18

GLYCOL DEHYDRATION

A number of liquids possess the ability to absorb water from gas. Yet, there are very few which meet the criteria for a suitable commercial process: are highly hygroscopic, do no solidify in a concentrated solution, are noncorrosive, do not form precipitates with gas constituents, are easily regenerated to a high concentration, can be separated easily, are essentially nonsoluble in liquid hydrocarbons, and are relatively stable in the presence of sulfur compounds and carbon dioxide under normal operating conditions.

Several of the glycols come the closest to meeting all of these criteria. Diethylene (DEG), triethylene (TEG) and tetraethylene (TREG) glycols all possess suitable traits. However, almost 100% of the glycol dehydrators use TEG.

DEG is somewhat cheaper to buy and sometimes is used for this reason. But, by the time it is handled and added to the units there is no real saving. Compared to TEG, DEG has a larger carry-over loss, offers less dewpoint depression and regeneration to high concentrations is more difficult. For these reasons, it is difficult to justify a DEG unit, although a few are built each year.

TREG is more viscous and more expensive than the other processes. The only real advantage is its lower vapor pressure which reduces absorber carry-over loss. It may be used in those relatively rare cases where glycol dehydration will be employed on a gas whose temperature exceeds about 50°C [122°F].

This chapter will concentrate on TEG, even though property data are shown in Appendix 18A for the several glycols. Some of the system characteristics apply also for all glycols.

THE BASIC GLYCOL DEHYDRATION UNIT

Figure 18.1 shows the basic glycol unit, regardless of the glycol used. Not shown is a full size separator ahead of the absorber, an essential piece of equipment. Also not shown is any cooling equipment that may be a part of the dehydration processes. When it is possible to cool the entering wet gas with air or suitable water ahead of the absorber, do so. Such cooling is the least expensive form of dehydration.

The entering wet (rich) gas, free of liquid water, enters the bottom of the absorber (contactor) and flows countercurrent to the glycol. Glycol-gas contact occurs on trays or packing. Bubble cap trays have been used historically but structured packing is more common today. The dried (lean) gas leaves the top of the absorber.

The lean glycol enters on the top tray or at the top of the packing and flows downward, absorbing water as it goes. It leaves rich in water.

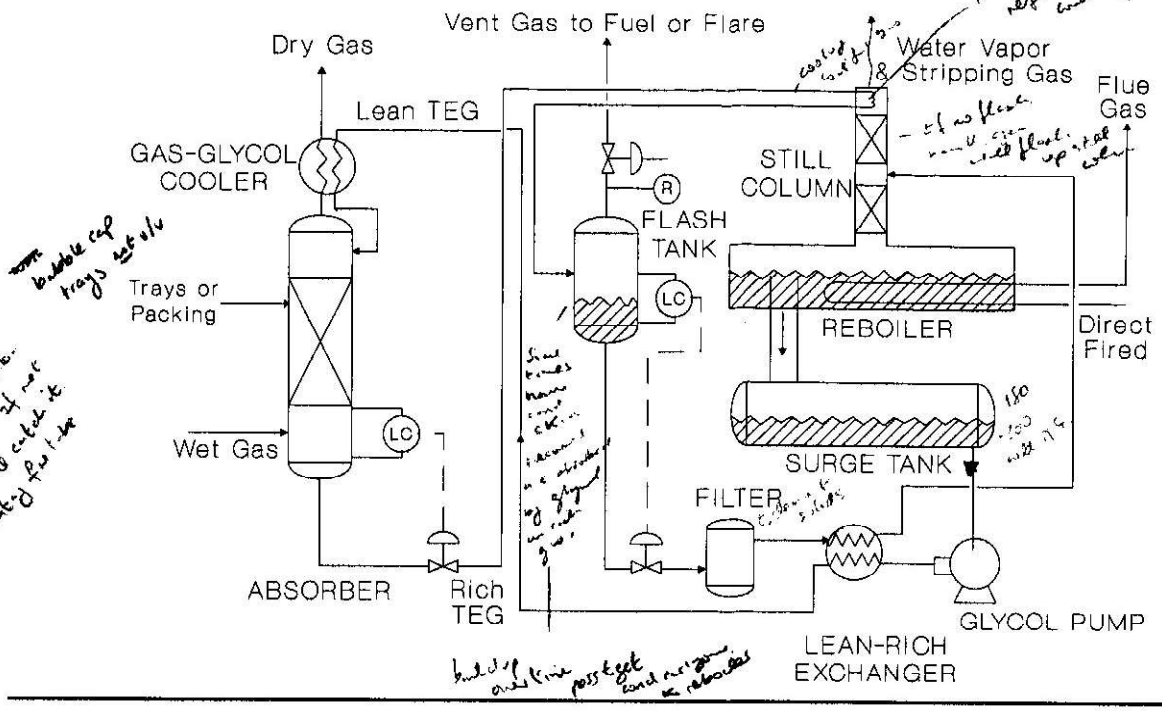


Figure 18.1 Basic Glycol Dehydration Unit

It is convenient to use the word "rich" to describe the bottom of the absorber and the word "lean" for the top. At the bottom, both the entering gas and glycol leaving are rich in water; at the top end they both are lean in water.

The rich glycol leaves the bottom of the absorber and flows to a reflux condenser at the top of the still column. The rich glycol then enters a flash tank where most of the volatile components (entrained and soluble) are vaporized. Flash tank pressures are typically 300-700 kPa [44-102 psia]. Leaving the flash tank the rich glycol flows through the glycol filters and the rich-lean exchanger where it exchanges heat with the hot lean glycol. The rich glycol then enters the still column where the water is removed by distillation.

The still column and reboiler are often called the regenerator or reconcentrator. This is where the glycol concentration is increased to the lean glycol requirement.

The regeneration unit shown is designed to operate at prevailing atmospheric pressure. The initial thermal decomposition temperatures of the glycols are

Glycol	Temperature
EG	165°C, 329°F
DEG	164°C, 328°F
TEG	206°C, 404°F
TREG	238°C, 460°F

These are the temperatures at which measurable decomposition begins to occur in the presence of air. DEG is no more stable than EG because it pyrolyzes in contact with carbon steel.

In the normal unit containing no air (oxygen), it has been found that one can operate the reboiler very close to the above temperatures without noticeable decomposition. So, they fix the composition of the lean glycol which leaves at its bubblepoint.

At the pressures involved, Raoult's Law applies:

$$x_w = \left(\frac{P}{P_v}\right)(y_w) \qquad (18.1)$$

Where: x_w = mol fr water in lean glycol
P = system pressure
P_v = water vapor pressure at reboiler temperature
y_w = mol fr water in the reboiler vapor (in equilibrium with x_w)

Once one has used the highest allowable temperature (to maximize vapor pressure, P_v), "P" and/or "y" must be lowered in value if lower water concentrations are needed. A vacuum pump or ejector may be used to lower pressure.

The addition of some other vapor to the reboiler will decrease the "y" for water. As shown in Figure 18.2(a), this may be accomplished with stripping gas. Any inert gas is suitable. A part of the gas being dehydrated, or exhaust from a gas-powered glycol pump (if used), is suitable. The quantity required is small. In theory, adding gas to a packed unit between the reboiler and surge tank is superior and will result in lower stripping gas rates. In commercial units it makes little difference how you get the gas into the reboiler so long as the quantity is right. It is common to use a distributor pipe along the bottom of the reboiler.

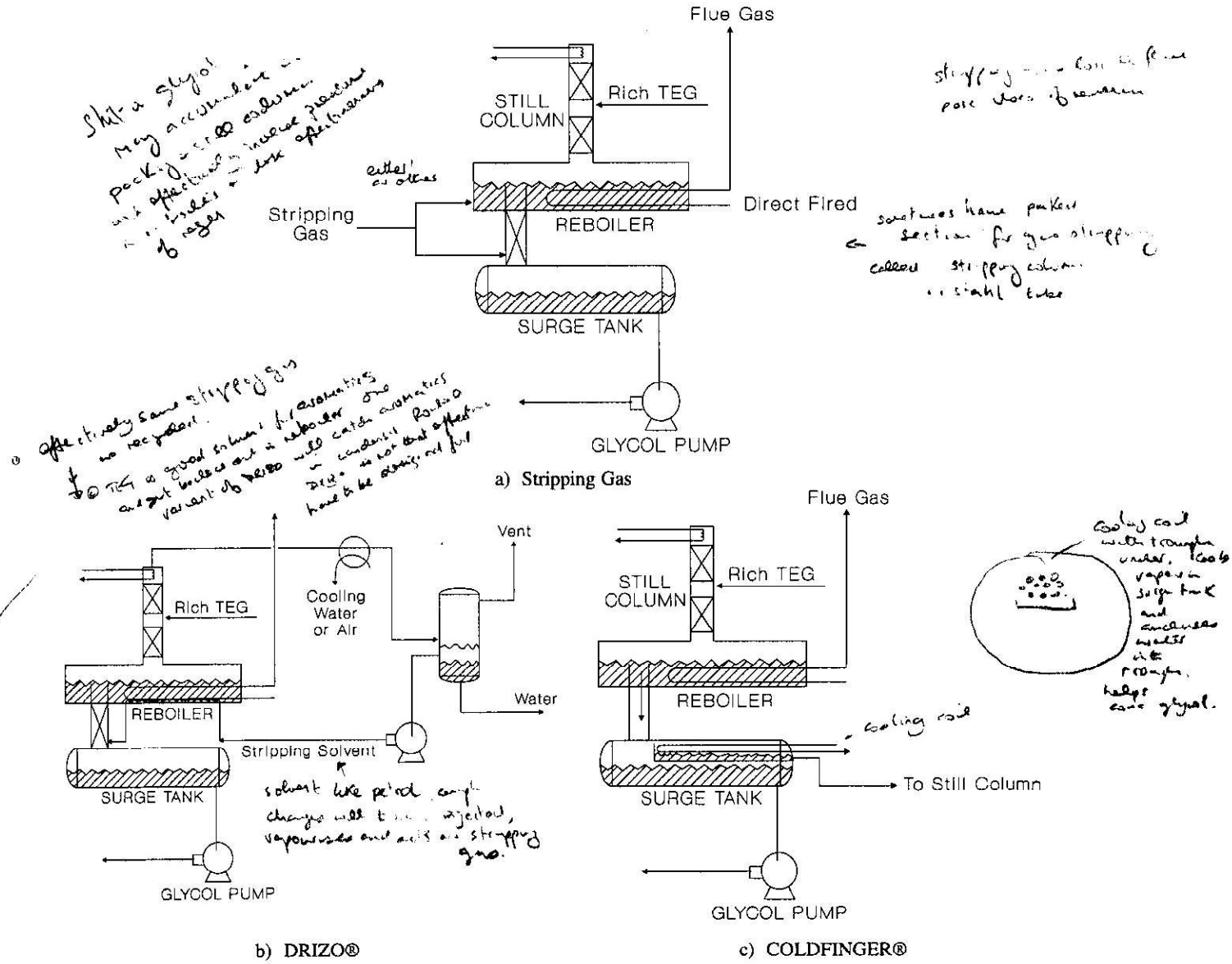


Figure 18.2 TEG Regeneration Alternatives

A second stripping gas alternative is close the stripping gas loop and use a material like iso-octane to the unit, as shown in Figure 18.2(b). It vaporizes at reboiler temperature but can be condensed and separated from the water in a 3-phase separator. The stripping solvent is then pumped back to the regenerator to complete the stripping loop. Sold under the trade name DRIZO®, this unit has the advantage of providing very high stripping gas rates with little or no venting of hydrocarbons. Glycol concentrations in excess of 99.99 wt% have been achieved with the DRIZO process. It has an added advantage of condensing and recovering aromatic hydrocarbons from the still column overhead. In fact, these units often operate with a stripping solvent which is not iso-octane but a mixture of aromatic, naphthenic and paraffin hydrocarbons in the C_5-C_8 range.

Figure 18.2(c) shows a third regenerator alternative called a COLDFINGER®. The COLDFINGER process achieves glycol enrichment by passing rich TEG through a cool "finger" inserted in the surge tank vapor space. This condenses a water-TEG mixture which is very rich in water. This mixture is drawn out of the surge tank by means of a trough below the "coldfinger" and is recycled back to the regenerator. The H_2O partial pressure in the vapor space is thus lowered and the lean glycol concentration increased. Lean TEG concentrations of 99.9 wt% have been achieved in COLDFINGER units without the use of stripping gas.

The unit shown in Figure 18.1 is typical. Figure 18.3 shows examples of two systems using TEG that incorporate additional features.

The upper flow sheet is for an offshore unit. The inlet scrubber is in the bottom of the absorber. Three-phase separation is required. The gas rises through a "chimney tray" to the absorber. The hydrocarbon and water are separated as shown. Three-phase separation saves on deck space and is less expensive, but many of the existing units are unsatisfactory because they provide inadequate separation.

The rich TEG from the chimney tray goes to a degassing pot (flash tank) which is operated at a high enough pressure to send the gas to fuel. In some systems the pressure is sufficient merely to enter the main flare system. The purpose of this is several fold: (1) use or dispose safely any volatile components picked up by the TEG in the absorber, and (2) minimize the presence of corrosive sulfur compounds and carbon dioxide in the high temperature reboiler.

The true solubility of paraffin hydrocarbons is very low in the glycols. But, separator carryover and entrainment does introduce hydrocarbons into the rich glycol. Many of these are "heavier" than air and can be a safety problem unless disposed of properly. In addition, aromatic components are very soluble in TEG. These can also be a safety concern when discharged to atmosphere at the top of the still column.

Both sulfur compounds and carbon dioxide are very soluble in water and react to some degree with the glycols. The degassing in the flash tank prior to the stripping column reduces their concentration and minimizes high temperature corrosion. This degassing is more efficient if the rich glycol is preheated first, as shown in the lower flow sheet in Figure 18.3.

External gas-TEG exchange is shown in the upper flow sheet, as opposed to external cooling in the lower one. Offshore it is suitable to use sea water cooling in plate exchangers, provided treated sea water is available for other purposes. In temperate latitudes aerial cooling also is a viable alternative.

An external glycol-glycol exchanger of the type shown in the lower flow sheet would be preferred if fuel is expensive. The closest economic temperature approach possible reduces reboiler heat load. Plate exchangers are widely used in this service.

Both flow sheets show a fired reboiler. The use of hot oil, steam, waste heat or electrical resistance coils are all suitable if they are readily available at the site. Oftentimes the use of electrical resistance offshore is cost-effective and safe.

No filter is shown on the upper flow sheet. It is on the low pressure side of the flash tank in the lower one. Location, pressure-wise, obviously affects cost. I prefer locating the filter at some point ahead of the

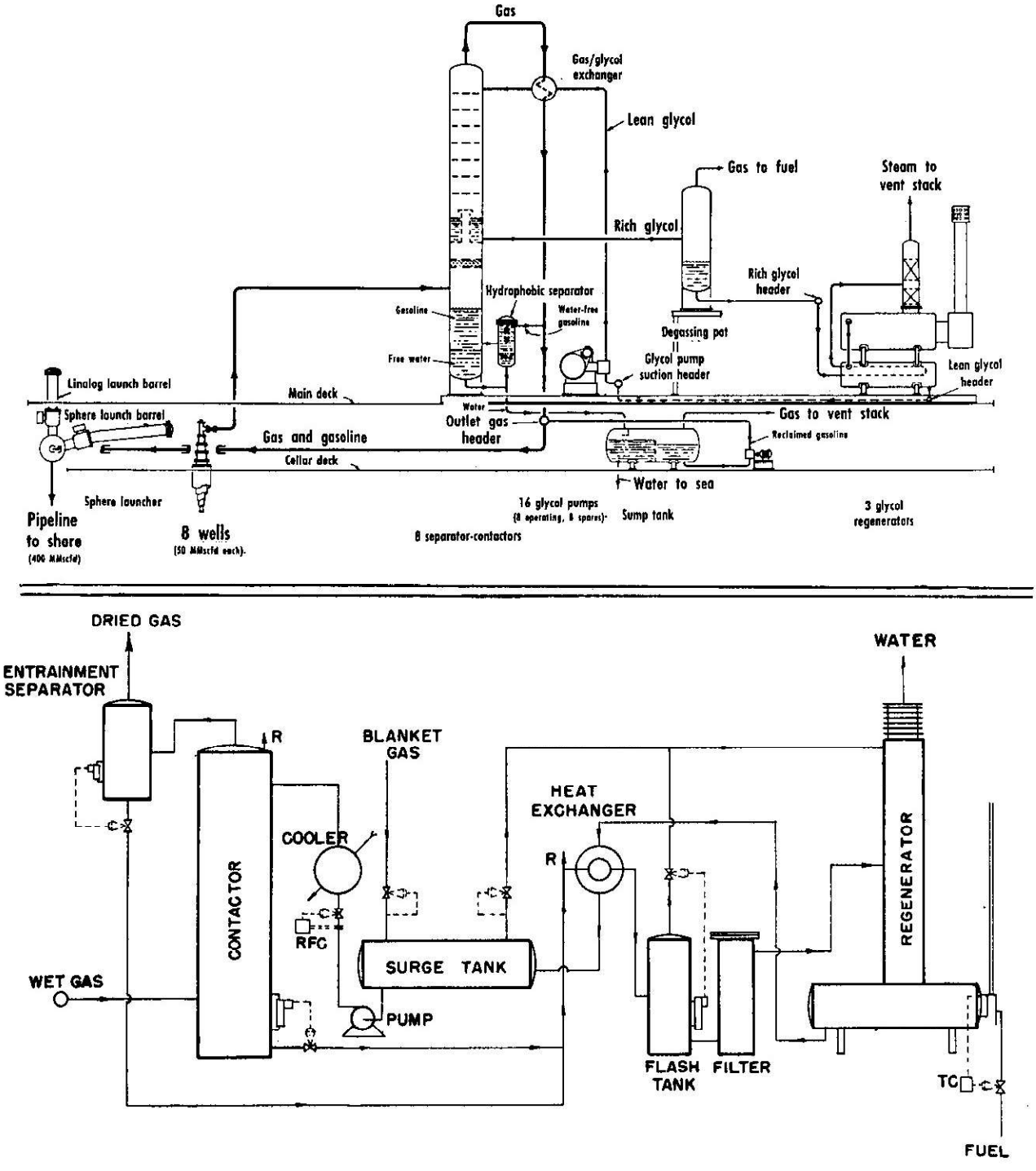


Figure 18.3 Flow Sheets for Two Different TEG Dehydration Systems

reboiler to minimize the "gunk" accumulating therein. For effective operation it is imperative that full-flow, glycol filters be installed in the system.

BASIC PROCESS DESIGN FACTORS

All factors controlling the behavior of absorption systems also apply for TEG dehydration. In fact, from a process viewpoint, TEG is one of the simpler absorption processes being employed in the petroleum industry.

In order to properly design a unit one needs to know maximum gas flow rate, maximum temperature and pressure, gas composition and required water dewpoint or content of the outlet gas. From these one can calculate:

1. The *minimum concentration* of TEG in the lean solution entering the top of the absorber required to meet outlet gas water specification.
2. The lean TEG circulation rate required to pick up from the gas needed amount of water necessary to meet the outlet gas water content specification.
3. The amount of absorber contact required to produce the necessary approach to equilibrium required in (1) above at the chosen circulation rate.

To obtain these answers it is necessary to have a vapor-liquid equilibrium correlation for a TEG-water system. From this basic input, one can size equipment and develop mechanical specifications.

The procedure that follows is very straightforward and can be performed manually. In all but a few exceptional applications, it will give results as reliable as more complex (appearing) methods. Following an outline of the basic calculation procedure, each major equipment component will be reviewed.

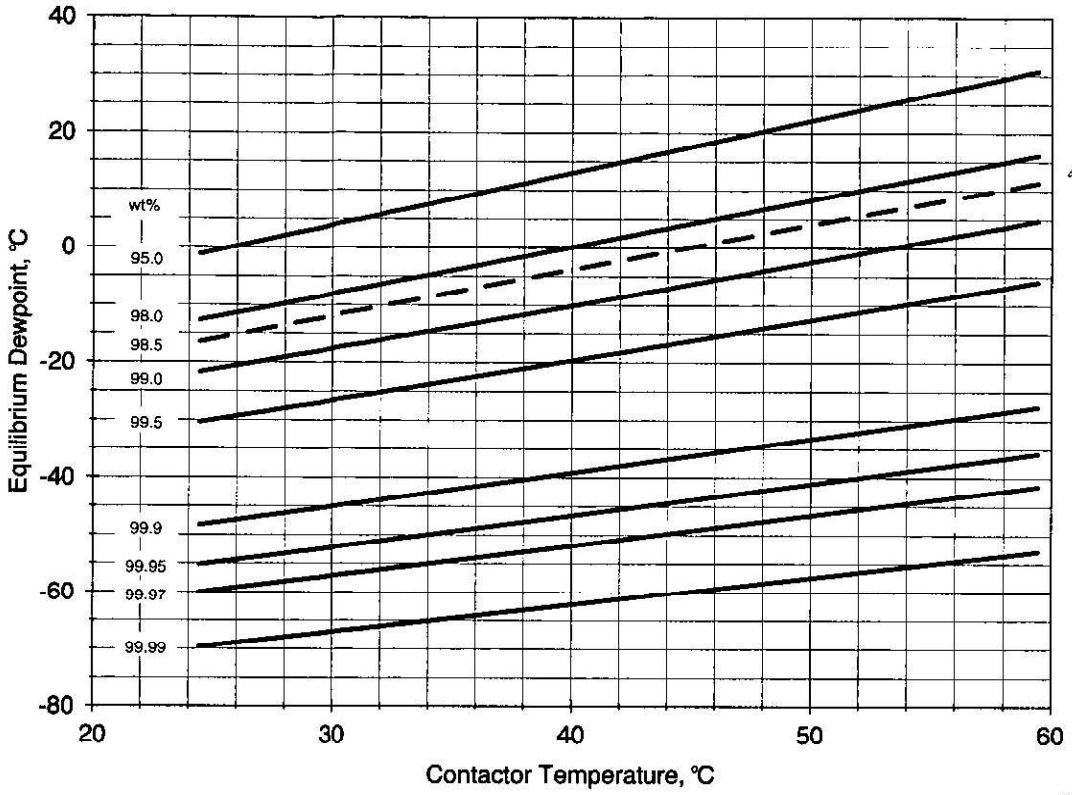
MINIMUM LEAN TEG CONCENTRATION

If water-saturated gas is placed in a static cell with a given concentration of TEG-water solution at a fixed P and T, equilibrium would be attained in time. Assuming the liquid had a sufficiently lower water concentration, water would transfer to this liquid from the gas. At equilibrium, the mol fraction water in the gas divided by its mol fraction in the liquid equals the K value for this system.

