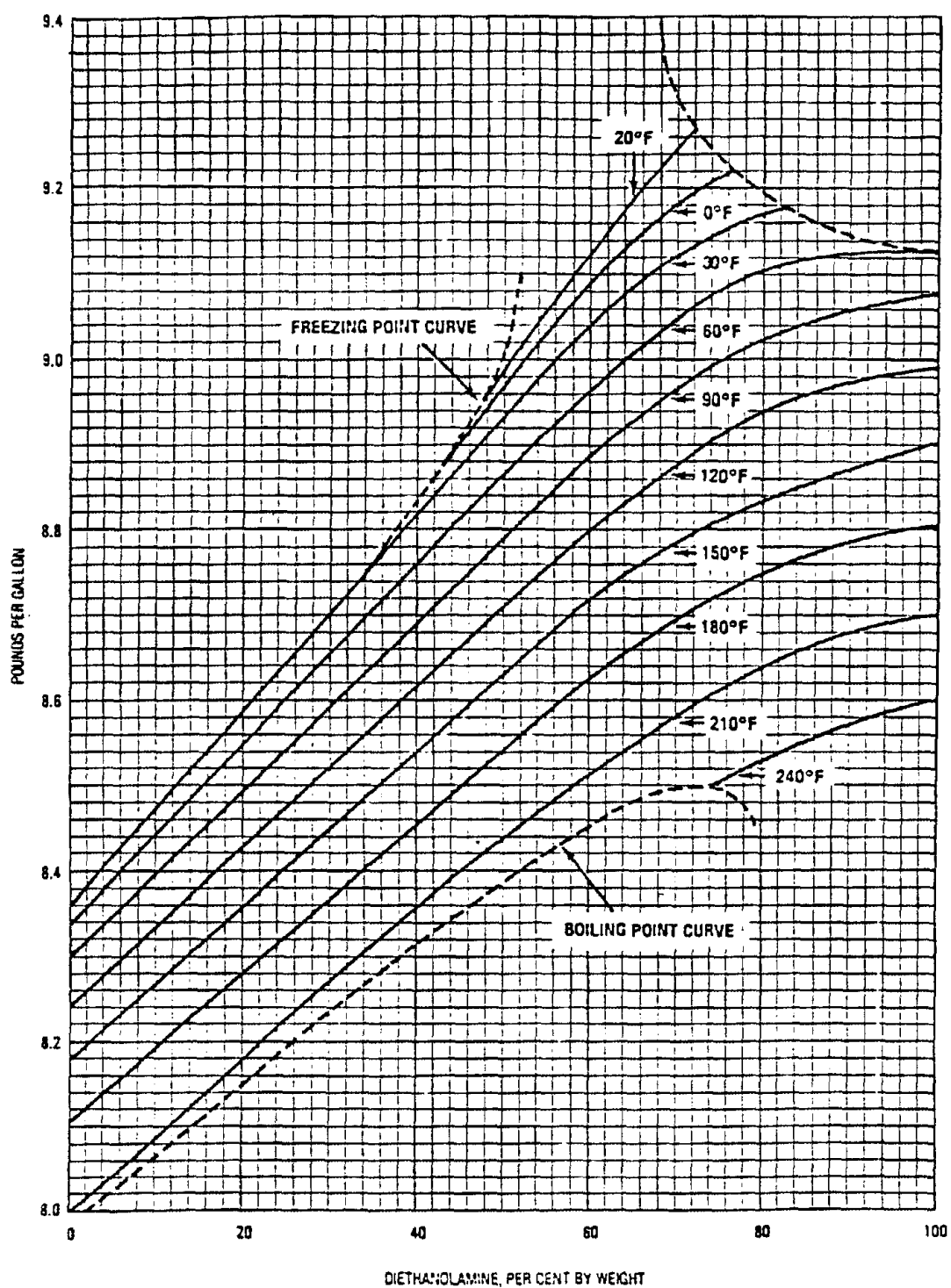


Figure 9.