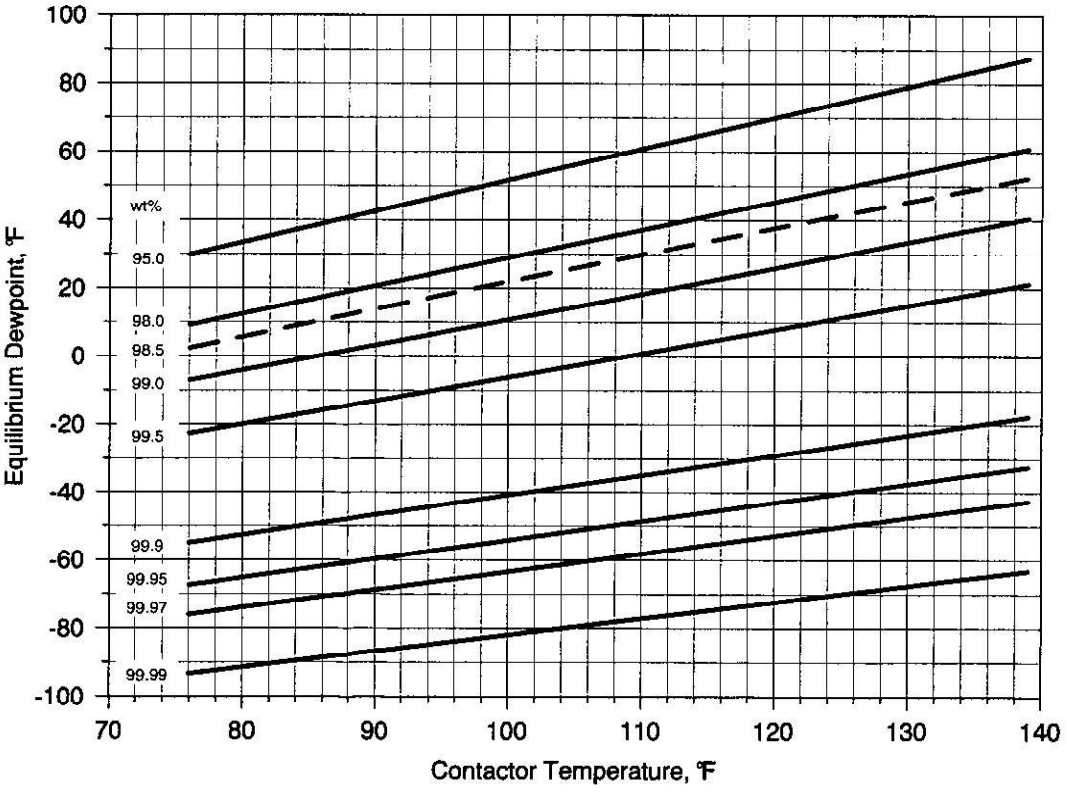
Figures 18.4(a) and 18.4(b) are based on equilibrium data published by Parrish, et. al.[18.7] Several equilibrium correlations[18.1,18.3-18.5,18.7] have been presented since 1950. Previous editions of this book presented an equilibrium correlation based on the work of Worley[18.1]. In general, the correlations of Worley[18.1], Rosman[18.5] and Parrish[18.7] agree reasonably well and are adequate for most TEG system designs. All are limited by the ability to measure accurately the equilibrium concentration of water in the vapor phase above TEG solutions. The Parrish correlation has been included in this edition because equilibrium water concentrations in the vapor phase were determined at infinite dilution (essentially 100% TEG). The other correlations use extrapolations of data at lower concentrations to estimate equilibrium in the infinite dilution region. The effect of pressure on TEG-water equilibrium is small up to about 13800 kPa [2000 psia][18.4].

A TEG absorber is essentially isothermal. The heat of solution is about 21 kJ/kg [91 Btu/lbm] of water absorbed in addition to the latent heat. But, the mass of water absorbed plus the mass of TEG circulated is trivial to the mass of gas. So, the inlet gas temperature controls. The temperature rise due to heat of absorption seldom exceeds 2°C [4°F] except when dehydrating at pressures below about 1000 kPa [145 psia]. In low pressure service some temperature adjustment may be desirable.

The diagonal lines represent weight % TEG in a TEG-water mixture entering the top of the absorber. What is the lowest water dewpoint one could attain with a given concentration at a given temperature?



(a)



(b)

Figure 18.4 Equilibrium H_2O Dewpoint vs. Temperature at Various TEG Concentrations

Example 18.1: What equilibrium water dewpoint could be obtained at 40°C with a lean glycol solution containing 99.5 wt % TEG?

In Figure 18.4 locate 40°C on the abscissa, go vertically to the 99.5 wt % line and then horizontally to the ordinate. Read –19°C.

This water dewpoint could be attained in a test cell but not in a real absorber. The gas and TEG are not in contact for a long enough time to reach equilibrium. Numerous tests show that a well designed, properly operated unit will have an actual water dewpoint 5.5-8.5°C [10-15°F] higher than the equilibrium dewpoint. This "approach" to equilibrium can be used to specify minimum lean glycol concentration. The procedure is as follows.

1. Establish the desired outlet water dewpoint needed from sales contract specifications or from minimum system temperature.
2. Subtract the approach from (1) to find the corresponding equilibrium water dewpoint.
3. Enter the value in (2) on the ordinate of Figure 18.4 and draw a horizontal line.
4. Draw a vertical line from the inlet gas temperature on the abscissa.
5. The intersection of the lines in Steps (3) and (4) establishes minimum lean TEG concentration required to obtain the water dewpoint in Step (1).

If water content is specified or calculated in mass per unit gas volume, a water content, pressure, dewpoint temperature correlation is required. Note that the equilibrium water dewpoints on the ordinate of Figure 18.4 are based on the assumption the condensed water phase is a metastable liquid. At low dewpoints the true condensed phase will be a hydrate. The equilibrium dewpoint temperature above a hydrate is higher than that above a metastable liquid. Therefore, Figure 18.4 may predict dewpoints which are colder than those which can actually be achieved. The difference is a function of temperature, pressure and gas composition but can be as much as 8-12°C [15-20°F]. When dehydrating to very low dewpoints, such as those required upstream of a refrigeration process, the TEG concentration must be sufficient to dry the gas to the hydrate dewpoint.

Example 18.2: The gas sales contract specifies an outlet water content of 100 kg/10^6 std m^3 at a pressure of 6.9 MPa. The inlet gas temperature is 40°C. What minimum lean TEG concentration is required?

Metric: For 100 kg/10^6 std m^3 and 6.9 MPa, the equivalent dewpoint from a correlation is –2°C. If we use an 8°C approach the equilibrium dewpoint is –10°C. From Figure 18.4 at –10°C and 40°C contact temperature, wt % TEG = 99.0.

English: At 104°F [40°C] and 1000 psia [6.9 MPa] the dewpoint is 28°F for a water content of 6 lb/MMscf. An approach of 14.4°F [8°C] gives an equilibrium temperature of about 14°F. From Figure 18.4(a), lean TEG concentration equals 99.0 wt %.

The dashed line in Figure 18.4 at about 98.5 wt% represents the concentration of lean TEG that can be produced routinely in a regenerator operating at standard atmospheric pressure and 204°C [400°F]. This is a safe value for design and specification purposes. Concentrations of 98.7-98.8 wt% are common; some to 99.1 wt% have been reported but represent a special case where incoming hydrocarbons provided natural stripping and/or the pressure was lower than standard atmospheric.

Since the capital cost of ordinary gas stripping accessories is trivial, they always should be included. Conditions can change to where they may be required.

It is necessary to fix a lean TEG concentration for subsequent calculations. For the first consideration, use the results from Figure 18.4. If the concentration obtained is less than 98.5 wt%, use 98.5 wt% for the calculation unless you plan to reduce the reboiler temperature below 204°C [400°F].

The minimum lean TEG concentration may not be the one used. A higher concentration than this may be specified to minimize circulation rate and optimize cost.

TEG REGENERATION

A given lean TEG concentration is produced in the reboiler and still column (regenerator) section by control of reboiler temperature, pressure and the possible use of a stripping gas. So long as no stripping gas is used, the concentration of the lean TEG leaving the reboiler is independent of the rich TEG entering.

When stripping gas is used, the concentration of rich TEG leaving the absorber is found by a water material balance around that absorber. By definition

$$\text{wt \% rich TEG} = \frac{\text{wt lean TEG}}{\text{wt lean TEG + wt water absorbed + wt water in lean TEG}}(100) \qquad (18.2)$$

The weight quantities in this equation may be found per unit of time or per unit of gas flow. In any case, the values used depend on circulation rate. This rate depends on dewpoint requirements, lean TEG concentration, amount of absorber contact and economics. The latter dictates a rather low circulation rate. This rate usually will be 16-40 liters of lean TEG solution per kg of water absorbed from the gas [2-5 U.S. gal/lb water]. The minimum rate is governed by the rate required for effective gas-liquid contact in the absorber; the maximum is limited by economics.

Because this regeneration takes place at low pressure, under ideal gas conditions, the calculation is very routine. Figure 18.5 has been calculated to predict regenerator performance.[18.2]

The minimum wt% lean TEG on the top abscissa is found from Figure 18.4. The wt% of rich TEG on the bottom abscissa is found from Equation 18.2. The rich TEG concentration can also be determined from Equation 18.3.

$$\underset{\text{wt \%}}{\text{Rich TEG}} = \frac{(\rho)\,(\text{Lean TEG})}{\rho + (1/m)} \qquad (18.3)$$

			Metric	English
Where:	ρ	= liquid density	1.12 kg/L	9.3 lb/U.S. gal
	m	= lean TEG rate Litres TEG / Kg water removed	L/kg	U.S. gal/lb
	Rich TEG	= wt% TEG in rich TEG solution		
	Lean TEG	= wt% TEG in lean TEG solution		

5

The diagonal lines in the lower left portion of Figure 18.[E#,G4F011754 represent various amounts of stripping gas. It is seldom that one would use more than 0.08 m^3 gas per liter of TEG [10 scf/U.S. gal]. At some point the practical impact of stripping gas diminishes with rate.

Three temperature lines are shown. Where high concentrations are desired, the specification of 204°C [400°F] is normal unless the gas being dehydrated contains oxygen. This is close to the thermal decomposition temperature (in air). In the usual case where the natural gas is oxygen free, the use of 204°C [400°F] has proven very satisfactory.

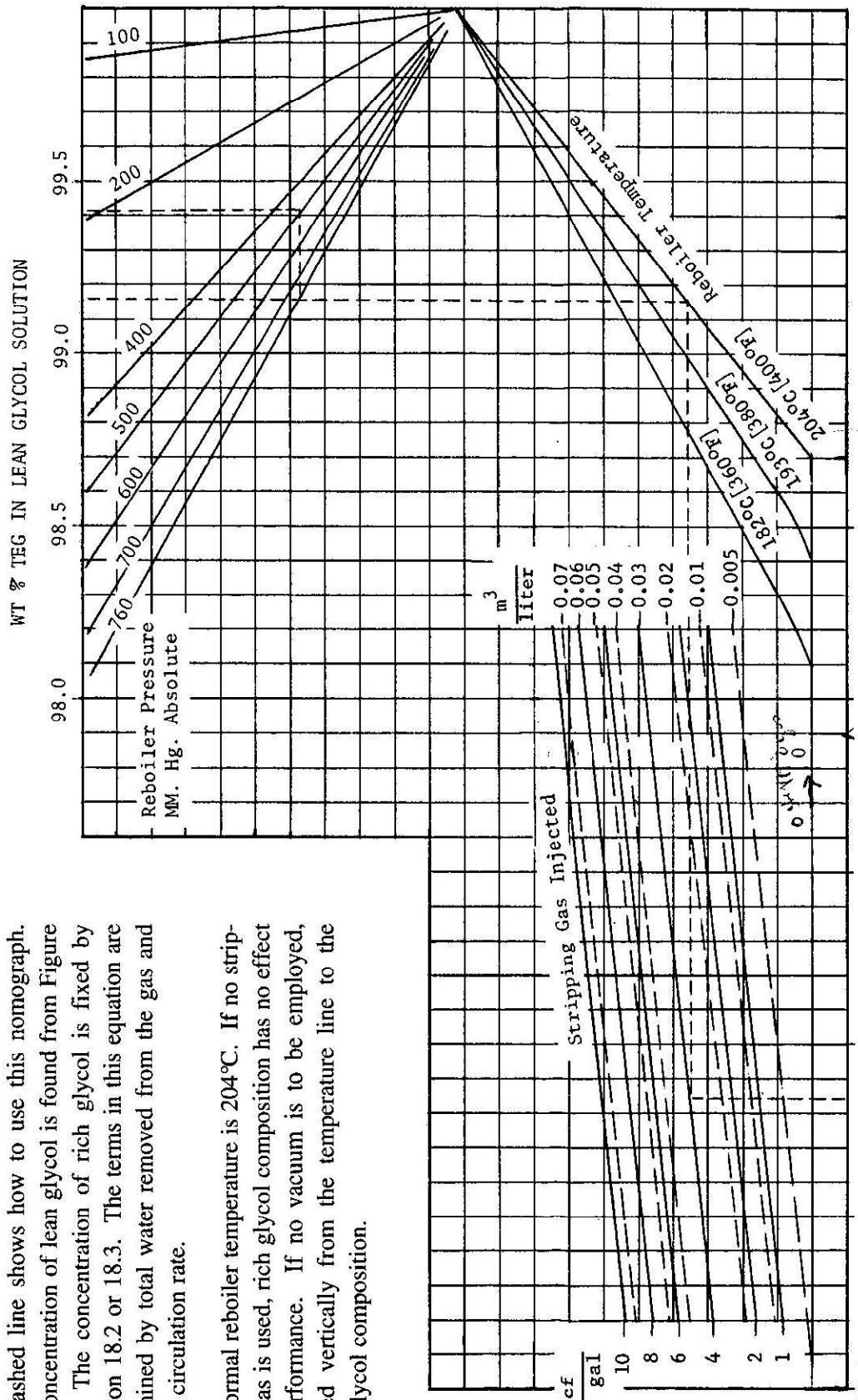


Figure 18.5 Nomograph for Estimating Regenerator Performance as a Function of Pressure, Reboiler Temperature and Stripping Gas

The dashed line shows how to use this nomograph. The concentration of lean glycol is found from Figure 18.4. The concentration of rich glycol is fixed by Equation 18.2 or 18.3. The terms in this equation are determined by total water removed from the gas and glycol circulation rate.

The normal reboiler temperature is 204°C. If no stripping gas is used, rich glycol composition has no effect on performance. If no vacuum is to be employed, proceed vertically from the temperature line to the lean glycol composition.

The diagonal lines at upper right in Figure 18.5 represent the effect of regeneration pressure in mm Hg,

760 mm Hg = 14.7 psia = 101.325 kPa
100 kPa = 1 bar = 750 mm Hg

Unless a vacuum is being used, it is customary to use the 760 mm Hg line for design calculations.

Notice that at 760 mm Hg pressure and a reboiler temperature of 204°C, Figure 18.5 shows a lean TEG concentration of 98.7 wt%. If in using Figure 18.4 you obtain a concentration less than this, use 98.7 wt% as the desired concentration when utilizing Figure 18.5.

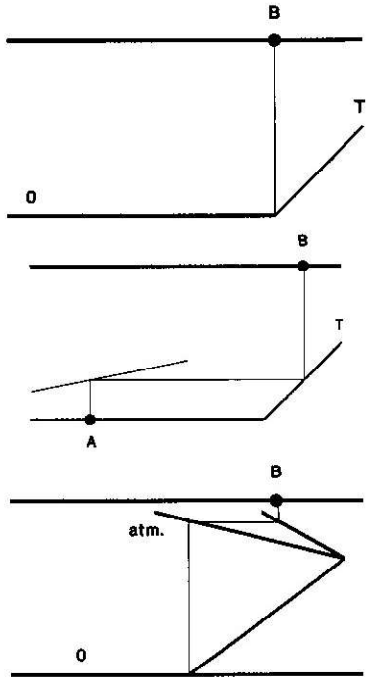
The general procedure for using Figure 18.5 is as follows:

1. Atmospheric Pressure, No Stripping Gas -

   Wt% rich glycol is not a variable. Proceed vertically from 0 stripping gas and temperature line intersection. You will read 98.7 wt% TEG at 204°C; 98.4 wt% at 193°C.

2. Atmospheric Pressure, Stripping Gas -
   a. Proceed vertically from B to temperature line and then horizontally.
   b. Proceed vertically from A.
   c. Intersection of two lines from A and B fixes amount of stripping gas.

3. Vacuum, No Stripping Gas -
   a. Proceed vertically from intersection of 0 gas line and temperature line to atmospheric line (760 mm Hg).
   b. Proceed horizontally from point in (a) to pressure line necessary to fix value of point B.



In that rare case where both stripping gas and vacuum are used, procedures (2) and (3) are combined.

Example 18.3: An example is shown on Figure 18.5 for use of stripping gas and vacuum. A 96.84 wt% rich glycol enters a regenerator using 0.03 m^3 of stripping gas per liter of glycol solution [4 scf/U.S. gal]. Proceeding to 204°C and then vertically, one reads 99.16 wt% if atmospheric pressure is used. If a vacuum is employed and the absolute pressure is 500 mm Hg, the lean glycol concentration is 99.41 wt%.

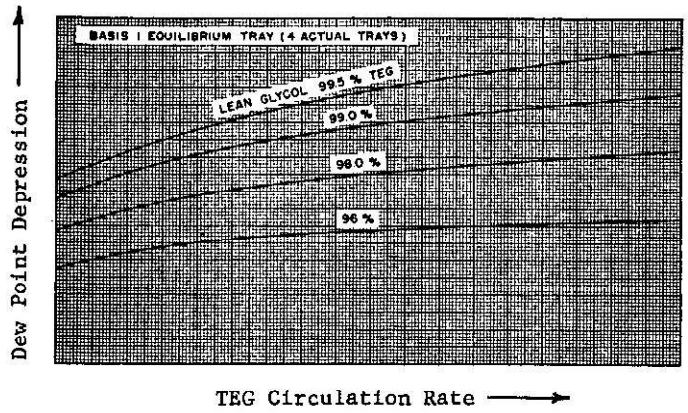
As a general rule, vacuum is avoided unless necessary to simplify unit operation. Vacuum pumps can be a nuisance. An ejector can be used to produce necessary vacuum in the right circumstances.

Figure 18.4 is based on 1 equilibrium stage in the regenerator. Most regenerators will contain more than 1 equilibrium stage, particularly if a stripping column is installed between the reboiler and surge tank. For this reason, actual stripping gas rates will typically be less than those predicted from Figure 18.4.

CIRCULATION RATE – ABSORBER CONTACTS

The above calculation is dependent on glycol circulation rate if stripping gas or vacuum are used. Although a number of circulation rates are possible, the minimum feasible one should be used. As circulation

rate increases, so does operating cost. The minimum feasible rate is fixed by absorber characteristics and cost.



The figure at left shows the effect of TEG concentration and circulation rate on dewpoint depression for a fixed amount of absorber contact of absorber contact. Notice that the curves become relatively flat at high circulation rates.

For ordinary pipeline water dewpoint control, the glycol circulation rate usually will be 16-40 liters per kg water absorbed from the gas [2-5 U.S. gal/lb water]. A circulation rate above this range can be justified economically only in special applications for it results in excess utility consumption.

For a given circulation rate a given number of absorber contacts are needed. The relationship between rate and amount of contact is very adequately described by the Kremser-Brown method described in Chapter 17. In the glycol application, mol fractions may be used in instead of regular absorption parameters because of the concentrations involved. The basic absorption equation thus may be rewritten as:

$$E_a = \frac{y_{N+1} - y_1}{y_{N+1} - y_0} = \frac{A^{N+1} - A}{A^{N+1} - 1} \qquad (18.4)$$

Where: y_{N+1} = mol fr water in entering wet gas
y_1 = actual mol fr water in dried gas leaving
y_0 = water content of dried gas if it is in *equilibrium* with the entering lean glycol (value is less than y_1)
A = absorption factor, A = L/(KV)
L = glycol circulation rate, moles/unit time
V = gas flow rate, moles/unit time
K = equilibrium constant for water between water in gas and water in a TEG-water solution, y = Kx
N = no. of theoretical plates in the absorber

The mol fraction water, y_w, is related to W, the mass of water per standard volume of gas by a fixed conversion factor. As noted in Chapter 6,

$y_w = 1.33(E\text{-}06)\ W$ Where: W = kg/106 std m3

$y_w = 2.11(E\text{-}05)\ W$ Where: W = lbm/MMscf

Thus, $$\frac{y_{N+1} - y_1}{y_{N+1} - y_0} = \frac{W_{N+1} - W_1}{W_{N+1} - W_0} \qquad (18.5)$$

The subscripts on "W" have the same significance as on "y."

For a given calculation the values of inlet water content, outlet water content, gas flow rate, and absorber pressure and temperature are fixed. Using a correlation for determining the equilibrium K value of water in a TEG-water system, values for y_0 (or W_0) and K are available. The only variables left in Equation 18.4 are L (the TEG circulation rate) and N (the number of theoretical trays). In theory, there are an infinite

number of combinations of L and N that satisfy Equation 18.4. In practice, the choices are limited by economics and absorber performance.

The cost of purchasing and operating any absorption unit is a function of circulation rate. It is thus good practice to operate at, or near, the minimum rate necessary to meet absorption specifications.

Figure 18.6 is a plot of Equation 18.4 that is convenient for manual calculations. This uses what could be called an *overall absorption factor*. The ratio L/V varies slightly throughout the absorber. L_0 is the rate of lean TEG entering the top tray and V_{N+1} is the gas rate entering the bottom tray. As a later numerical example will illustrate, the variation of L/V will have a calculable, but usually nonsignificant, effect on unit design.

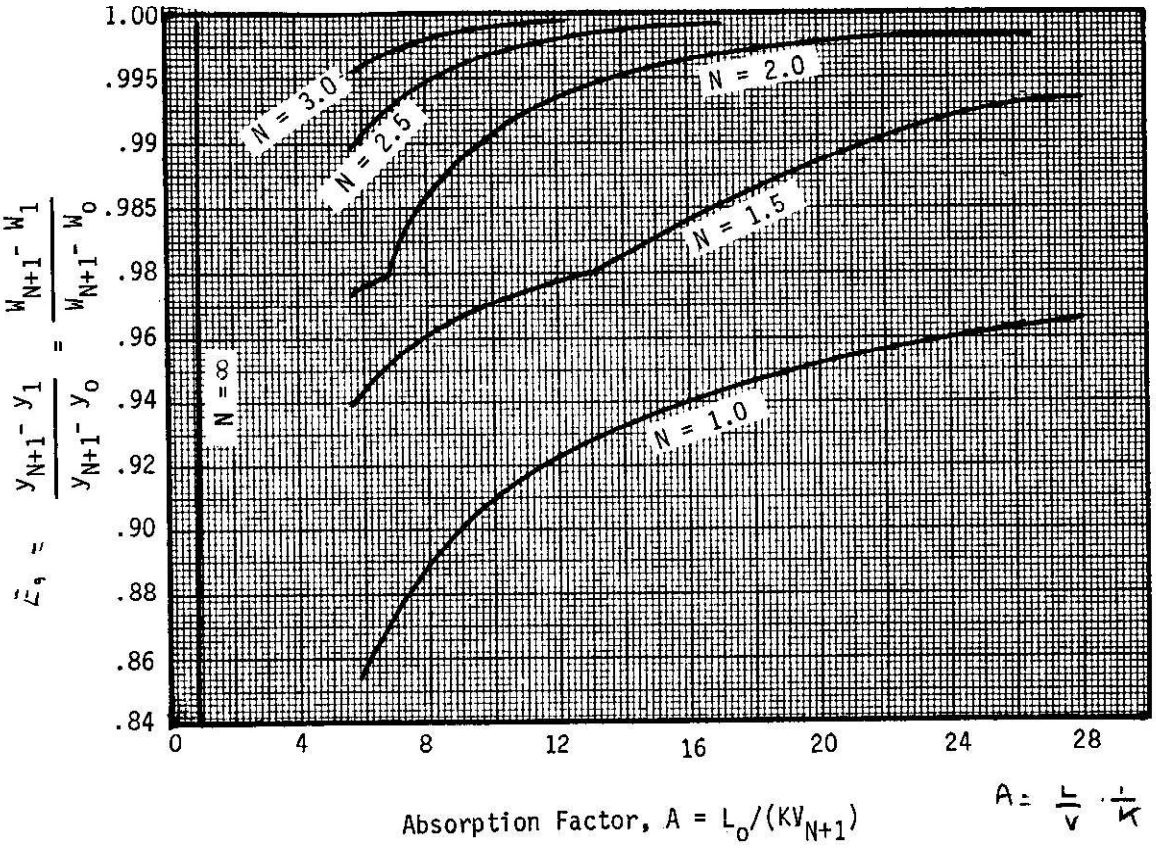


Figure 18.6 Plot of Kremser-Brown Equation

The left-hand ordinate of Figure 18.6 could be called *absorption efficiency*. It is the actual amount of water removed, divided by the maximum amount removable. The values of N encompass the range of theoretical trays usually employed. The line for N equals infinity represents the minimum absorption factor, e.g., minimum circulation rate. All curves for finite values of N become asymptotic to this line. Note that the scale changes on the ordinate at 0.98.

Calculation of Lean TEG Rate for a Given Absorption Efficiency and N -

1. Calculate y_0 (or W_0)
2. Determine absorption efficiency
3. Use Equation 18.4 or Figure 18.6 to find absorption factor A for a given value of N
4. Knowing V_{N+1} and K, solve A for L_0, the lean TEG circulation rate

Calculation of N for a Given Lean TEG Rate and Absorption Efficiency -

1. Calculate y_0 (or W_0)
2. Determine absorption efficiency
3. Calculate absorption factor A
4. Determine N from Equation 18.4 or Figure 18.6

It is usual to repeat the calculation to obtain three lean glycols rate/absorber contact values that satisfy the required absorption efficiency. The final choice is economic. This usually involves selection of standard modules to make up the unit.

This calculation should be made at the lowest pressure and highest temperature anticipated for the entering wet gas, to obtain the maximum water loading. Historically, the tendency has been to choose a design temperature lower than that actually obtained.

The overall tray efficiency in a well-designed TEG unit will vary from 25-40%. It is recommended that 25% be used for most applications. This provides an affordable safety factor to help compensate for the inherent errors in the design specifications.

Equilibrium Relationships

Various studies have been made of the equilibrium behavior of water in the TEG-water system.[18.3-7] All provide rather consistent data. The use of an activity coefficient (γ) is a convenient and reliable method for calculating K. Using this relationship

$$K = (y_w)(\gamma) = (B)(W)(\gamma) \tag{18.6}$$

Where:
- K = equilibrium constant for water in a TEG-water system
- y_w = mol fr water in the gas at saturation over 100% liquid water (from regular water content correlation)
- γ = activity coefficient for water in the TEG-water system as found from Figure 18.7
- W = water content on a mass per volume basis, at saturation, as found from a regular water content correlation
- B = 1.33(E-06) when W = kg/10^6 std m^3 (measured at 15°C and 100 kPa)
  = 2.11(E-05) when W = lbm/MMscf (measured at 60°F and 14.7 psia)

Notice that γ and thus K vary with TEG concentration and temperature, which in turn varies throughout the absorber. An average K at average concentration cannot be found until the circulation rate is fixed. So, a simple trial-and-error calculation is involved. One can assume the inlet lean TEG concentration as a first try. For most dehydration applications the increase in K from the lean to rich TEG is roughly proportional to the increase in L/V, so the absorption factor (A = LV/K) remains relatively unchanged.

In the absorption efficiency term

$$y_0 = K\,x_0 \quad \text{and} \quad W_0 = (W)(\gamma)(x_0) \tag{18.7}$$

Where: x_0 = mol fr water in the lean TEG entering the absorber

This may be calculated from X_{gl}, the weight percent TEG in the lean solution entering the absorber. This must be not less than the minimum value required from Figure 18.4.

$$x_0 = \frac{(100 - X_{gl})/18}{[(100 - X_{gl})/18] + (X_{gl}/150)} \tag{18.8}$$

Equation 18.8 is shown graphically in Figure 18.8.

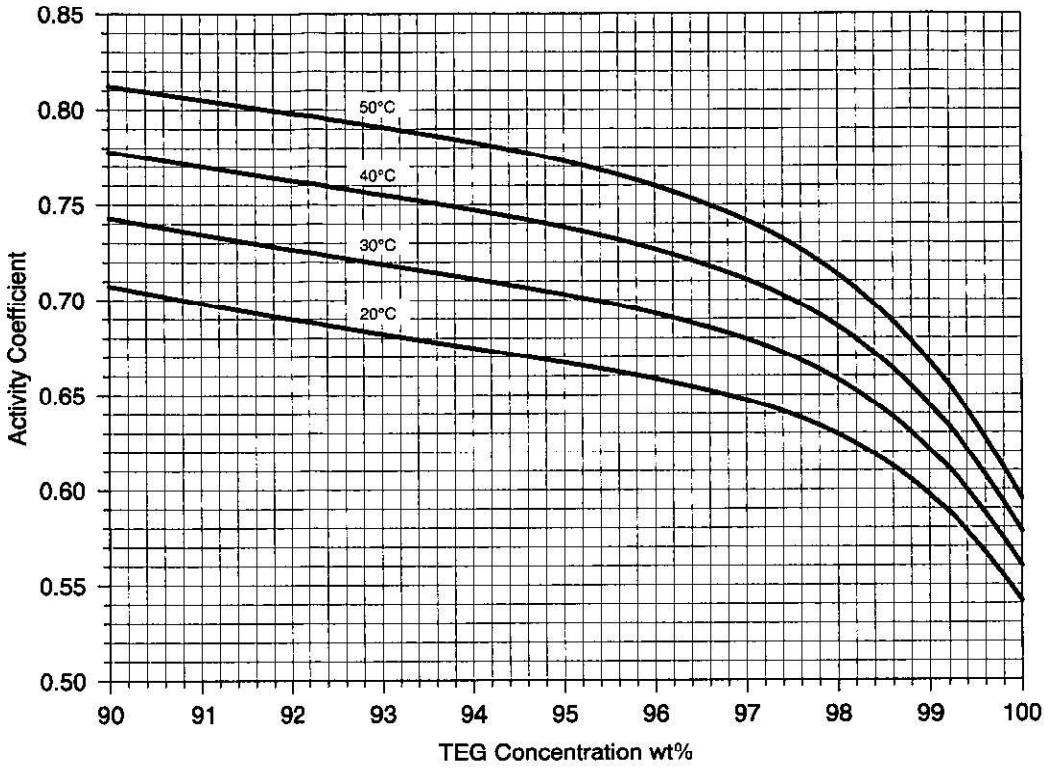


Figure 18.7 Activity Coefficient for H_2O Concentration at Various Temperatures

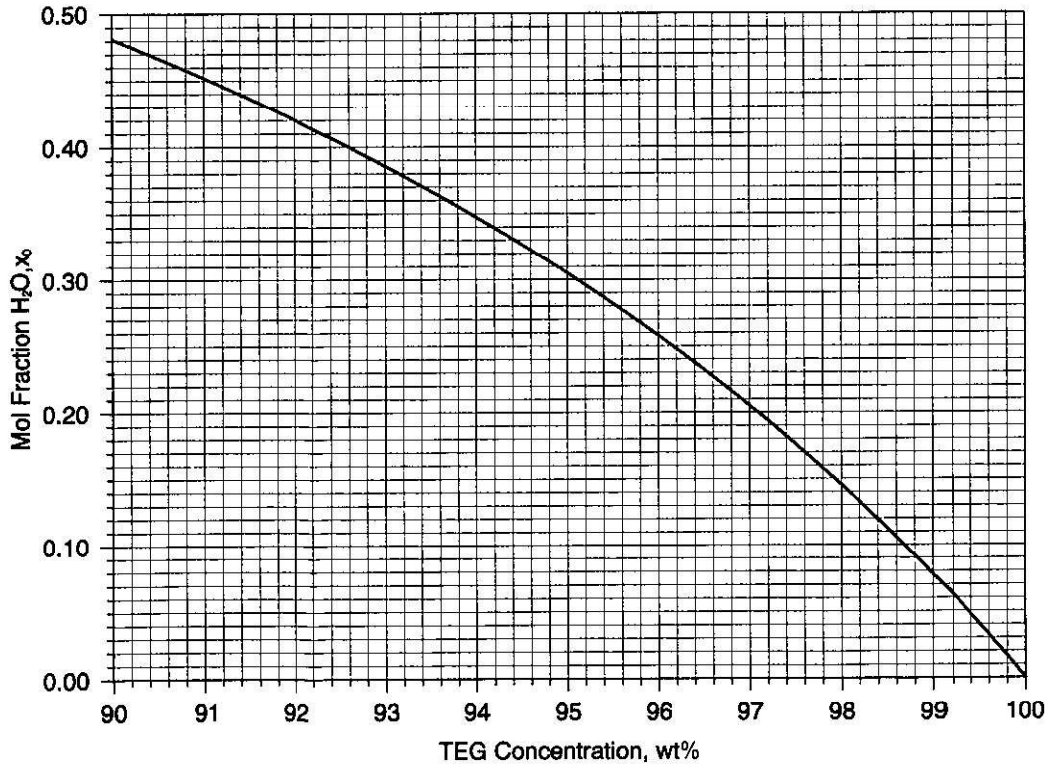


Figure 18.8 Equation 18.8 Mol Fraction H_2O vs. TEG Concentration

The above procedure using the Kremser-Brown approach to absorption is as good as a tray-to-tray balance around the absorber. As reviewed in Chapter 17, this is true because there is little gas shrinkage and A is essentially constant throughout the tower.

The use of other equilibrium K values will have little effect on contactor design. The required lean glycol concentrations may differ but the difference is normally less than the random error in process specifications and is statistically insignificant.

Example 18.4: Calculate the circulation rate of 98.7 wt% lean TEG needed to dry 10^6 std m^3/d of gas at 7.0 MPa and 40°C in a six tray absorber (1.5 theor. tray) to achieve an exit gas water content of 117 kg/10^6 std m^3. The inlet water content is 1100 kg/10^6 std m^3 (saturated gas).

1. From Equation 18.8, $x_0 = 0.099$
2. From Figure 18.7, $\gamma = 0.66$
3. W is the water content of saturated gas at 7.0 MPa and 40°C or 1100 kg/10^6 std m^3 in this case.
4. From Equation 18.7, $W_0 = (1100)(0.66)(0.099) = 71.9$ kg/10^6 std m^3
5. The left-hand side of Figure 18.6 is: $(1100 - 117)/(1100 - 71.9) = 983/1048 = 0.956$
6. From Figure 18.6, for N = 1.5, A = 7.3

(In order to solve for L one must recognize that it is different at each point in the absorption tower. The conservative approach is to assume the gas volume is constant and solve for L_0 from A.. This will yield a circulation rate sufficiently close to a more rigorous calculation.)

7. $L_0 = (A)(K)(V_{N+1})$
   From Equation 18.6, $K = (1.33 \times 10^{-6})(1100)(0.66) = 0.000\ 967$
   V = 1739 kmol/h
   So, $L_0 = (7.3)(9.67 \times 10^{-4})(1739) = 12.3$ kmol/hr
8. MW lean glycol = (0.099)(18) + (0.901)(150) = 137
9. kg TEG/h = (12.3)(137) = 1685
10. Density of TEG is 1.12 g/cm^3 = 1.12 kg/liter
    Circulation rate is 1681/1.12 = 1500 liter/h
    In one hour (1100 – 117)/24 or 41.0 kg H_2O is absorbed.
    Circulation rate is 1500/41 = 36.6 liter/kg H_2O absorbed.

In traditional English units the calculation follows the same format.

1., 2. The same
3. W = 67 lb/MMscf
4. $W_0 = (0.66)(67)(0.099) = 4.38$ lb/MMscf
5. $(67 - 7)/(67 - 4.38) = 0.958$
6. A = 7.5
7. $K = (2.11 \times 10^{-5})(67)(0.66) = 0.000931$
   V = (34.9)(110) = 3839 lb-mol/hr
   $L_0 = AKV_{N+1} = (7.5)(9.31 \times 10^{-4})(3839) = 26.8$ lb-mol/hr
8. MW = 137
9. lb/TEG/hr = (26.8)(137) = 3672
10. Density of TEG is about 9.3 lb/U.S. gal
    Circulation rate is 3672/9.33 = 394 U.S. gal/hr
    In one hour a total of 92 lb of water is absorbed.
    Circulation rate is 394/92 = 4.3 U.S. gal/lb water absorbed

Example 18.4 illustrates the calculation procedure outlined above and used in the accompanying computer program.

When using the Kremser-Brown method, the terms V and L must be expressed in molar units. For the glycol solution this requires estimation of the MW. The molecular weight of a TEG water solution may be calculated as follows:

$$MW = 18\ x_0 + 150\ (1 - x_0) \tag{18.9}$$

The actual circulation rate will be different from this because operating conditions always differ to some degree from those specified. This number will be used to select a pump size. It is then sound practice to choose other components to have a capacity compatible with that of the pump.

For the example case, would we buy a 1.5 theoretical tray absorber? Probably not! The circulation rate calculated is toward the high end of the economic range. A 7 or 8 actual tray (1.75–2.0 theoretical trays) might well be specified to provide valuable flexibility and inexpensive "insurance."

ABSORBER DESIGN

The absorber will be sized using the criteria outlined in Chapters 11 and 17. Special consideration must be given to the low circulation rate, glycol viscosity and its foaming tendencies.

A basic decision is whether to use some kind of tray or packed tower. With tray towers the choice is between valves and bubble caps. The former is more efficient at design capacity, but at lower flow rates glycol "weeping" may produce unsatisfactory water dewpoints. Bubble caps certainly are a safe choice in service where widely fluctuating gas flow rates are anticipated.

Regardless of the type of tray, a minimum spacing of 24 inches is recommended. It is essential that a stable foam not fill the gas space between trays to prevent excess glycol loss. This spacing also allows a suitable liquid level in the downcomers.

Tray hydraulics design is critical because of the low circulation rate. Liquid can by-pass caps or valves in some areas of the tray, ineffective gas-liquid contact can occur with low gas rates, and liquid levels can be unstable. In situations like this, absorber performance can vary markedly with gas and liquid rates. A higher than calculated liquid rate may be necessary to provide the tray efficiency required.

Remember that the minimum TEG concentration found from Figure 18.4 assumes that the tower provides the contact required, e.g., the proper number and efficiency of trays. The result desired is achievable with that concentration only if both the mechanical design of the absorber and the circulation rate are proper. On the other hand, if you don't have at least that concentration, the result is unattainable, regardless of the amount of contact or circulation rate.

Random packing has been used successfully for gas-liquid contact in a glycol absorber but is not generally recommended. One can encounter liquid distribution problems. If undue foaming occurs, the tower can flood at lower than normal gas rates and cause excess glycol losses. Solids in the gas tend to plug the packing.

The use of structured packings is standard practice in glycol dehydration service today. Some of the more common types include Mellapak, Montzpak and Flexipak and Gempak. Structured packings offer the advantage of considerably smaller diameter towers as compared to trayed contactors for the same gas rate. This feature can significantly reduce capital costs, especially offshore. In addition, glycol losses may be reduced due to less agitation of the glycol solution at the top of the absorber. Mass transfer is somewhat better than trays but the real savings is in tower diameter.

For sizing packed glycol contactors using structural packing, the following parameters are useful.

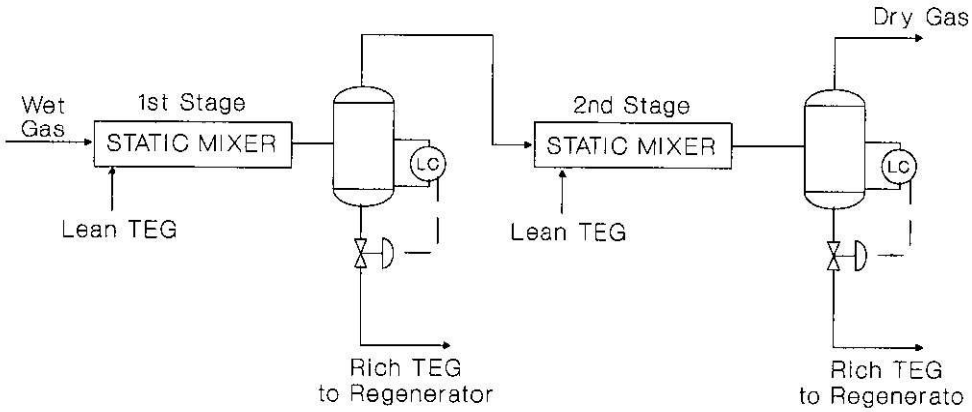
	Metric	English
K_s	0.1 m/s	0.33 ft/sec
HETP	1.5–2.0 m	60–80 in.

Courtesy Nutter Engineering

Structured packing consists of prefabricated elements approximately 0.2 m [8 in.) thick. Each section is oriented 60° or 90° relative to the adjacent unit to insure good liquid distribution. Sealing is provided at the vessel wall with wall wipers which come with the packing. Two sections of structured packing are shown to the left.

One of the primary applications of structured packing has been to increase the gas handling capacity of an existing trayed contactor. Retrofits increasing absorber capacity by 100% have been reported. When retrofitting a contactor adequate pump and regenerator capacity must also be checked.

Some vendors offer an absorber other than a conventional vertical unit. One design uses two or three cocurrent contactors in series separated by scrubbers. The cocurrent contractors are static mixers. This design often has a lower installed weight when compared to a conventional contactor, and may offer a cost advantage when a high dewpoint depression is not required.



Static mixers have also been used upstream of conventional contactors to add some portion of a theoretical stage to the unit.

REGENERATION AND HEAT EXCHANGE

The glycol circulated must be heated to reboiler temperature and then cooled before re-entering the absorber. Efficient rich glycol-lean glycol heat exchange will minimize fuel and/or utilities cost.

The detailed calculation involves a heat and material balance around the regeneration system for the maximum anticipated glycol circulation rate. The reboiler heat load depends on the efficiency of exchange.

The Reboiler

Commonly a direct-fired reboiler is used. The outside temperature of the fire tube surface, covered by glycol, is surprisingly cool, if the unit is properly fired. Figure 18.9 shows one temperature profile obtained on test.

Outside surface temperature may be lower than steam or hot oil units because of high film resistance on the low pressure gas side. This temperature is important to prevent cracking of any hydrocarbons present and degradation of the glycol.

To maintain proper skin temperature, prevent "hot spots" and obtain satisfactory fire tube life, it must have sufficient area. The following are recommended:

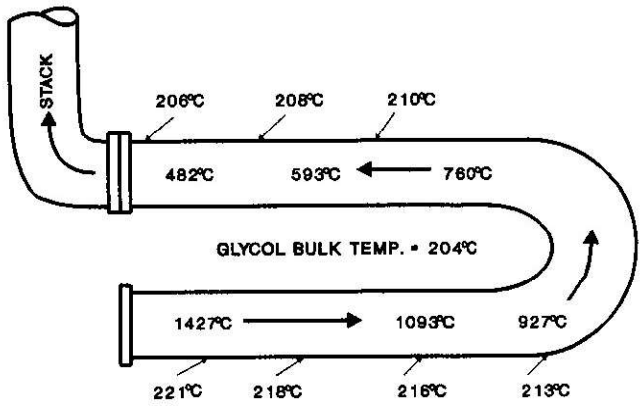


Figure 18.9 Typical Temperature Profile in Gas Fired Glycol Reboiler

Max. heat flux across fire tube wall	25 kW/m^2, [8000 Btu/hr-ft^2]
Recommended heat flux for max. life	20 kW/m2, [6000 Btu/hr-ft2]
Burner capacity	30 kW/m^2, [10 000 Btu/hr-ft^2]

Notice that the burner possesses extra capacity to obtain firing flexibility.