# Specific Heats of Aqueous Diethanolamine Solutions

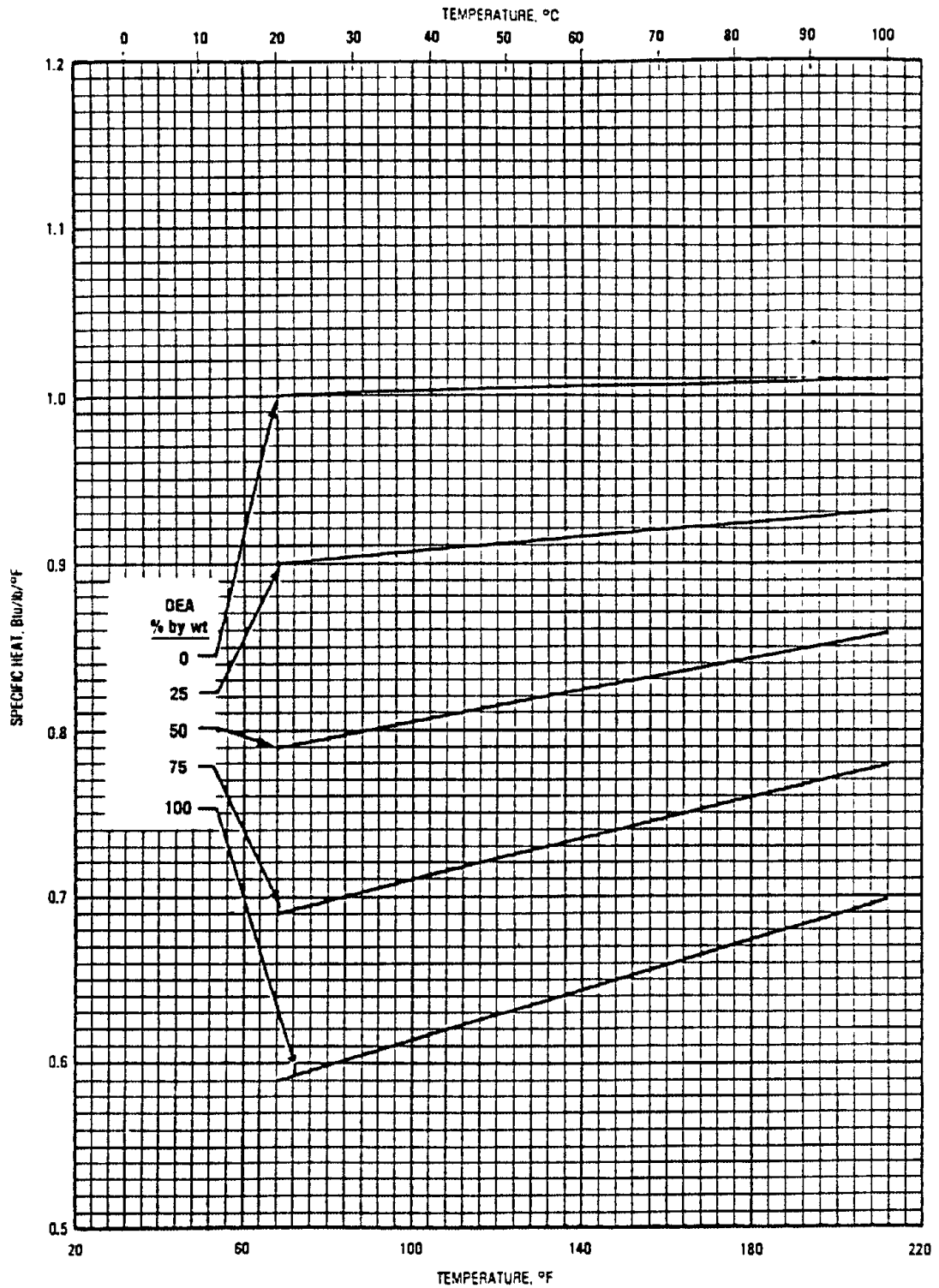
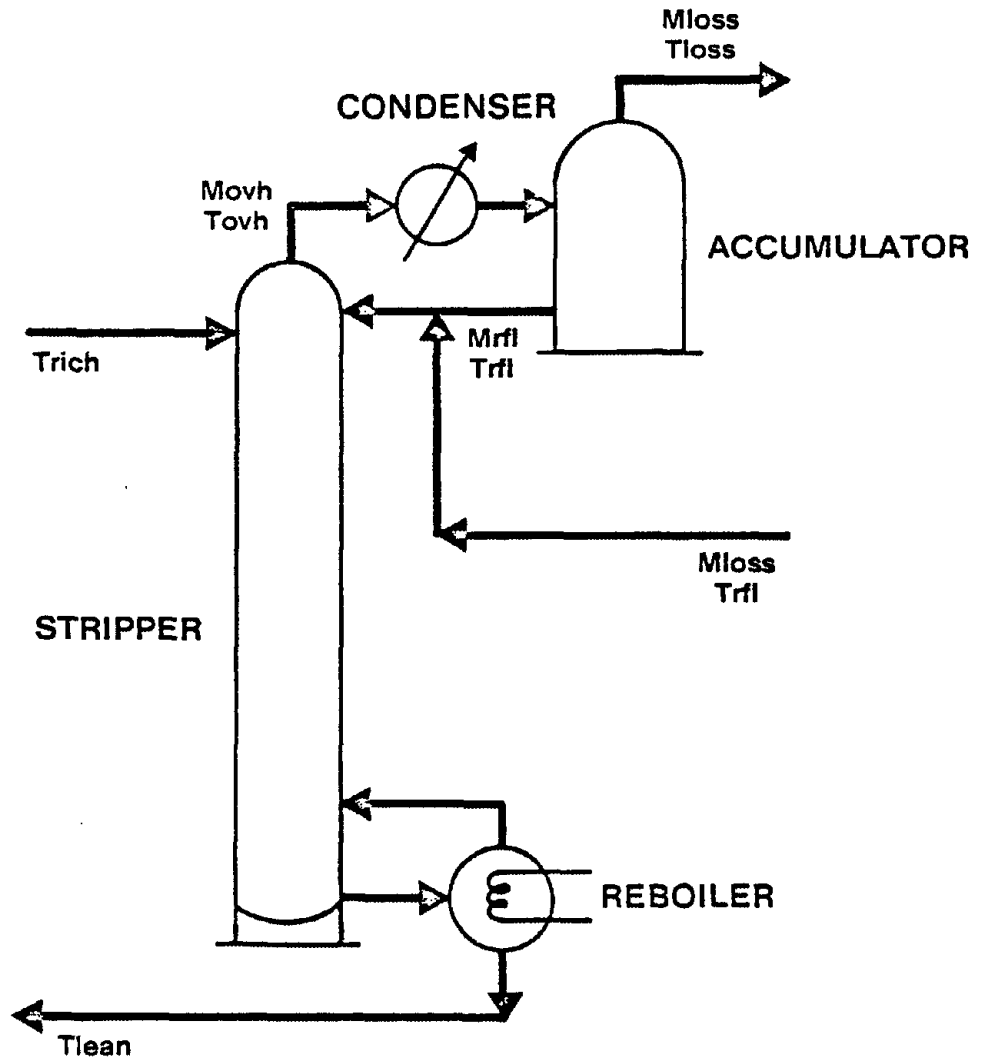