The typical heat balance will indicate a reboiler heat load of 390–450 kJ/liter of TEG circulated [1400–1600 Btu/U.S. gal]. Experience has shown that extra heating capacity is desirable. Based on the maximum pump capacity, I recommend that the minimum reboiler rating be

560 kJ/liter TEG [2000 Btu/U.S. gal TEG]

The direct fired reboiler is very efficient but there can be safety problems, particularly offshore. Hot liquid, steam, electrical resistance coils and waste heat can be used. The choice depends on what else is on the platform. The heat load of the glycol unit is rather small so it seldom justifies a separate source.

The Still Column

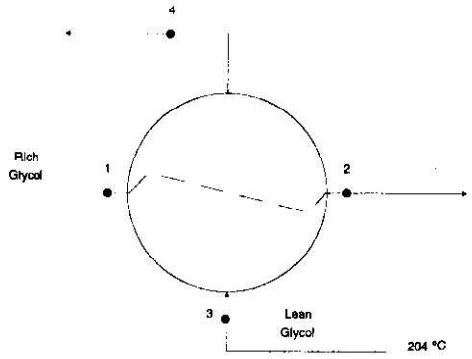
This is a packed column except in large sizes. The upper part of this is really a rectification section to prevent glycol loss. No formal amount of reflux is necessary with TEG. Just enough is needed to keep the packing wet. Since the vapor load is low, the sizing of this column is not critical. It should, however, conform generally to the diameter approximated in Equation 18.10.

$$d = (A)(m)^{0.5} \qquad (18.10)$$

		Metric	English
Where:	d = diameter of packed tower	cm	in.
	m = glycol circulation rate	L/min	U.S. gal/min
	A = empirical constant	11.9	9.1

Glycol–Glycol (Lean-Rich) Heat Exchanger

This is the basic heat exchanger. Its efficiency has a direct effect on reboiler heat load. The rich glycol from the absorber enters at about the temperature of the inlet gas (Pt. 1). The lean glycol from the regenerator (Pt. 3) enters usually at about 204°C [400°F]. The temperature of the lean glycol at Pt 4 should not be greater than 60–65°C [140–149°F].



In most cases a 15-20°C approach in the heat exchanger is desirable. If it is too high the reboiler and glycol cooler duties will increase. In this exchanger

$$Q_{3-4} = Q_{1-2} = m_1 (h_2 - h_1) = m_3 (h_3 - h_4) \qquad (18.11)$$

The easiest way to make this enthalpy calculation is to look up the average specific heat of the glycol in Appendix 18A and multiply it by ΔT across the heat exchanger to find Δh for the lean mixture. The temperature of the rich glycol entering the heat exchanger will be about the same as that of the entering wet gas.

If an efficient glycol-glycol exchanger is used there may be no need for an additional cooler on the lean glycol stream. A cooling coil in the top of the absorber is not recommended for any application other than small wellhead units. The most common types of glycol-glycol exchangers are pipe-in-pipe and plate. The first are used on small units, while the latter find extensive use in larger units and offshore. Plate exchangers provide effective heat exchange but are very susceptible to fouling in dirty service. Clean filtered glycol is imperative if plate exchangers are used.

FILTERS

Good filtration is critical. The full-flow type is preferred. I recommend two filters in parallel, with no by-pass lines, so that full filtration is assured.

A cloth fabric element that is capable of reducing solids to about 100 ppm by weight is preferred. Paper and fiberglass elements generally have proven unsatisfactory. Filter size in a properly operated glycol system should be 5–10 μm. Larger sizes 25–50 μm may be required during startup and in dirty service.

It may be impossible to judge the effectiveness of filtration by color alone. Even well filtered glycol probably will be black. But, removal of most of the solids will reduce corrosion, plugging and deposits in the reboiler, and may reduce foaming losses. Good filtration is critical for satisfactory performance. It is desirable to measure the pressure differential across the filter and change the element when it reaches about 170 kPa [25 psi].

The use of a carbon purifier downstream from the filter often is recommended. This will produce essentially water-white glycol. Maintenance of this color has proven desirable because it tends to increase dehydration efficiency and minimum foaming, a major source of glycol loss.

Aromatic hydrocarbons are often present in the rich glycol entering the regenerator and will be adsorbed on the carbon filter. They will quickly reach equilibrium loading on the carbon filter although it is likely they are eventually displaced (to some extent) by heavier hydrocarbons. Because of this high aromatic content, changeout of carbon filters requires special precautions to avoid unnecessary exposure of benzene and toluene to workers.

In some units the carbon filter is installed in the lean TEG stream upstream of the contactor to avoid significant aromatic loading.

Coal-based activated carbon should be used because wood-based charcoal tends to break up in use. This carbon can be placed in a metal canister or fill a vessel. In either case, good screens are needed to prevent carbon loss into the system. Said carbon particles, much like iron sulfide, tend to promote a stable foam.

Glycol filters are only effective when used. In especially dirty glycol systems, filters are often bypassed to avoid frequent filter change-out. The problems with this should be obvious. If filter plugging is

excessive, try larger filter size and look for source of problem (e.g., poor inlet separation, degradation, corrosion products, etc.).

PUMPS

A number of types of positive displacement pumps have been used in glycol service. In small units, variations of chemical feed pumps have been used. A Kimray pump of the type shown in Figure 18.10 is used commonly when a gas-powered pump is desired. They have a unique power recovery feature that minimizes the amount of power gas required. In many cases, the exhaust power gas can be used as stripping gas or burned as fuel.

Electric powered plunger type, triplex pumps also are used commonly. These provide a steady flow rate to the absorber. Hardened or chrome plated plungers usually are recommended. Scoring and pitting has been a problem. Piston speeds should be kept below 0.6 m/s [120 ft/min].

INLET SEPARATION

You cannot afford the dehydrator if you cannot afford to place an effective separator on the gas inlet. Salt water will enter the reboiler, evaporate, and coat the walls (causing fire-tube failure) or fill up the unit. This happens frequently on wells that supposedly do not produce salt water "officially."

A good separator also should remove the bulk of the compressor oil, drilling mud, corrosion inhibitors, pipeline dirt, formation solids, and the like, which are somewhat incompatible with glycol unit operation. A full-sized unit meeting the criteria in Chapter 11 should be used.

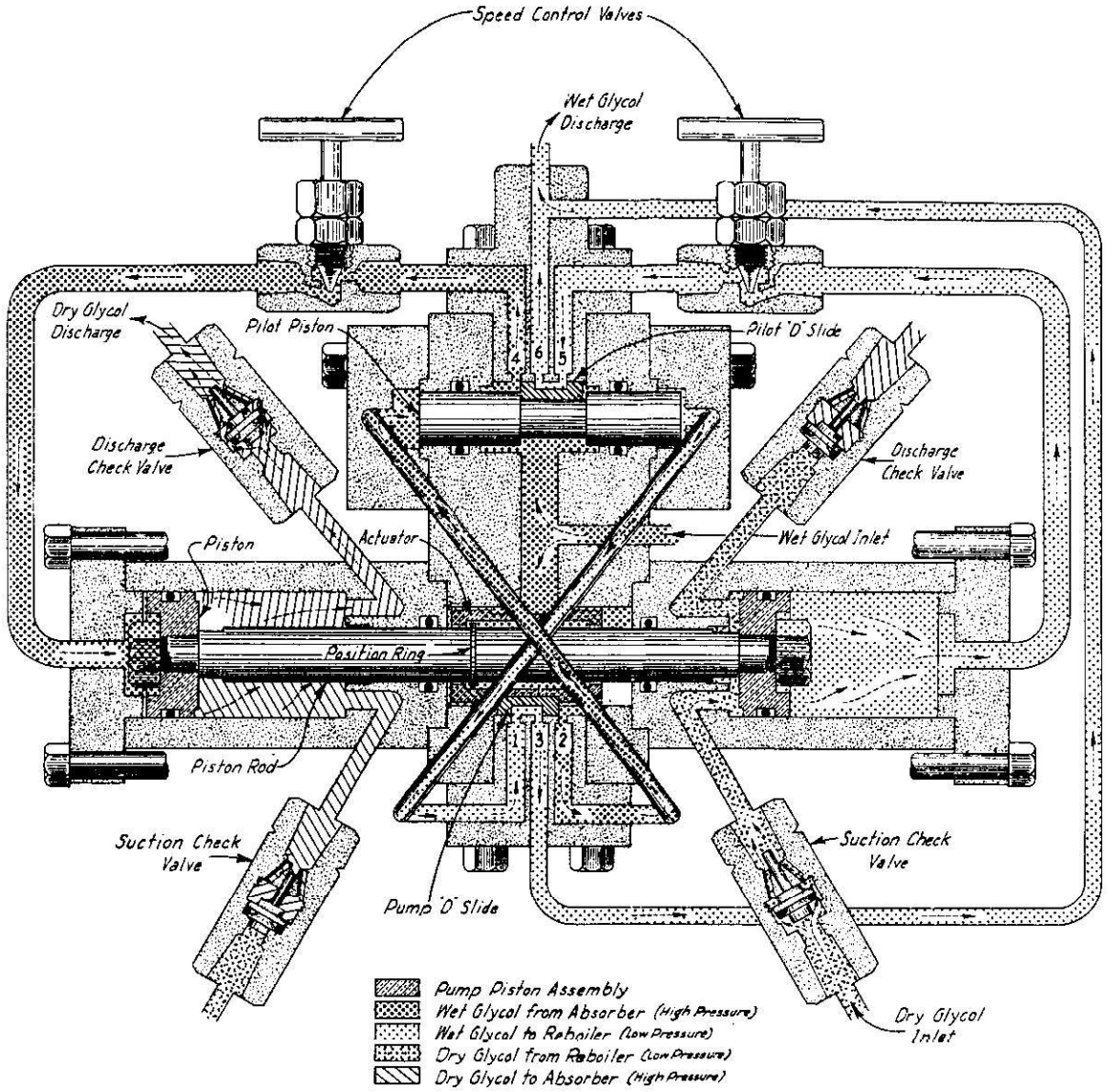
Placing the separator in the bottom of the glycol absorber may be satisfactory but seldom is there enough height to provide performance equivalent to a regular separator. Consider this carefully and do not be too idealistic. In some circumstances this approach represents poor economy.

OPERATING PROBLEMS

The glycol unit should be essentially trouble-free. It seldom is. Many of the problems stem from inadequate design and/or operational faults. The basic simplicity of the unit and the availability of "standard" units tends to obscure the need for attention to mechanical design details. The glycols are very reactive chemically and need to be protected from contamination.

One common symptom of many problems is excess glycol loss. This loss is due to one, or a combination, of the following:

1. Foaming
2. Degradation
3. Salt plugging the regenerator still column
4. Inadequate mist extraction
5. Inadequate absorber design for flow conditions
6. Loss of glycol from pinholes in a gas-glycol coil in the top of the absorber or in a chimney tray above a separator section in the bottom of the absorber
7. Spillage of glycol or pump leakage
8. Lean glycol to absorber is too hot



OPERATION:

The Kimray glycol pump is double acting, powered by Wet Glycol and a small quantity of gas at absorber pressure.

Wet Glycol from the absorber flows through port #4 and is throttled through the SPEED CONTROL VALVE to the left end of the Pump Piston Assembly, moving this assembly from left to right. Dry Glycol is being pumped from the left cylinder to the absorber while the right cylinder is being filled with Dry Glycol from the reboiler. At the same time Wet Glycol is discharging from the right end of the Pump Piston Assembly to a low pressure or atmospheric system.

As the Pump Piston Assembly nears the end of its stroke, the POSITION RING on the PISTON ROD contacts the right end of the ACTUATOR. Further movement to the right moves the ACTUATOR and PUMP "D" SLIDE to uncover port #1 and communicate ports #2 and #3. This exhausts Wet Glycol from the left end of the PILOT PISTON through ports #2 and #3 to the low pressure Wet Glycol system. At the same time port #1 (which was communicated with port #3) admits Wet Glycol to the right end of the PILOT PISTON. This causes the PILOT PISTON and PILOT "D" SLIDE to be driven from right to left.

In its new position the PILOT "D" SLIDE uncovers port #5 and communicates ports #4 and #6. This exhausts Wet Glycol from the left end of the Pump Piston Assembly through ports #4 and #6 to the low pressure Wet Glycol system. Port #5 (which was communicated with port #6) now admits Wet Glycol through the right hand SPEED CONTROL VALVE to the right end of the Pump Piston Assembly.

The Pump Piston Assembly now starts the stroke from right to left. It follows the above procedure with reversed directions of flow.

Figure 18.10 Operation of the Kimray Glycol Pump

Glycol likes to foam. It will foam whenever allowed to. Ordinary foaming may not be critical if the unit is carefully designed. Any foam tends to be more stable when aromatics and/or sulfur compounds are present. Metallic sulfides and sulfites, and degradation products, all contribute to the problem.

Foams are only broken using surface and time, or chemicals. Tray spacing must be large enough so that foam cannot fill up the space between trays and form a continuous liquid phase. A mist extractor does not break foam effectively. Once foam fills the absorber, there is a continuous liquid phase for glycol to go out overhead.

Use of an antifoam agent can reduce the problem. Figure 18.11 shows the effect of adding trioctylphosphate to maintain a concentration of 500 ppm. There are many antifoam agents available. One that works in one unit may not work equally well in another. Some trial-and-error testing of an antifoam agent, and concentration of that agent, is often necessary.

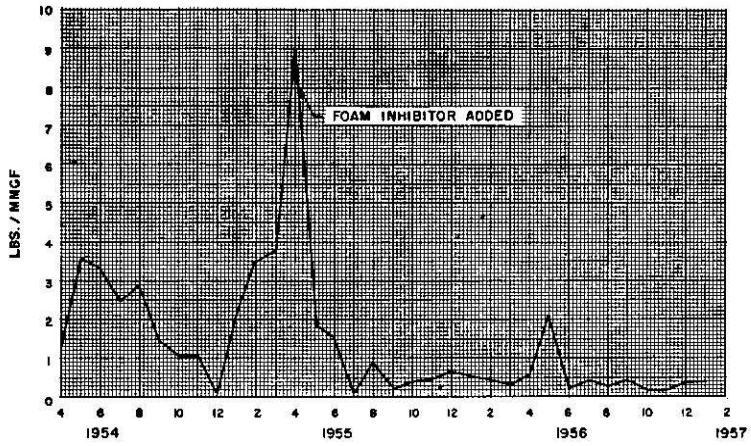


Figure 18.11 Possible Effect of Foam Inhibitors in TEG Systems[18.8]

Avoid adding too much antifoam agent. If too much is added it may accelerate foaming. Set up a careful control policy so operators keep unit concentration within the limits specified.

Degradation is a natural occurrence and is accelerated in the presence of sulfur compounds. The answer is effective filtration. Degradation products contribute to foaming but they also are major sources of corrosion problems. The best filtration system uses a regular filter to remove the large "chunks" and then an activated carbon filter to remove hydrocarbons as well as fine contaminants that pass through the first filter. The initial cost is higher but the carbon filter may offer a favorable benefit cost/ratio.

Salt is a continuing problem. Good separation ahead of the absorber is mandatory. Any salt arriving at the regenerator deposits either in the still column or in the reboiler. It is common for packed still columns to plug up to the point glycol is lost overhead. If this does not occur, salt can plug the reboiler and cause failure. Not providing good separation is inexcusable.

The water vapor in gas is relatively fresh but is slightly saline. NaCl is soluble in TEG to some degree. At 50°C about 3.3 kg will dissolve in 100 kg of TEG. So, some salt is always present. The soluble salt hydrolyzes to HCl and lowers the pH of the glycol.

Corrosion–Erosion

Glycols are very reactive with sulfur compounds. The resultant materials tend to polymerize and form "gunk" which is very corrosive. Also, the glycol pH becomes lower. Corrosion inhibitors alone cannot solve

the problem satisfactorily. The real solution is good mechanical design and good filtration supplemented by a corrosion inhibitor.

Good design involves factors like control of fluid velocities, long radius ells and a host of little details that too seldom are done properly. In many cases, good mechanical design will eliminate the need for expensive alloy steels.

If feasible to do so, the glycol pH should be maintained above 6.0. Some become so preoccupied keeping it at 7.0 or above that they add copious amounts of caustic, sodium carbonate and the like to the unit. The result is seldom satisfactory. Adjustment of pH is proper but the cure can be worse than the disease if it is overdone.

Corrosion inhibitors which plate out on metal surfaces and form a film can be effective in minimizing corrosion. Many materials are available. A product called Nacap has been used often. Some have used the amines effectively.

Figure 18.12 shows one result of using a corrosion inhibitor in a glycol system.

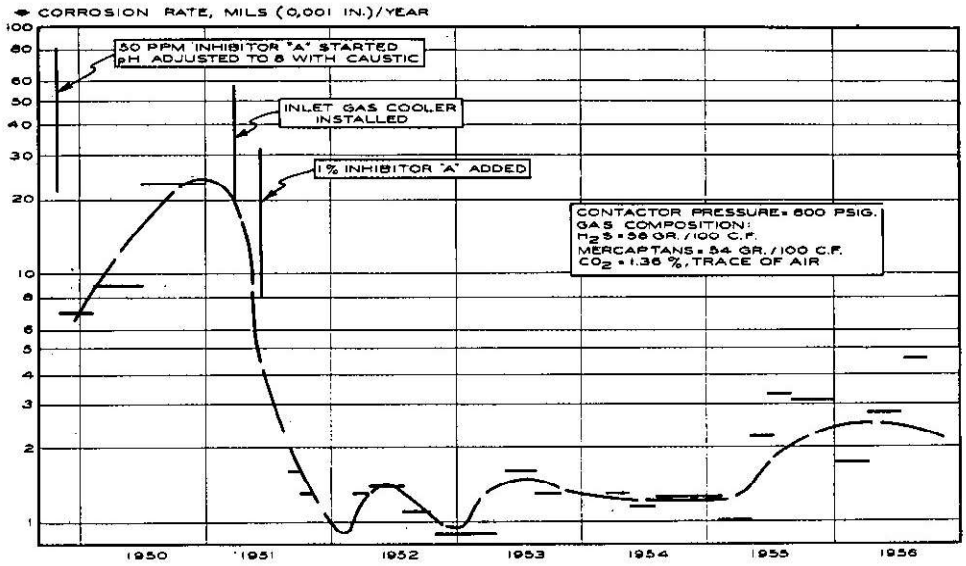


Figure 18.12 Possible Effect of Corrosion Inhibitors in TEG Systems[18.8]

Notice that corrosion was not eliminated; it merely was reduced to a satisfactory level. In a corrosive environment, the total elimination of corrosion is an unrealistic goal. The proper goal is reducing it to economically tolerable levels.

Figure 18.13 shows the solubility of H_2S in TEG.[18.9] This is true absorption that takes place in the absorber. It lowers pH and provides a mechanism for reactions. Figure 18.14 shows solubility of CO_2 in a 96.5 wt% TEG solution.[18.10] Solubility of CO_2 in pure TEG is approximately 20% higher. Reference 18.11 provides additional data on the solubilities of H_2S and CO_2, as well as C_1, C_2 and C_3 in TEG.

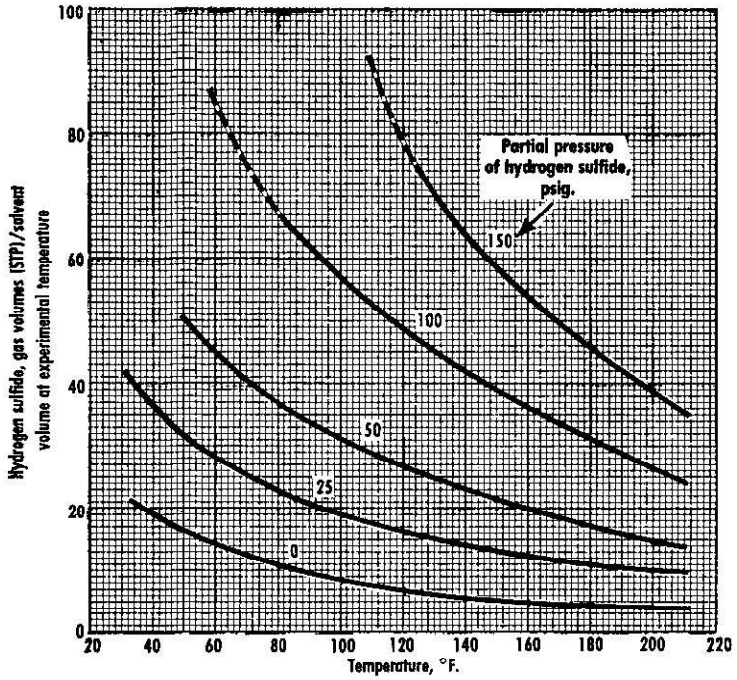


Figure 18.13 Solubility of Hydrogen Sulfide in TEG at Various Partial Pressures [30-230°F][18.8]

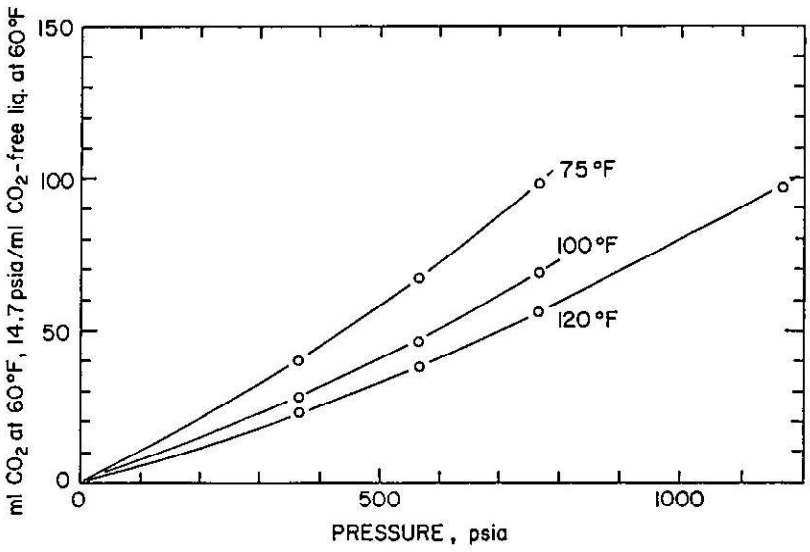


Figure 18.14 CO_2 Solubility in TEG 3.5 wt% H_2O

AROMATIC ABSORPTION

The affimity for aromatics by TEG has long been recognized. The UDEX process was used for many years in refineries and chemical plants to extract aromatic hydrocarbons from paraffins with TEG.

In gas dehydration service, TEG will absorb limited quantities of aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylene) from the gas. these components are often abbreviated as BTEX. Quantifying the absorption levels has become more important in recent years due to increased restrictions on aromatic emissions from glycol units. To date, little published equilibrium data is available.[18.14,18.15]

Based on data from Reference 18.15, predicted absorption levels for BTEX components vary from 5-10% for benzene to 20-30% for ethylbenzene and xylene. Absorption is favored at higher pressures and lower temperatures, and increased TEG concentration and circulation rate.

The bulk of absorbed aromatics will be vented with the water vapor at the top of the regenerator. In some cases these aromatics can be condensed and recovered, however the effectiveness of condensation declines rapidly with increasing stripping gas rates.

In these cases, many operators use a partial condenser to condense the water and pipe the volatile hydrocarbons to an incinerator or to the reboiler as fuel. Back pressure on the regenerator is minimized by the use of an eductor – which is often the fuel gas valve on the reboiler.

Another mitigation measure which looks promising is to strip the aromatics from the TEG with a small stripping gas stream at the flash tank. The stripping vapors are then at a sufficiently high pressure to allow recycling to a compressor or use in a remote fuel gas system.

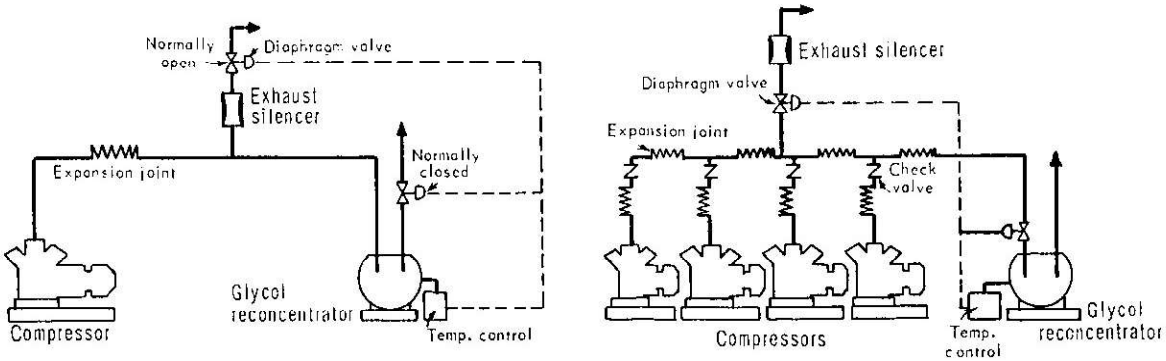
Others have proposed using membranes or activated carbon but these methods are not yet commercial.

This problem is one which requires careful attention in the design phase. Environmental considerations are increasingly driving the selection and operation of process equipment. In some cases the use of a dry desiccant unit (albeit at a higher capital cost) may be a lower cost alternative to glycol given the environmental impact of these BTEX emissions.

CONTROLS

The control system usually is rather simple. A regular displacement type level control is used on the absorber and flash tank. A back-pressure valve on the gas outlet may be required to maintain a stable pressure in the absorber. A manual bypass around the absorber is desirable to aid in the startup and shutdown of the unit. In some units standby methanol injection is provided so that gas flow can be maintained when the unit is down.

In a gas-fired reboiler the use of dual thermostats is very satisfactory. With other heat sources, a controller using only proportional mode usually is satisfactory. Figure 18.15 shows two systems used for waste heat control.



Former method of glycol concentration

Concentrator using two-control-valve arrangement

Figure 18.15 Two Systems Using Waste Heat for Regeneration[18.12]

The right portion of Figure 18.15 also shows some of the controls employed.

Figure 18.16 is a schematic of a glycol unit on a platform involving the separation of water condensate from gas, free water disposal and gas dehydration. A remote monitoring and control system is used for routine operations.

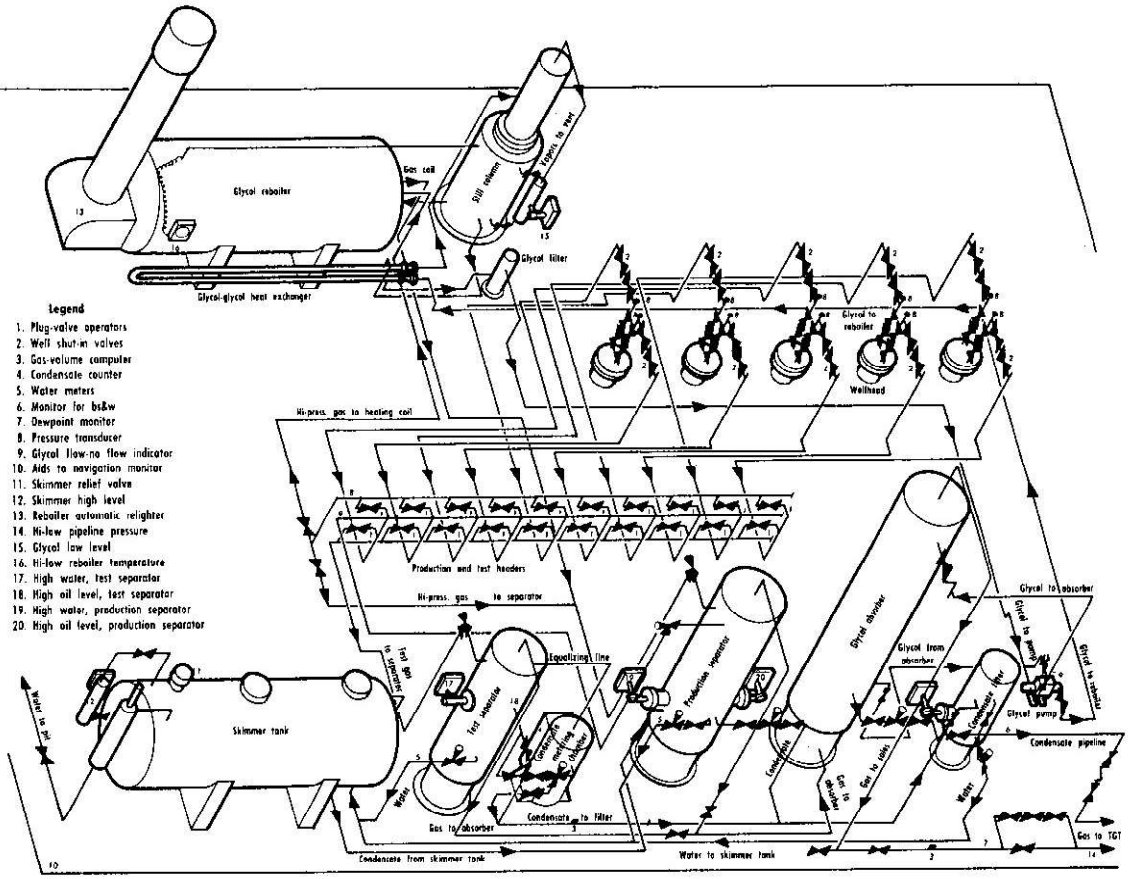


Figure 18.16 Layout of One Offshore Platform for Dehydration[18.13]

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18.14 Fitz, C. W. and Hubbard, R. A., "Quick Manual Calculation Estimates Amount of Benzene Absorbed in Glycol Dehydrator," *OGJ*, (Nov. 23, 1987), p. 72.

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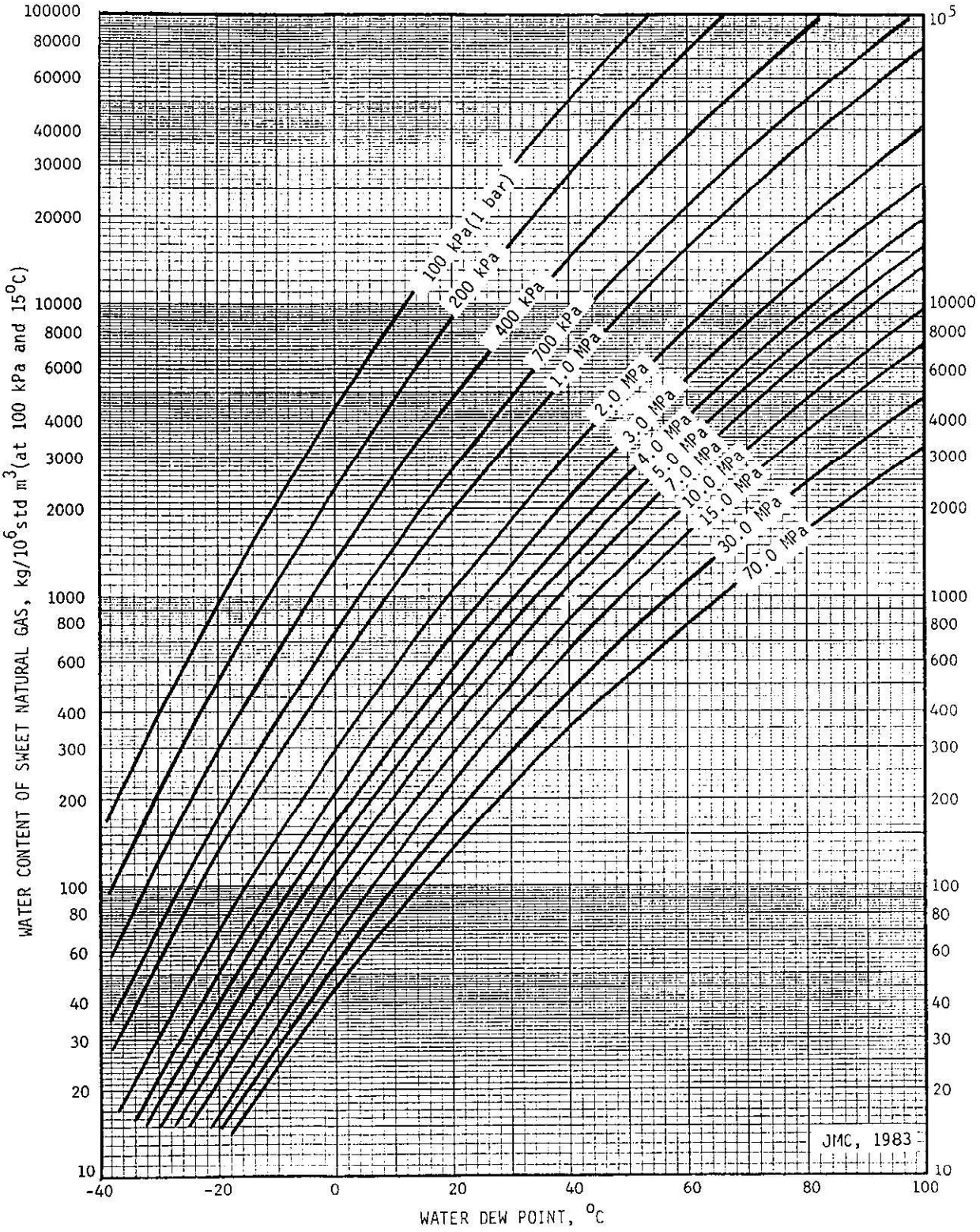
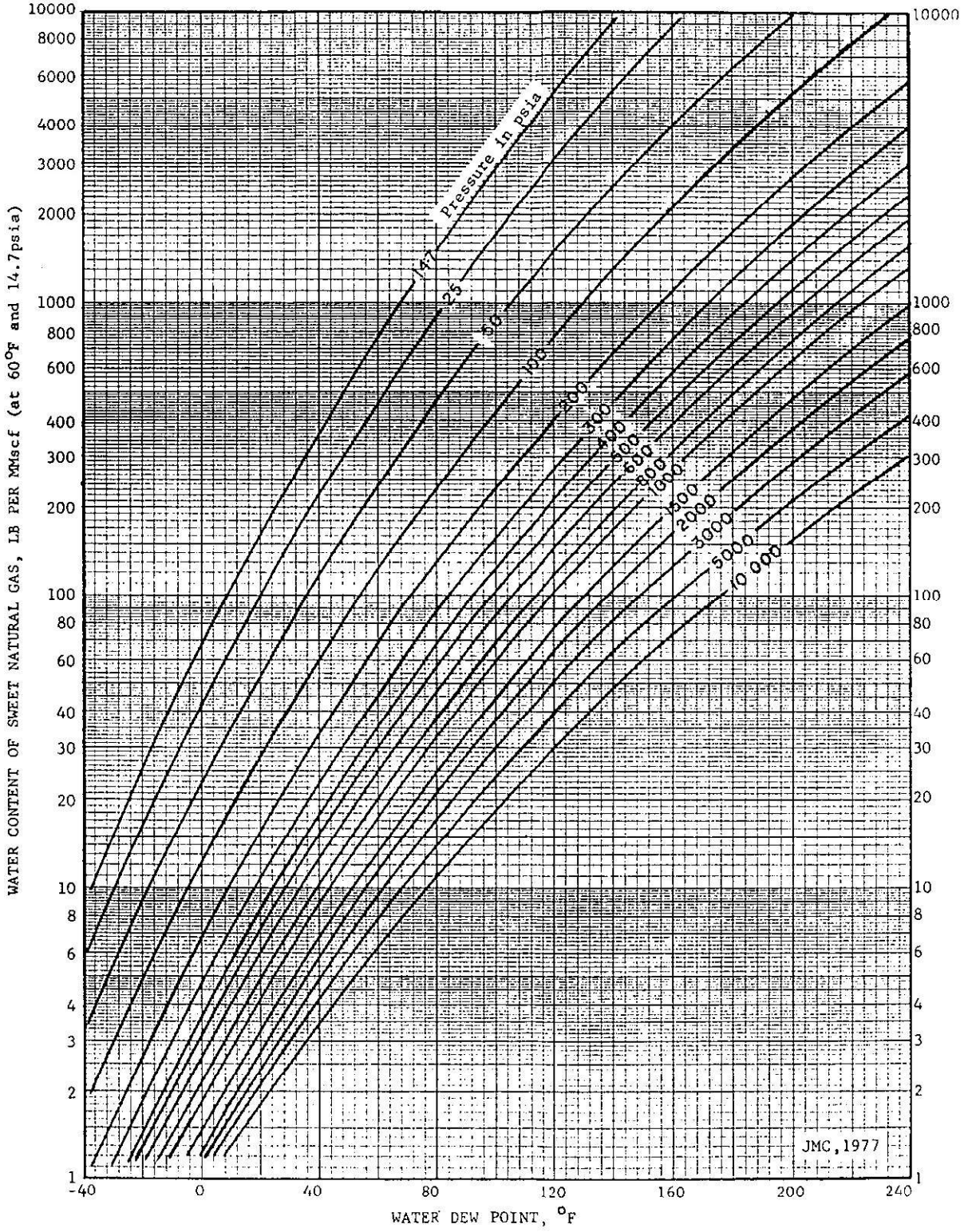
APPENDIX 18A

GLYCOL PROPERTIES AND WATER CONTENT CHARTS FROM CHAPTER 6.



Water Content of Sweet, Lean Natural Gas. (Metric)



Water Content of Sweet, Lean Natural Gas. (English)

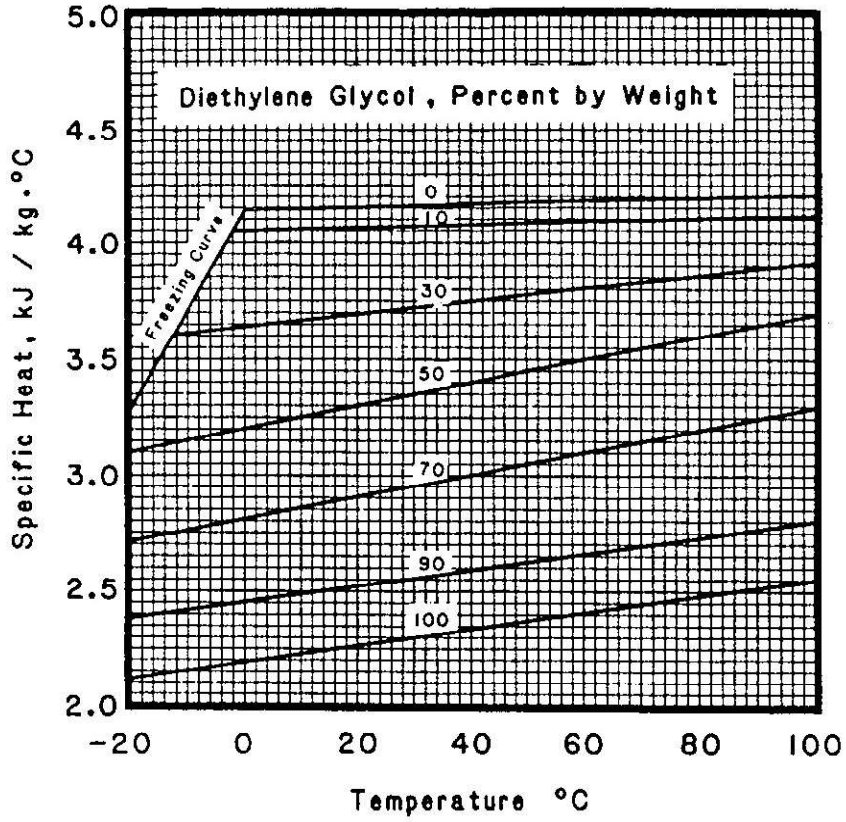
Physical Properties of Glycols

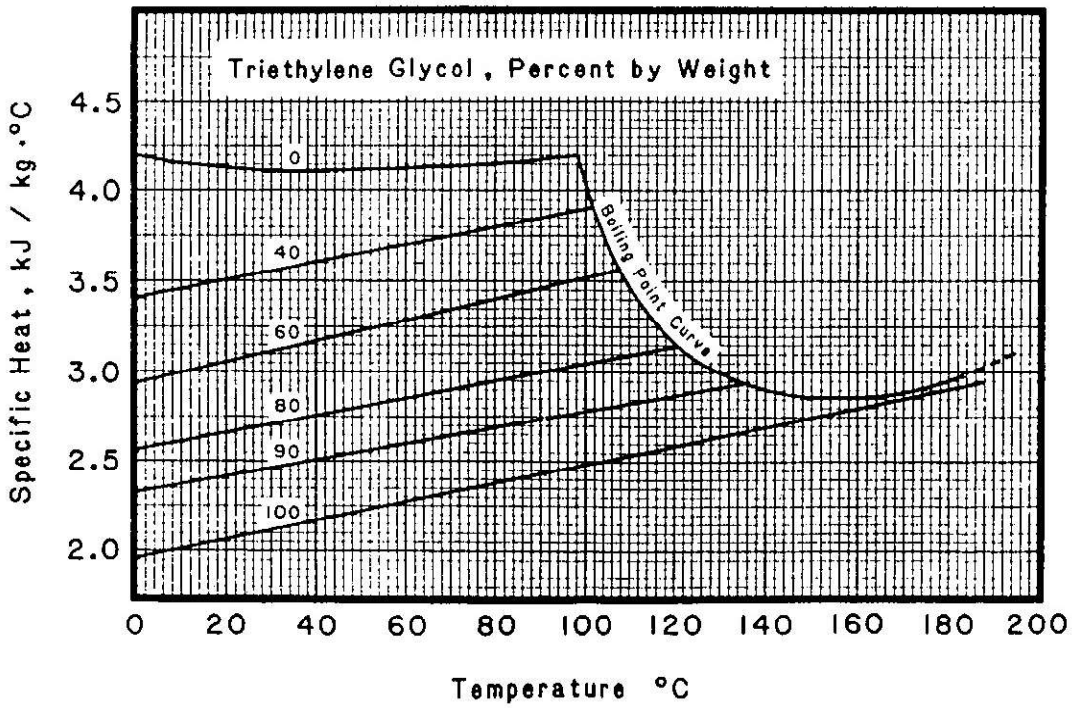
	EG	DEG	TEG
Formula	$C_2H_6O_2$	$C_4H_{10}O_3$	$C_6H_{14}O_4$
Molecular Weight	62.1	106.1	150.2
Boiling Point at 760 mm Hg °F	387.1	472.6	545.9
Boiling Point at 760 mm Hg °C	197.3	244.8	288
Vapor Pressure at 25°C, mm Hg	0.12	0.01	0.01
Density at 25°C , g/cm^3	1.110	1.113	1.119
at 60°C , g/cm^3	1.085	1.088	1.092
Pounds per Gallon at 25°C	9.26	9.29	9.34
Freezing Point, °C	-13	-8	-7
Pour Point, °C	-	-54	-58
Viscosity in Centipoises at 25°C	16.5	28.2	37.3
At 60°C	4.68	6.99	8.77
Surface Tension at 25°C Dynes/cm	47	44	45
Refractive Index at 25°C	1.430	1.446	1.454
Specific Heat at 25°C	0.56	0.55	0.53
Flash Point, °C (COC)	116	138	160
Fire Point, °C (COC)	119	143	166