Figure 10.

# AMINE REGENERATOR



Movh, Mloss, Mrfl = mass flow rate of water  
 Trich, Tovh, Tloss, Trfl, Tlean = stream temperatures

Figure 11.

# Surface Tensions of Aqueous Diethanolamine Solutions from 75 to 125° Fahrenheit

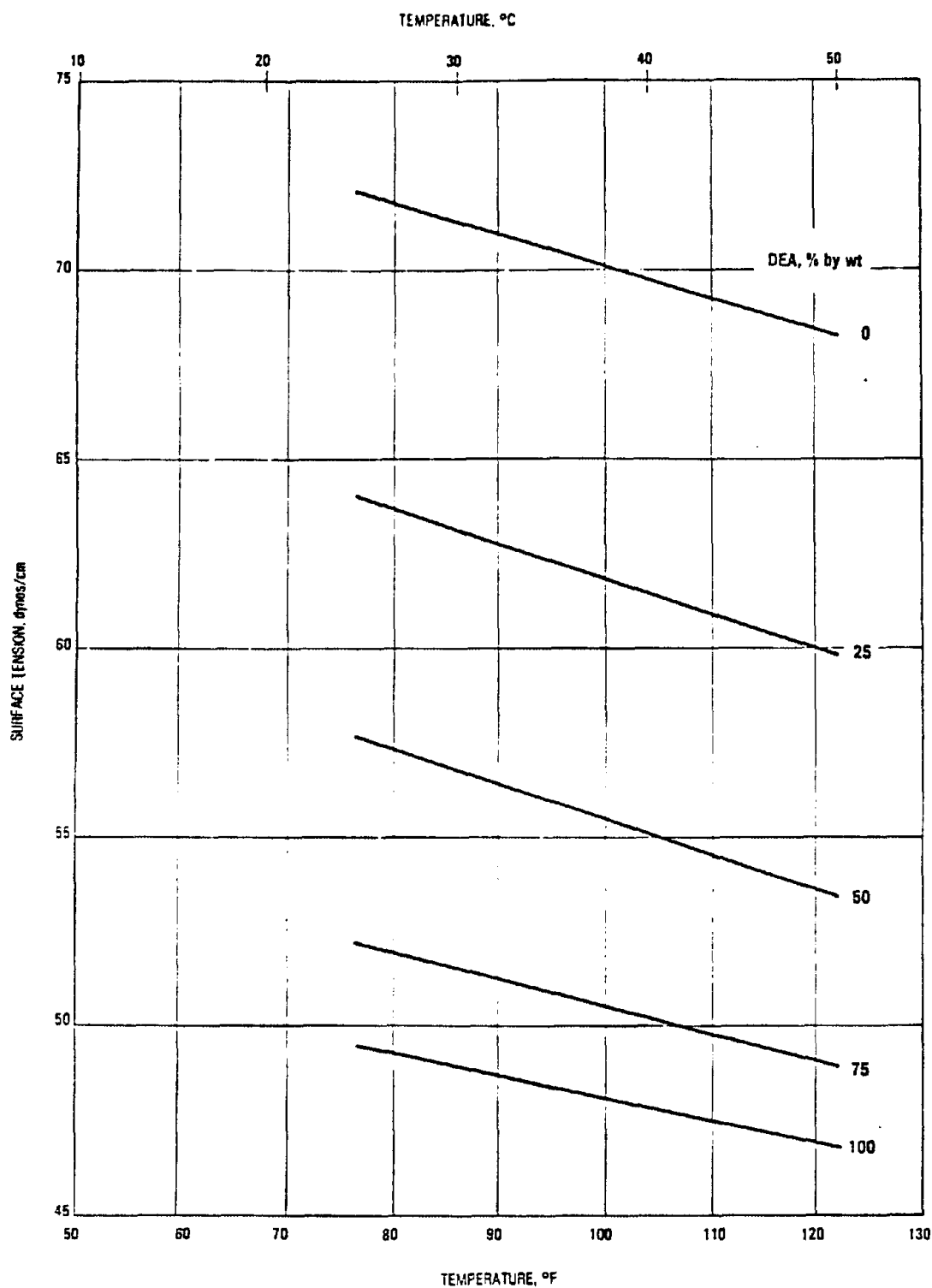


Figure 12.

# AMINE PLANT DESIGN CASES

* DESIGN CONDITIONS *						* DESIGN RESULTS *				
CASE	GAS FLOW MMSCFD	PRESSURE PSIA	CO <sub>2</sub> MOLE %	H <sub>2</sub> S MOLE %	AMINE WEIGHT %	CIRC. RATE GPM	RICH LOADING	REBOILER HEAT DUTY	ABSORBER DIAMETER FT	STRIPPER DIAMETER FT
							<u>MOLE ACID GAS</u> <u>MOLE AMINE</u>	MMBTU/HR		
1	100	1000	4.5	0.5	30 % DEA	751	0.5	37.8	6.3	7.4
2	100	1000	2.25	0.25	30 % DEA	398	0.46	19.0	6.2	5.3
3	50	1000	4.5	0.5	30 % DEA	376	0.5	18.9	4.4	5.2
4	100	500	4.5	0.5	30 % DEA	839	0.45	39.2	7.4	7.6
5	100	250	4.5	0.5	30 % DEA	949	0.40	40.7	8.8	7.7
6	100	1000	4.5	0.5	15 % DEA	933	0.55	41.7	6.3	7.8
7	100	250	4.5	0.5	15 % DEA	1119	0.47	44.2	8.8	8.1

FIGURE 13