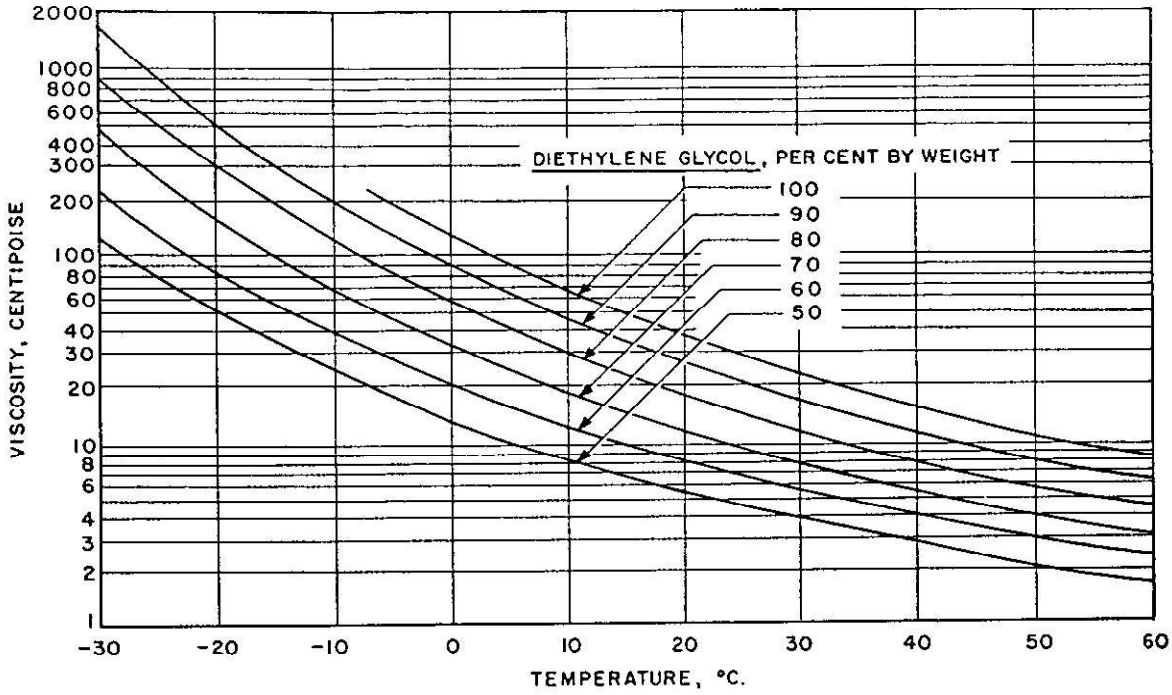
HEAT TRANSFER FACTORS FOR GLYCOL

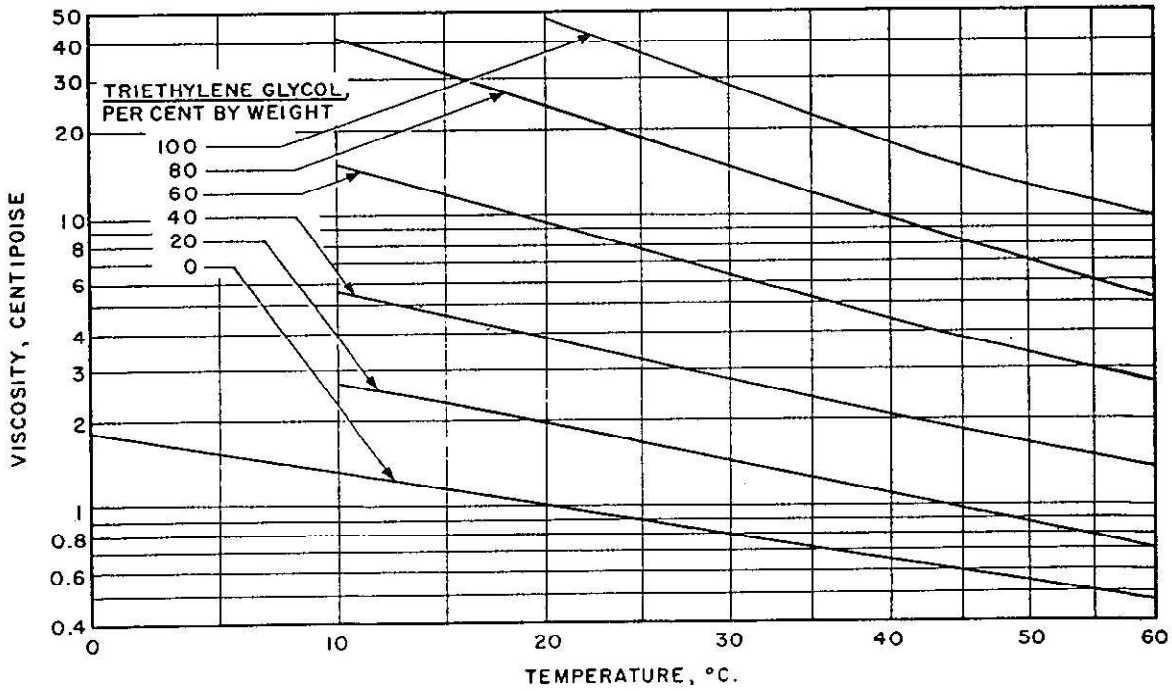
Material	Liquid Heating or Cooling		Vapor Heating or Cooling	Condensing Vapor	Boiling Liquids
	Re < 2100	Re > 2100			
Ethylene Glycol	0.49	0.12	0.60	0.18	0.30
Diethlene Glycol	0.50	0.11	0.60	0.17	0.30
Triethylene Glycol	0.49	0.09	0.60	0.15	0.30

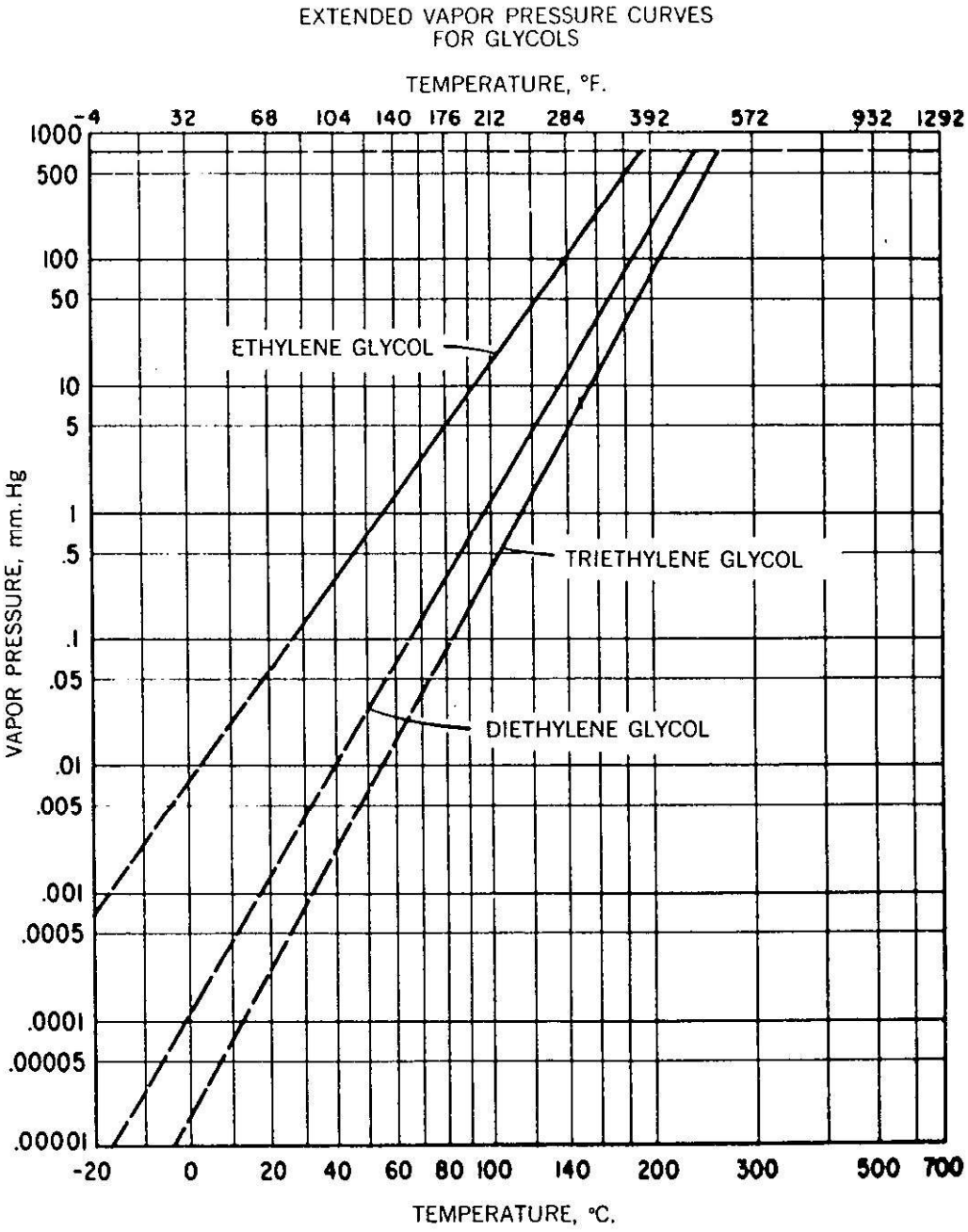
The water factor = 1.0. Multiply heat transfer coefficients for water by the factor shown to obtain glycol coefficient for the service involved.

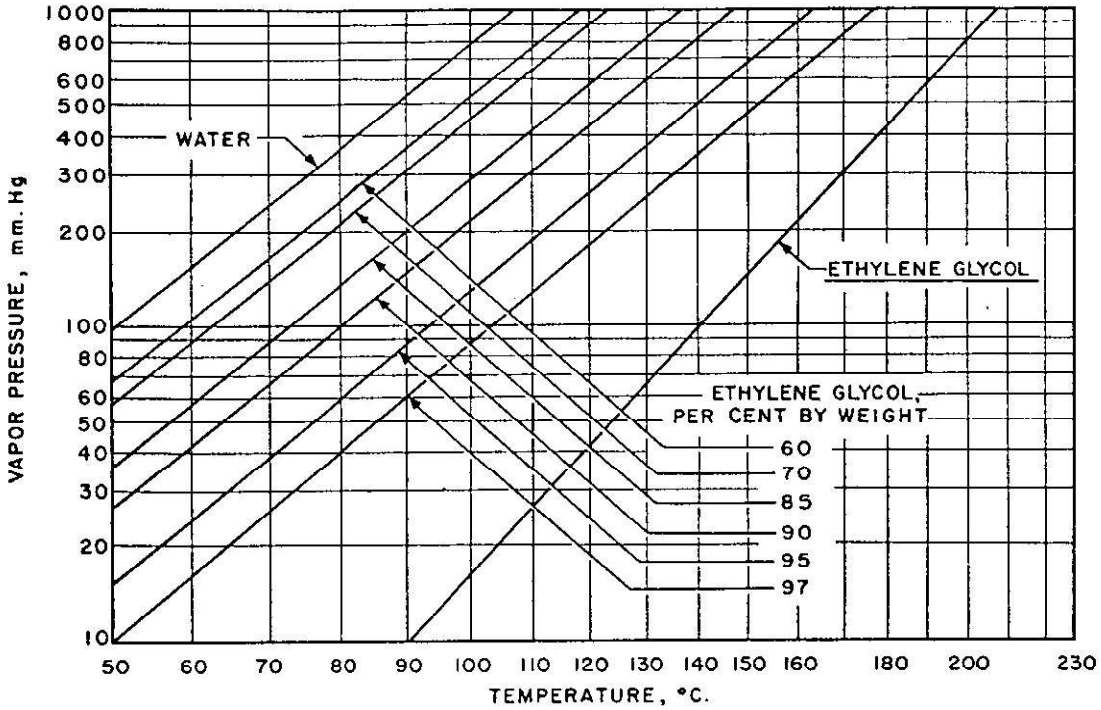

Diethylene Glycol, Percent by Weight
0
10
30
50
70
90
100
Freezing Curve
Specific Heat, kJ / kg.°C
5.0
4.5
4.0
3.5
3.0
2.5
2.0
-20
0
20
40
60
80
100
Temperature °C

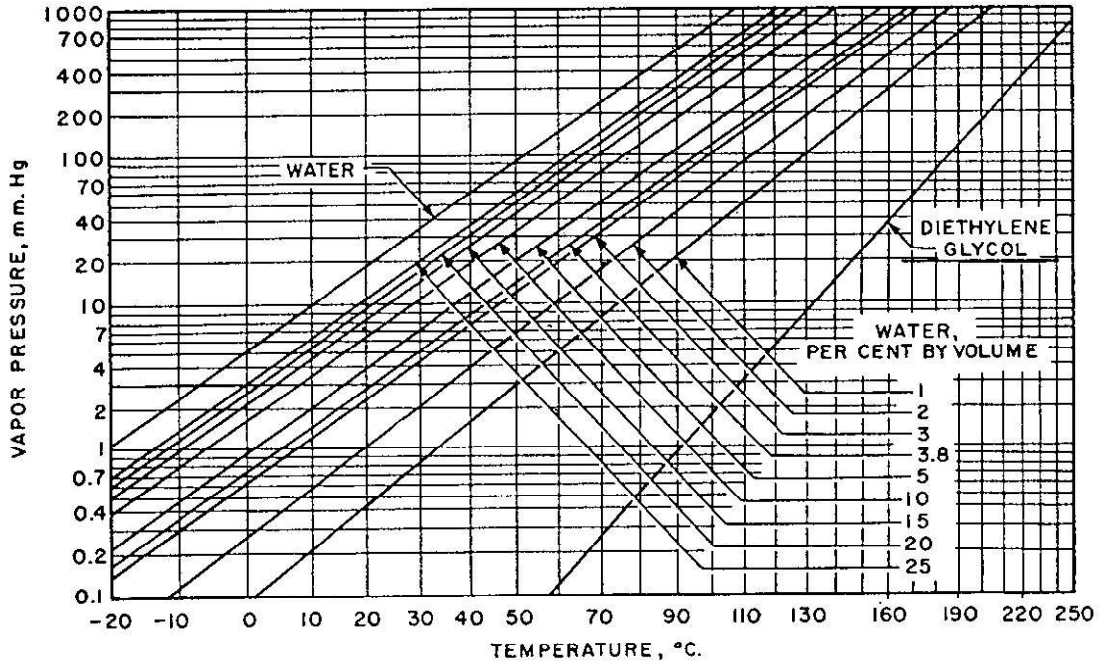

Triethylene Glycol, Percent by Weight
0
40
60
80
90
100
Boiling Point Curve
Specific Heat, kJ / kg.°C
4.5
4.0
3.5
3.0
2.5
2.0
0
20
40
60
80
100
120
140
160
180
200
Temperature °C

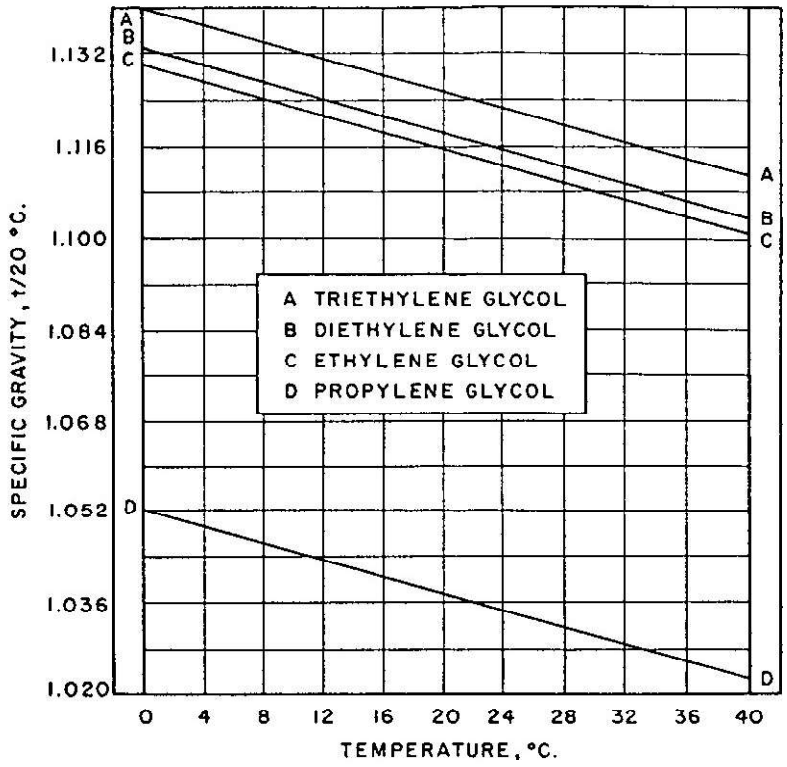

VISCOSITY, CENTIPOISE
2000
1000
800
600
400
300
200
100
80
60
40
30
20
10
8
6
4
3
2
1
DIETHYLENE GLYCOL, PER CENT BY WEIGHT
100
90
80
70
60
50
-30
-20
-10
0
10
20
30
40
50
60
TEMPERATURE, °C.

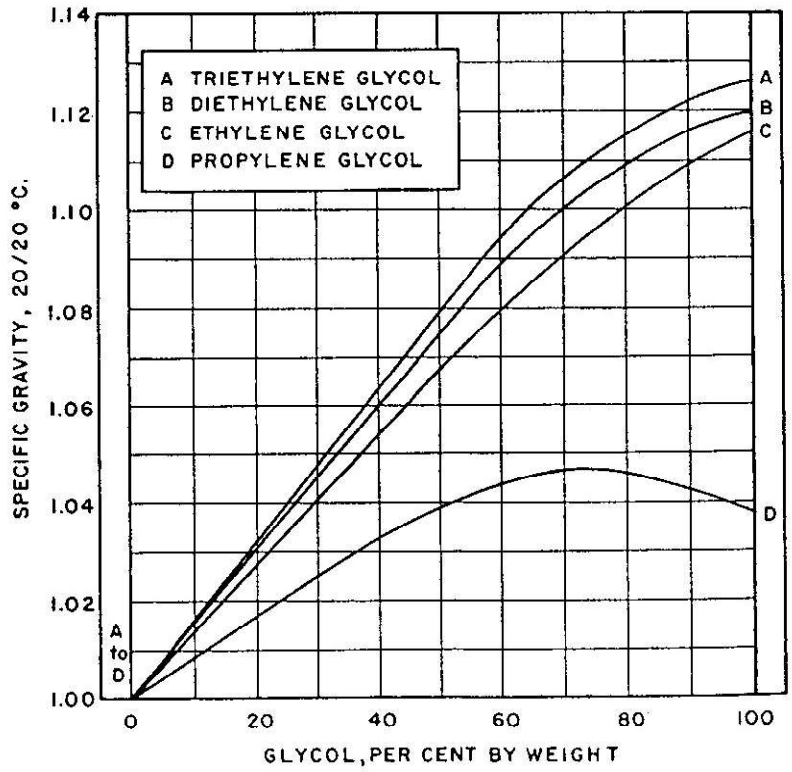

VISCOSITY, CENTIPOISE
50
40
30
20
10
8
6
4
3
2
1
0.8
0.6
0.4
TRIETHYLENE GLYCOL, PER CENT BY WEIGHT
100
80
60
40
20
0
0
10
20
30
40
50
60
TEMPERATURE, °C.

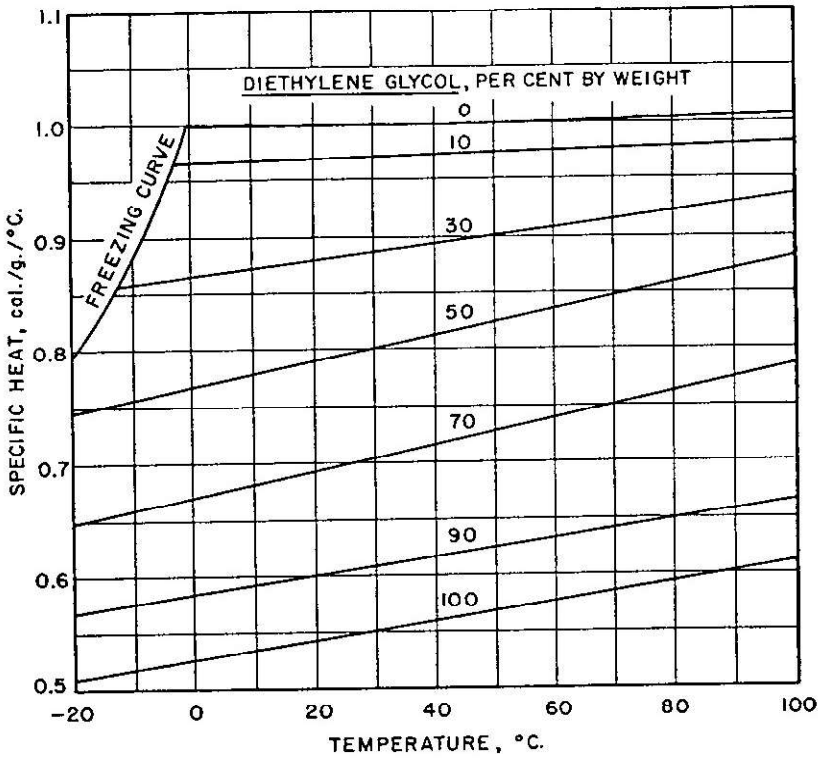

EXTENDED VAPOR PRESSURE CURVES
FOR GLYCOLS
TEMPERATURE, °F.
-4
32
68
104
140
176
212
284
392
572
932
1292
1000
500
100
50
10
5
1
.5
.1
.05
.01
.005
.001
.0005
.0001
.00005
.00001
VAPOR PRESSURE, mm. Hg
ETHYLENE GLYCOL
TRIETHYLENE GLYCOL
DIETHYLENE GLYCOL
-20
0
20
40
60
80
100
140
200
300
500
700
TEMPERATURE, °C.

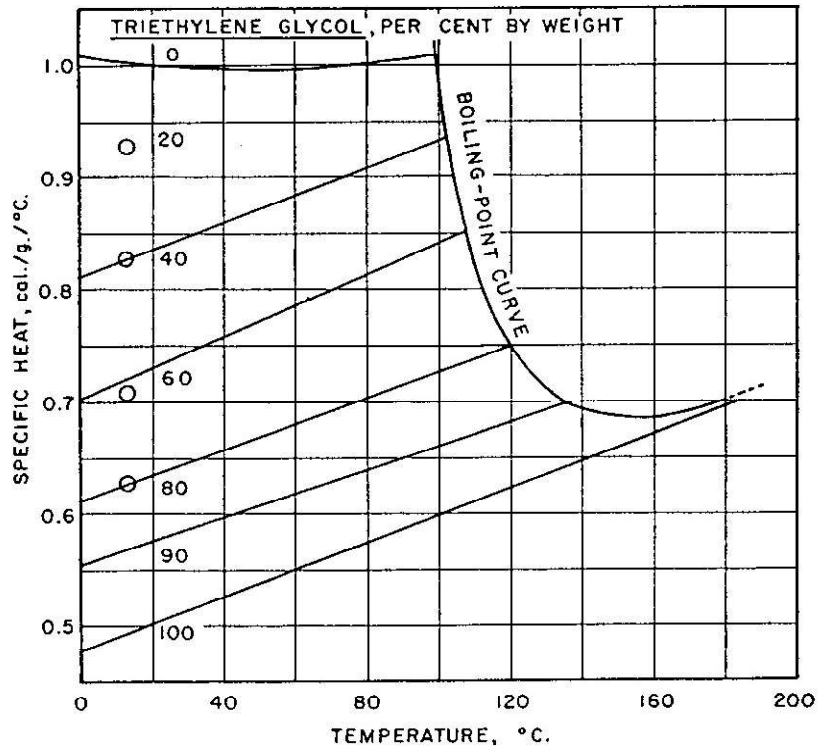

VAPOR PRESSURE, mm. Hg
1000
800
600
500
400
300
200
100
80
60
50
40
30
20
10
WATER
ETHYLENE GLYCOL
ETHYLENE GLYCOL, PER CENT BY WEIGHT
60
70
85
90
95
97
50 60 70 80 90 100 110 120 130 140 150 160 180 200 230
TEMPERATURE, °C.

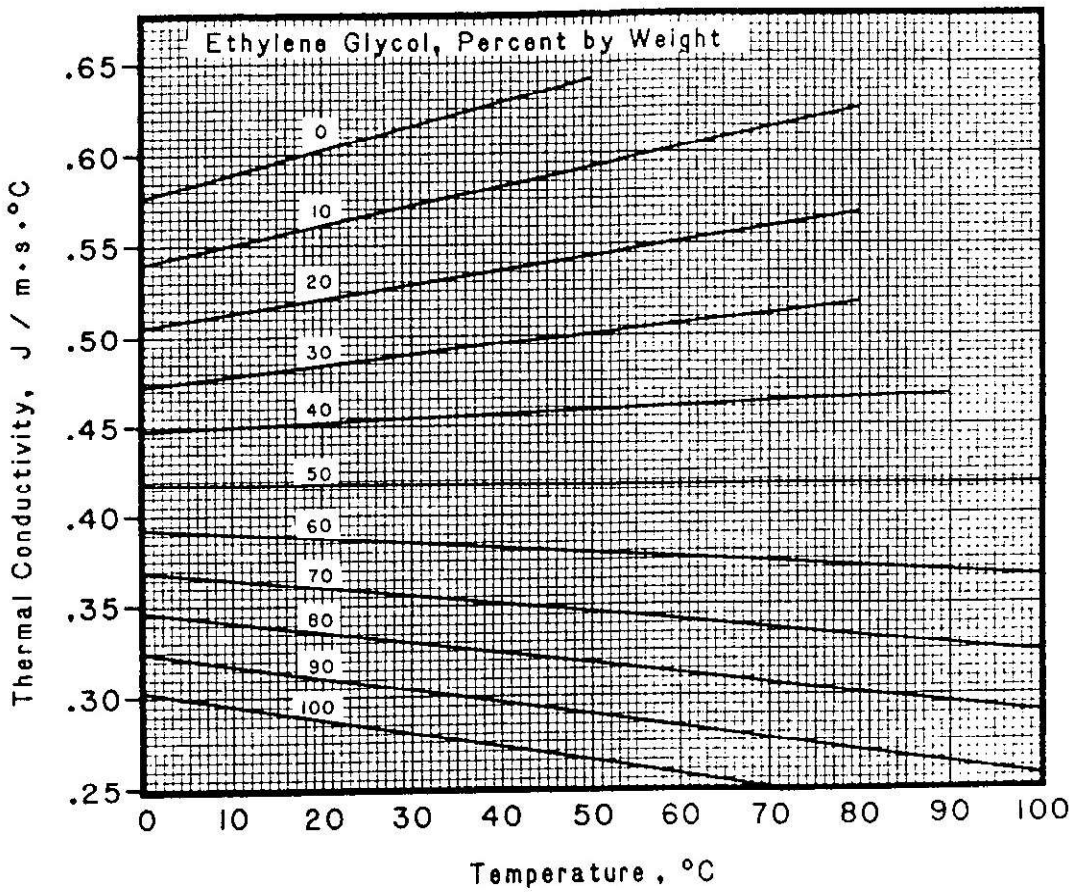

VAPOR PRESSURE, mm. Hg
1000
700
400
200
100
70
40
20
10
7
4
2
1
0.7
0.4
0.2
0.1
WATER
DIETHYLENE GLYCOL
WATER, PER CENT BY VOLUME
1
2
3
3.8
5
10
15
20
25
-20 -10 0 10 20 30 40 50 70 90 110 130 160 190 220 250
TEMPERATURE, °C.

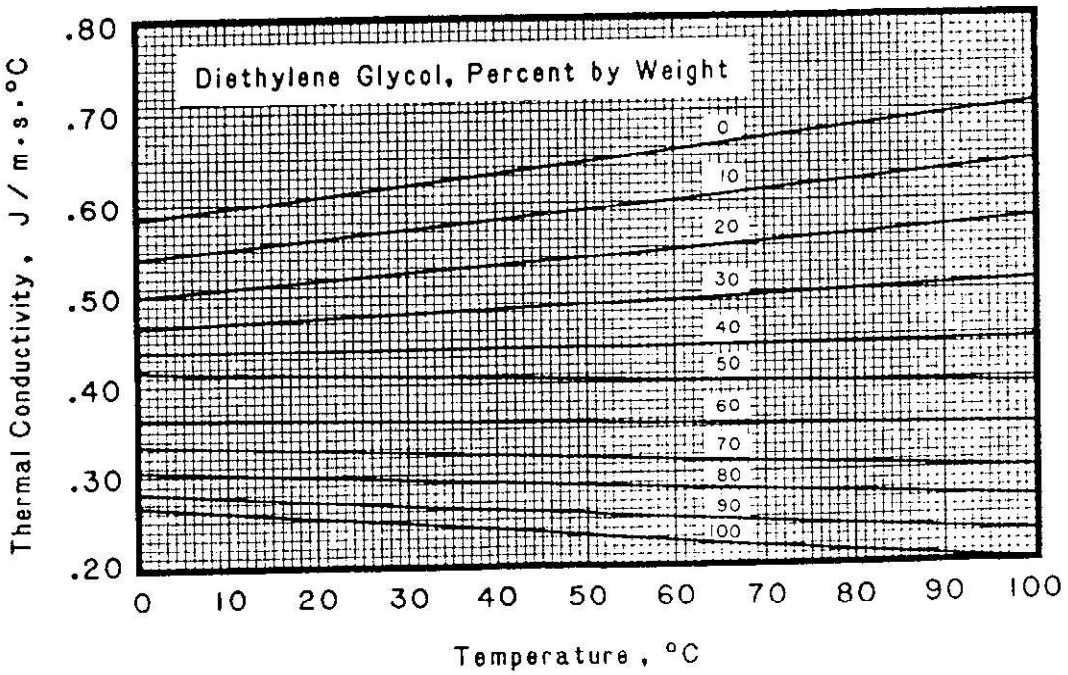

A
B
C
1.132
1.116
1.100
1.084
1.068
1.052
D
1.036
1.020
SPECIFIC GRAVITY, t/20 °C.
A TRIETHYLENE GLYCOL
B DIETHYLENE GLYCOL
C ETHYLENE GLYCOL
D PROPYLENE GLYCOL
A
B
C
D
0 4 8 12 16 20 24 28 32 36 40
TEMPERATURE, °C.

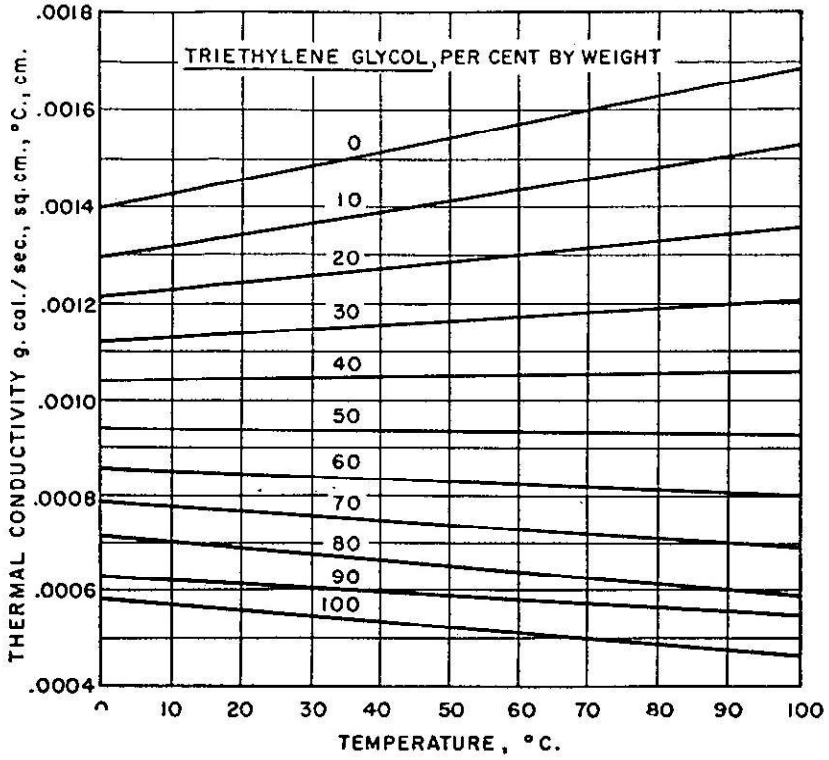

1.14
1.12
1.10
1.08
1.06
1.04
1.02
1.00
SPECIFIC GRAVITY, 20/20 °C.
A TRIETHYLENE GLYCOL
B DIETHYLENE GLYCOL
C ETHYLENE GLYCOL
D PROPYLENE GLYCOL
A
B
C
D
A to D
0 20 40 60 80 100
GLYCOL, PER CENT BY WEIGHT

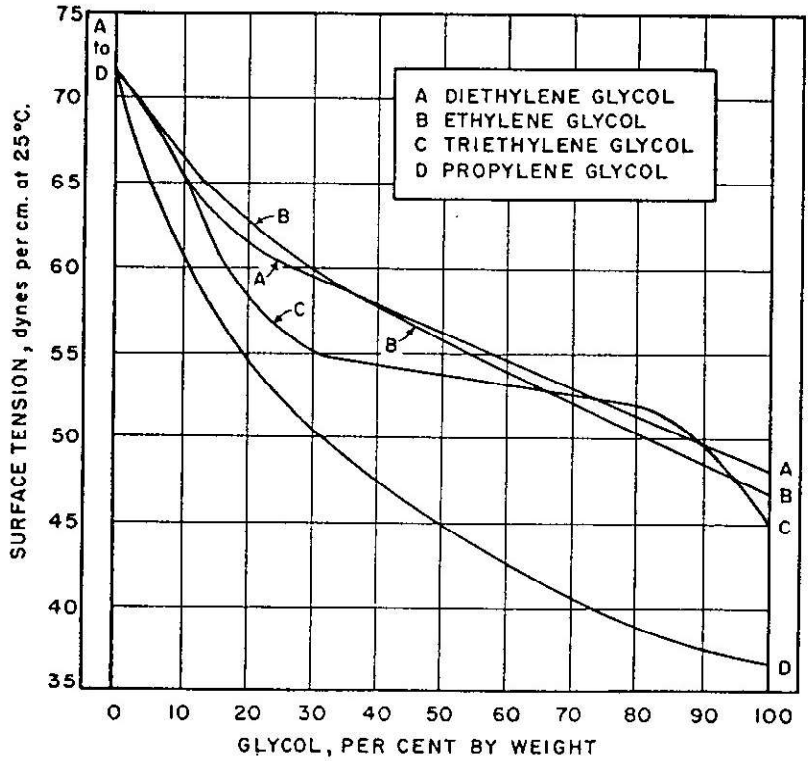

DIETHYLENE GLYCOL, PER CENT BY WEIGHT
0
10
30
50
70
90
100
FREEZING CURVE
SPECIFIC HEAT, cal./g./°C.
1.1
1.0
0.9
0.8
0.7
0.6
0.5
-20
0
20
40
60
80
100
TEMPERATURE, °C.


TRIETHYLENE GLYCOL, PER CENT BY WEIGHT
0
20
40
60
80
90
100
BOILING-POINT CURVE
SPECIFIC HEAT, cal./g./°C.
1.0
0.9
0.8
0.7
0.6
0.5
0
40
80
120
160
200
TEMPERATURE, °C.


Ethylene Glycol, Percent by Weight
0
10
20
30
40
50
60
70
80
90
100
Thermal Conductivity, J / m • s • °C
.65
.60
.55
.50
.45
.40
.35
.30
.25
0 10 20 30 40 50 60 70 80 90 100
Temperature, °C


Diethylene Glycol, Percent by Weight
0
10
20
30
40
50
60
70
80
90
100
Thermal Conductivity, J / m • s • °C
.80
.70
.60
.50
.40
.30
.20
0 10 20 30 40 50 60 70 80 90 100
Temperature, °C


TRIETHYLENE GLYCOL, PER CENT BY WEIGHT
0
10
20
30
40
50
60
70
80
90
100
THERMAL CONDUCTIVITY g. cal./sec., sq.cm., °C., cm.
.0018
.0016
.0014
.0012
.0010
.0008
.0006
.0004
0 10 20 30 40 50 60 70 80 90 100
TEMPERATURE, °C.


A DIETHYLENE GLYCOL
B ETHYLENE GLYCOL
C TRIETHYLENE GLYCOL
D PROPYLENE GLYCOL
A to D
SURFACE TENSION, dynes per cm. at 25°C.
75
70
65
60
55
50
45
40
35
0 10 20 30 40 50 60 70 80 90 100
GLYCOL, PER CENT BY WEIGHT
A
B
C
D

NOTES:

19

ADSORPTION DEHYDRATION AND SWEETENING

Adsorption describes any process wherein molecules from the gas are held on the surface of a solid by surface forces. Adsorbents may be divided into two classes – those which owe their "activity" to surface adsorption and capillary condensation, and those which react chemically. The latter group finds limited application in natural gas processing and will not be discussed herein. The former (physical adsorption) requires use of an adsorbent material which probably has the following characteristics:

1. Large surface area for high capacity.
2. Possesses "activity" for the components to be removed.
3. Mass transfer rate is high.
4. Easily and economically regenerated.
5. Good activity retention with time.
6. Small resistance to gas flow.
7. High mechanical strength to resist crushing and dust formation.
8. Fairly cheap, non-corrosive, non-toxic, chemically inert and possesses a high bulk density.
9. No appreciable change in volume during adsorption and desorption, and should retain strength when "wet."

Any commercial adsorbent will have a total surface area of 500 to 800 sq. meters per gram [2 400 000 to 3 900 000 sq. ft. per lb.]. One pound can easily be held in your cupped hands. This fantastic appearing area is only achieved by producing a material with large interior surface resulting from capillaries or a crystalline-type lattice. The exterior surface of the particles is almost negligible.

The materials which meet the above requirements may be divided into several general categories:

Bauxite – naturally occurring mineral composed primarily of Al_2O_3.
Alumina – a purer, manufactured version of bauxite.
Gels – composed largely of SiO_2 or alumina gel; manufactured by chemical reaction.
Molecular Sieves – a calcium-sodium alumino-silicate (zeolite).
Carbon (charcoal) – a carbon product treated and activated to have adsorptive capacity.

(Only listed are those materials commonly used for bulk treating.)

All but carbon are used for dehydration. Carbon has desirable properties for hydrocarbon removal and adsorption of certain impurities but possesses negligible water capacity. The first four desiccants are listed in the order of their capital cost. As might be expected, the higher-priced materials possess desirable

characteristics that may justify their cost. For one thing, capacity increases with cost, although it is not proportional to it. The final choice must be based on equipment costs, service life, applicability to process needs, etc. Undue preoccupation with initial cost can therefore be misleading. On the other hand, purchasing molecular sieves, the most versatile of the adsorbents, might be equally illogical because of their higher cost. Choosing the proper adsorbent for a given service inevitably involves a rational compromise between cost and need. Too often this choice is made poorly (bias and habit seemingly predominating). The purchaser should actively participate in this choice. (Vendors also suffer from bias and habit.) For routine applications where several materials will suffice, the choice is often not automatic. In most adsorption plants proper design and operation is more critical than choice of adsorbent. A rather abortive attempt to adapt "standard" units to non-standard service accounts for too many of the problems encountered.

Desiccant Properties

Summary of Typical Desiccant Properties

Property	Grade 03 Silica Gel	Mobilbead R	Mobilbead H	H-151 Alumina Gel	F-1 Alumina	4A-5A Molecular Sieves
Surface Area, m^2/g	750-830	550-650	740-770	350	210	650-800
Pore Volume, cm^3/g	0.40-0.45	0.31-0.34	0.50-0.54	0.35	0.21	0.27
Pore Diameter, °A	21-23	21-23	27-28	43	26	(1)
Bulk Density, kg/m^3	721	785	721	833-881	801-881	689-721
Sp. Ht., kJ/(kg·°C)	0.92	1.05	1.05	0.84	1.0	0.96

Notes: (1) Types 4A and 5A contain cavities 11.4°A in diameter with circular openings 4.2°A in diameter (opening size for adsorption). 10^8 angstroms (°A) = 1 cm.

(2) The values in Column 1 of the above table can be converted to English units using the following conversion factors:

Surface area, $ft^2/lbm = 4885 (m^2/g)$
Pore Volume, $in^3/lbm = 27.7 (cm^3/g)$
Bulk Density, $lbm/ft^3 = 0.0624 (kg/m^3)$
Specific Heat, Btu/(lbm-°F) = 0.24 (kJ/kg·°C)

The potential capacity per unit volume is a product of bulk density times the available area for adsorption. In essence, monolayer adsorption occurs. An examination of the above shows why the gels have a higher effective capacity than the aluminas.

The pore opening at the surface of the desiccant must be large enough to admit the molecules being adsorbed to the interior of the particle where most of the surface area exists. In the internal pores of the gels are capillaries of the diameter range shown. With molecular sieves, the internal pores are crystalline cavities larger than the openings on the surface.

In the table following are shown the *nominal diameter* of common molecules involved in hydrocarbon system adsorption. This is called the nominal diameter because the molecules are not spheres and their ability to enter a given size opening depends on their direction of approach. Also, they are flexible and can "squeeze" through an opening to some degree.

Molecule	Nominal Diameter, °A	Molecule	Nominal Diameter, °A	Molecule	Nominal Diameter, °A
Hydrogen	2.4	Hydrogen Sulfide	3.6	Propane	4.9
Carbon Dioxide	2.8	Methanol	4.4	nC_4-nC_{22}	4.9
Nitrogen	3.0	Methane	4.0	iC_4-iC_{22}	5.6
Water	3.2	Ethane	4.4	Benzene	6.7

The various commercial desiccants can be divided into three broad categories: alumina, gel and molecular sieves. Within each are a series of trade names.

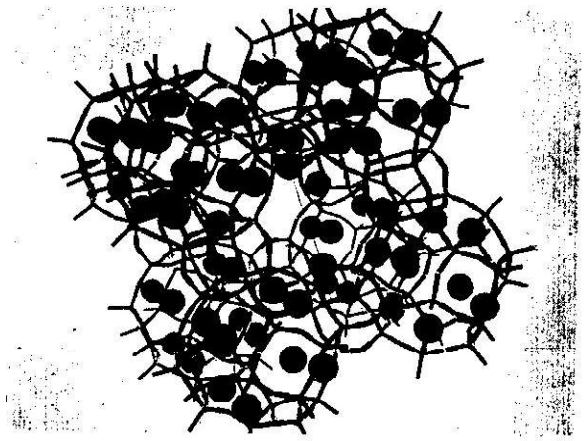
Alumina is a hydrated form of aluminum oxide (Al_2O_3). When manufactured it is essentially iron free. In its natural state (bauxite) it contains varying amounts of iron. It is *activated* by driving off part of the hydrated water adsorbed on the surface. $Al_2O_3 \cdot 3H_2O$ the hydrated version would be heated to from say $Al_2O_3 \cdot 1\ H_2O$, leaving the particle short of its equilibrium water content.

Gel is a granular, amorphous solid. Silica Gel is the generic name for a gel manufactured from sulfuric acid and sodium silicate. It is essentially 100% silicon dioxide (SiO_2). Other gels like *alumina gel* may be largely a form of Al_2O_3. Other gel type desiccants are some combination of these two.

Molecular Sieves are alkali metal crystalline aluminosilicates very similar to natural clays. 4A molecular sieves are composed of Na_2O_3, Al_2O_3 and SiO_2. Types 3A and 5A are produced by ion exchange of about 75% of the Na ions by potassium and calcium ions. Type 10X is produced from 13X by ion exchange of about 75% of the Na ions by Ca ions. All types have a pH of about 10 and are stable in the pH range of 5-12.

The affinity for water is based on the previous environment. However, polarity of the water molecule also plays an important part. Molecular sieves have electric charges on the inner surfaces of the crystal cavities, which are attracted to similar charges on polar molecules. Such molecules, including hydrogen sulfide, ammonia, carbon monoxide, methylamine, and the alcohols, are adsorbed in preference to non-polar molecules. Similarly, molecular sieves show a preference for "unsaturated" hydrocarbons, in which some of the carbon atoms are joined together by double or triple chemical bonds. This is because these compounds contain loosely bound electrons which give them polar characteristics resembling those of water molecules. As an example, if a mixed stream of ethane (a saturated hydrocarbon) and ethylene (an unsaturated hydrocarbon) is passed through a molecular sieve bed, eighty percent of the molecules adsorbed will be ethylene.

The A type sieves have a crystalline zeolite structure consisting of intracrystalline voids as shown at right. All adsorption takes place in these voids. The voids are 11.4 °A in diameter and are connected by openings 4.2 °A in theoretical diameter (pore diameter). The effective pore diameter is determined by the cation and its position in the structure. The maximum diameter of molecules that can enter the crystalline structure and be adsorbed are as follows:



Type	Molecule Diameter - °A
3A – potassium zeolite	3
4A – sodium zeolite	4
5A calcium zeolite	5
10X – calcium zeolite	8
13X – sodium zeolite	10

The X type sieves vary from the A type in the internal character of the crystalline structure. Their adsorption characteristics are the same. The X type can adsorb all molecules adsorbed by the A type with somewhat higher capacity. 13X can adsorb large molecules such as aromatics.

The selective capacity of molecular sieves for different sizes of molecules is important. To a degree, one can exclude those sizes too large to enter the crystal. This is why a 3A or 4A sieve might be used for drying. Sieves are likewise used for high temperatures because their capacity does not decrease as much as gel or alumina above 38°C. Table 19.1 summarizes the characteristics of regular molecular sieves.

TABLE 19.1
Basic Characteristics of Molecular Sieves

Basic Type	Nominal Pore Diameter (Angstroms)	Available Form	Equilibrium H_2O Capacity (% wt)*	Molecules Adsorbed**	Molecules Excluded	Applications
3A	3	Powder 1/16-in. Pellets 1/8-in. Pellets	23 20 20	Molecules with an effective diameter <3 angstroms, including H_2O and NH_3	Molecules with an effective diameter >3 angstroms, e.g. ethane	The preferred Molecular Sieve adsorbent for the comercial dehydration of unsaturated hydrocarbon streams such as cracked gas, propylene, butadiene, and acetylene. It is also usedfor drying polar liquids such as methanol and ethanol.
4A	4	Powder 1/16 in. Pellets 1/8-in. Pellets 8 x 12 Beads 4 x 8 Beads 14 x 30 Mesh	28.5 22 22 22 22 22	Molecules with an effective diameter <4 angstroms, including ethanol, H_2S, CO_2, SO_2, C_2H_4, C_2H_6, and C_3H_6	Molecules with an effective diameter >4 angstroms, e.g. propane	The preferred Molecular Sieve adsorbent for static dehydration in a closed gas or liquid system. It is used as a static desiccant in household refrigeration systems; in packaging of drugs, electronic components and perishable chemicals; and as a water scavenger in paint and plastic systems. Also used commercially in drying saturated hydrocarbon streams.
5A	5	Powder 1/16-in. Pellets 1/8-in. Pellets	28 21.5 21.5	Molecules with an effective diameter <5 angstroms, including n-C_4H_9OH**, n-C_4H_{10}**, C_3H_8 to $C_{22}H_{46}$, R-12	Molecules with an effective diameter >5 angstroms, e.g. iso compounds and all 4 carbon rings	Separates normal paraffins from branched-chain and cyclic hydrocarbons through a selective adsorption process.
10X	8	Powder 1/16-in. Pellets 1/8-in. Pellets	36 28 28	Iso paraffins and Olefins, C_6J_6, Molecules with an effective diameter <8 angstroms	Di-n-butylamine and larger	Aromatic hydrocarbon separation
13X	10	Powder 1/16-in. Pellets 1/8-in. Pellets	36 28.5 28.5	Molecules with an effective diameter <10 angstroms	Molecules with an effective diameter >10 angstroms, e.g. $(C_4F_9)_3N$	Used commercially for general gas drying, air plant feed purification (simultaneous removal of H_2O and CO_2) and liquid hydrocarbon and natural gas sweetening (H_2S and mercaptan removal).

For acid environments where the pH of the adsorbed water is below 5, AW300 and AW500 are used. These molecular sieves have the following properties.

Properties	AW300	AW500
Bulk Density, kg/m^3	888	728
Pellet Density, kg/m^3	1386	1165
Nominal Pore Size, °A	4	4
Avg. Heat of Adsorption, kJ/kg	3377	3377
Sp. Ht., kJ/kg·°C	0.63 at –51°C 0.80 at 38°C 1.00 at 238°C	

Desiccant Choice

The choice is primarily an economic exercise. The aluminas are the cheapest but require larger towers for a given water load, which increases capital cost and heat load. Molecular sieves are the most versatile but they are many times more expensive than gel or aluminas relative to their capacity for water. In effect, sieves have to be justified by factors like high inlet gas temperature, sour gases, outlet dewpoints that are below those of other desiccants and more selective separation requirements.

Any desiccant containing significant amounts of iron, like bauxite, is not very suitable for hydrocarbon streams that contain even trace (but measurable) amounts of sulfur compounds. Silica gel is a very suitable desiccant for use with low percentages of sulfur compounds. In any case where the pH of the adsorbed water will be 5 or less, an AW type sieve must be used.

Pressure Loss

The pressure drop across the entire unit normally is specified. Use a realistic value, not just some standard specification plucked from a file drawer. Unit cost is sensitive to pressure drop.

The pressure loss across the bed should be trivial compared to that across the unit. Most of it is in the piping manifold, switching valves and across controls. Allowing a higher pressure drop enables the designer to reduce the size of these components.

THE BASIC SYSTEM

Figure 19.1 shows the simplest dry desiccant system. It consists of two towers containing desiccant. One is drying while the other is regenerating.[19.1] During regeneration all adsorbed materials are desorbed by heat to prepare the tower for its next cycle on-stream.

At the time shown, Tower 2 is drying. The main gas stream flows into the top of the tower and out the bottom. The filter shown is not used in all systems. As later discussions will detail, the regeneration cycle consists of two parts – heating and cooling. During the heating portion the regeneration gas is heated to 200-315°C [400-600°F]. The temperature depends on the desiccant being used and the character of the material being adsorbed.

The regeneration gas by-passes the heater to cool down the bed once the desiccant bed has been heated to the desired level. This cooling normally ceases when the bed is 10-15°C [18-27°F] higher than the inlet gas temperature.

The regeneration gas leaving the tower is cooled to condense the materials desorbed. After these are separated the gas usually returns to the main inlet gas stream. This regeneration gas will be 5-15% of the total throughput, with 10% being a good average. In gas dehydration, flow normally is always downward because of the higher allowable velocity in this direction. Upward regeneration is preferred even though it requires more valves and piping. Most bed contamination occurs at the top. By regenerating upward, the "steam" produced from the lower part of the bed helps remove the contamination. It can be removed without spreading throughout the bed. Cooling is optional. Upflow cooling saves two switching valves per tower (since unheated regeneration gas may be used), but requires dry gas. Downflow cooling (same direction as adsorption) is preferred if the cooling gas contains water.

There are three basic sources of regeneration gas in gas dehydration:

1. Inlet gas.
2. A closed cycle separate from the stream being dehydrated.
3. Dry effluent (tail) gas from the unit.

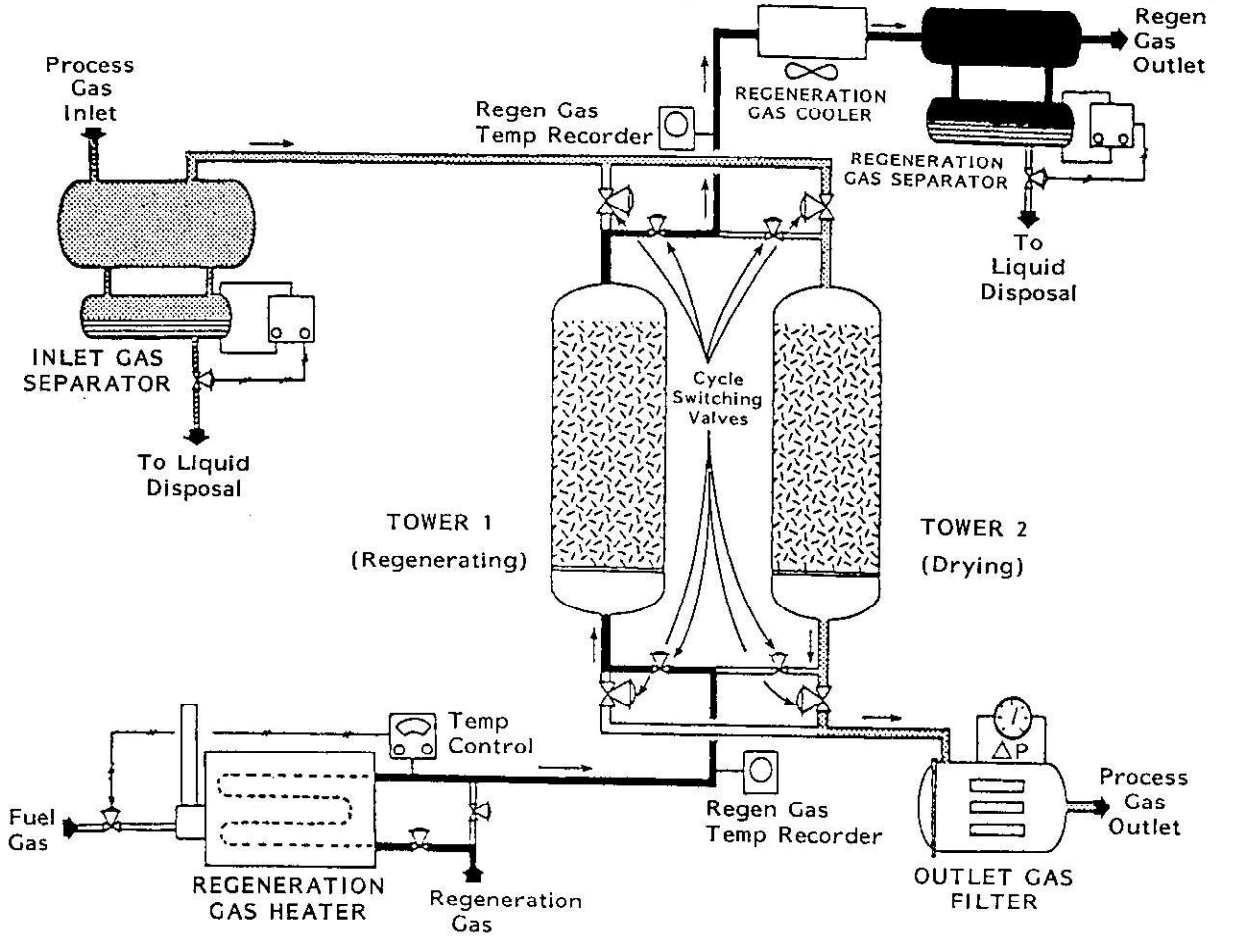
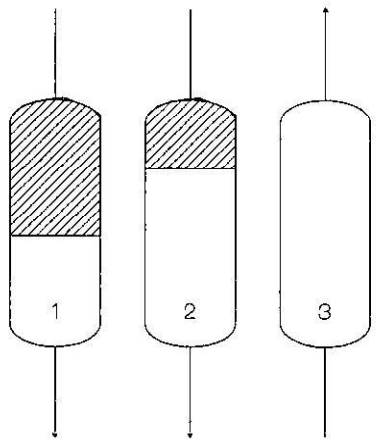


Figure 19.1 Flow Sheet of a Basic Two-Tower Dry Desiccant Unit

(1) involves some degree of re-saturation of the bed during cooling which limits the minimum water dewpoint achievable; (2) requires a separate piping system, and a compressor, and is not used very often; (3) is the most efficient, more costly than (1), but the norm in cryogenic drying service.

Most large dry desiccant units for natural gas drying contain more than two towers to optimize the economics. One design factor is the number of towers.

There are several ways one can use multiple towers. As shown in the illustration below using three towers, two are in-stream in parallel with the third being regenerated and cooled.



In this illustration, the shaded area inside towers 1 and 2 shows the progress of water adsorption in the bed or the portion of the bed which is essentially saturated with water. Below this area, the desiccant is capable of adsorbing more water. The bottom of this area represents the position of the adsorption front as it moves down through the bed with time.

The front in bed 1 is lower than in bed 2 because it has been on stream longer. When the leading edge of this front reaches the outlet, bed 1 will be switched to regeneration and beds 2 and 3 will be on

stream. Thus, at any one time, the two dehydrating towers possess different degrees of saturation. By the time bed 2 is ready for regeneration, bed 1 must be ready to go back on-stream.

The operating sequence of the towers on stream is:

1 and 2, 2 and 3, 1 and 3, 1 and 2, ad infinitum.

A similar arrangement could be used with four towers, with three on stream at a time. Obviously, the flow arrangement affects the cycle time chosen.

Figures 19.2 and 19.3 show a different use of a three-tower system as well as illustrating different regeneration/cooling arrangements.

Figure 19.2(a) uses by-passed wet gas for regeneration in what is called an open cycle. A portion of this wet gas is by-passed and goes to the tower which has been regenerated but is ready for cooling. The bed being cooled pre-heats the gas to the heater to save on fuel. The gas leaves the heater at a temperature suitable for regeneration and enters the top of the wet tower ready for regeneration. The gas leaving flows to a condenser-cooler. Liquids formed are separated and the gas returns to the inlet main gas stream. This cooling/heating process uses the least amount of equipment, gives maximum heat efficiency and minimizes pressure drop. However, the condensation efficiency is not as high as for some other arrangements.

In Figure 19.2(b) the regeneration gas is heated, enters the regenerating tower, is cooled and then enters the tower requiring cooling. The warmed gas leaving the tower exchanges heat with the entering regeneration gas and then returns to the main stream. This heating/cooling system has a better condensation efficiency than cooling/heating. However, it requires an extra heat exchanger. It also pre-saturates the bed being cooled more than the cooling/heating system.

Figure 19.3(a) shows the use of inlet gas for regenerating and the effluent gas for cooling. In this system complete regeneration must be achieved before cooling a bed or desorbed components can enter the plant outlet. It requires more equipment than any of the other processes and uses more regeneration gas. This must be justified by good condensation efficiency and reduced pre-saturation. The latter may be particularly important if recovery of the lighter hydrocarbons is desired.

Figure 19.3(b) uses closed cycle regeneration with effluent gas cooling. Closed cycle regeneration offers the advantage of very good condensation efficiency. It has been found that placing the tower to be cooled in the closed cycle is an unsatisfactory practice. The closed cycled obviously is more complex and more expensive but it may sometimes be justified for hydrocarbon dewpoint control.

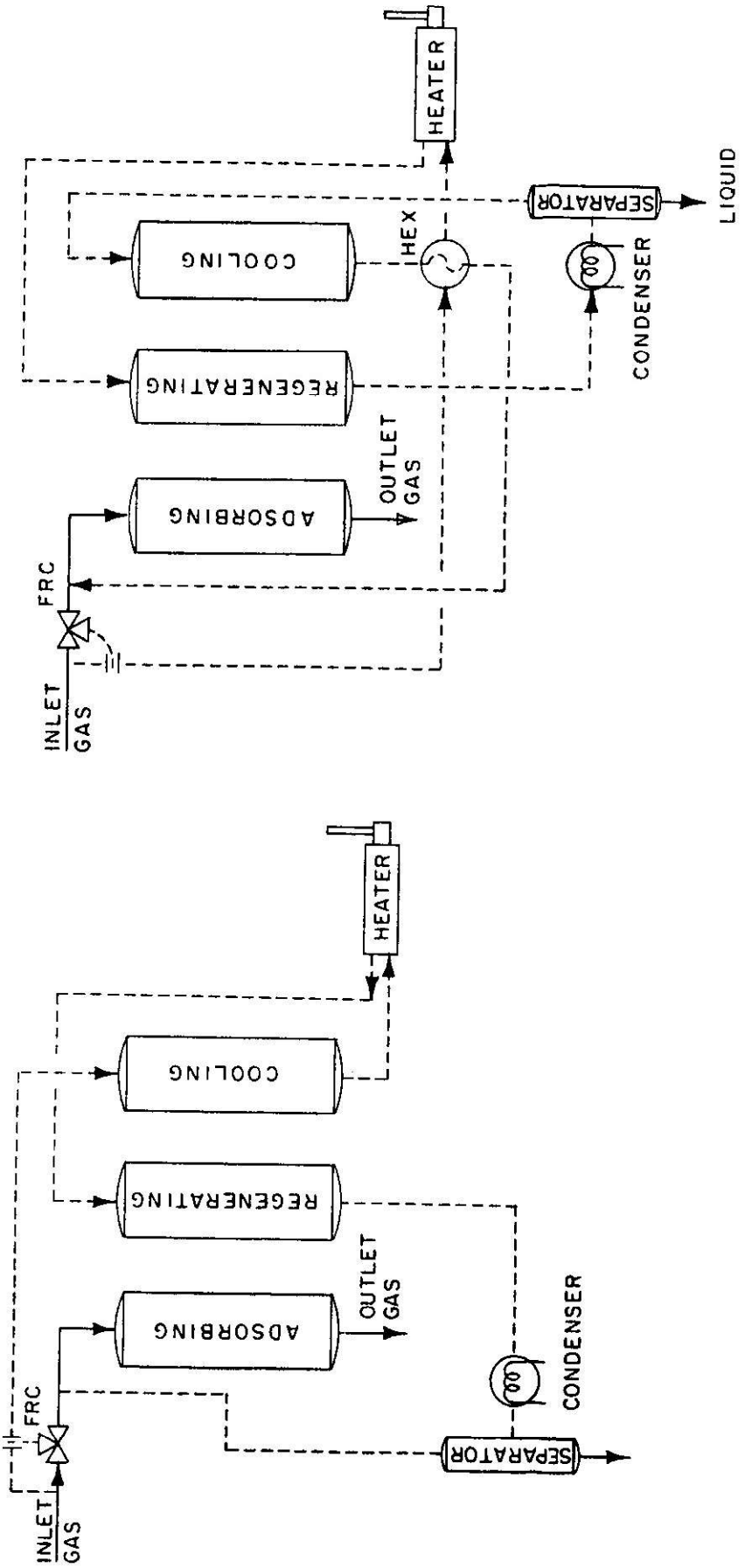
Shown on page 376 is a piping manifold for a three tower plant using a general configuration like that shown in Figure 19.2 and 19.3. Two-way valves are shown. Three-way valves are sometimes used, but are not recommended. This illustrates the basic type of layout required. It is important that the valves not leak.

All of these systems shown regenerate at essentially full line pressure, using hot gas. In some small units it may be feasible to use heating coils imbedded in the bed. In this case, enough carrier gas must be used to carry out the water vapor formed.

One can also reduce tower pressure to regenerate. Some air driers use this approach, which requires no heater. Carrier gas is needed to once again carry out the water vapor. One must reduce pressure slowly enough to eliminate desiccant breakage. This approach has not been used, so far as I know, for large natural gas driers.

One of the major operating costs in dry desiccant plant is for heater fuel. if it is available, waste heat may be used. Another improvement over traditional efficiency may be obtained by use of better insulations of towers, piping and valves.

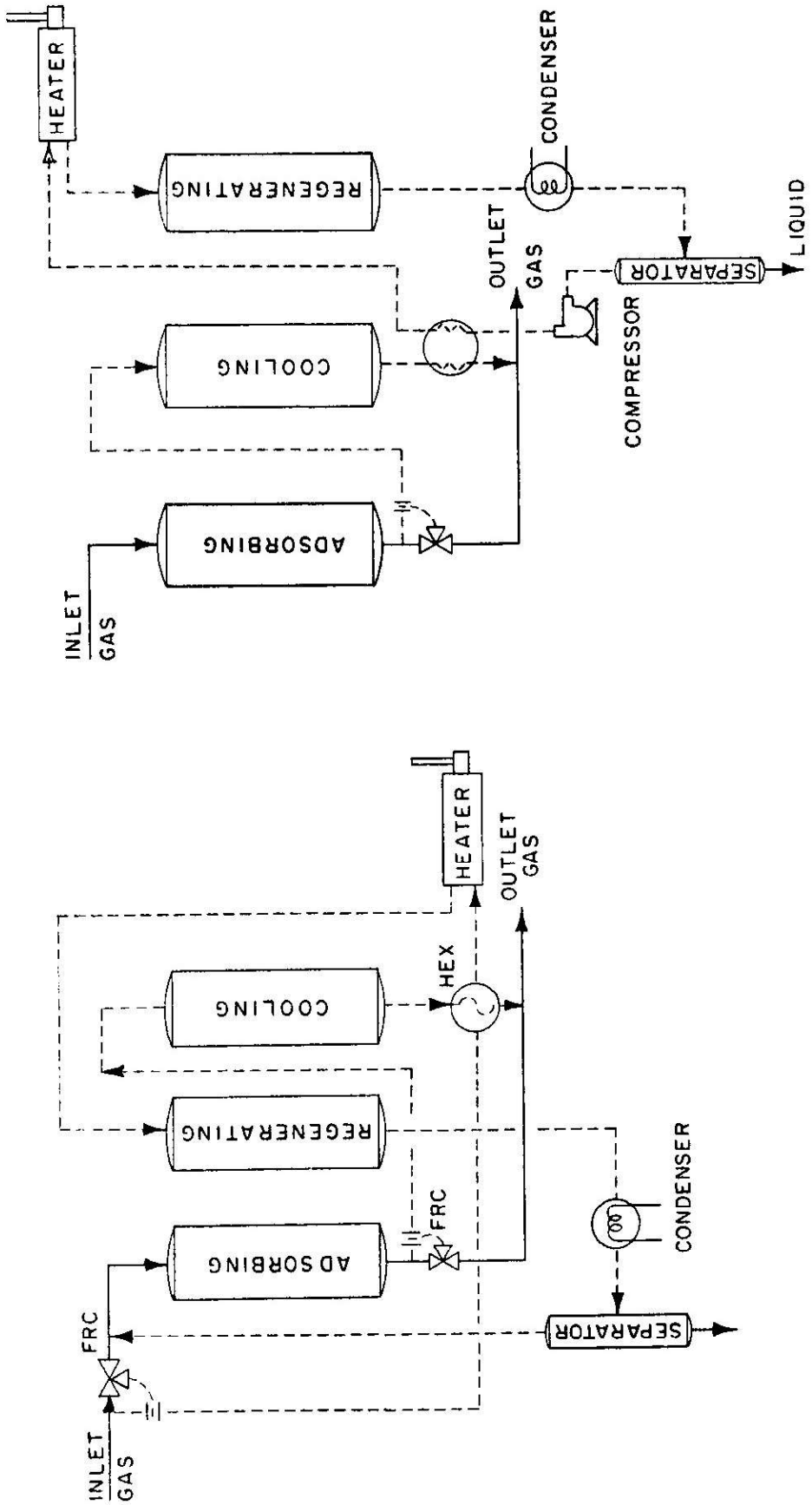
A more detailed discussion of desiccant plants and their operations is available in Reference 19.1.



(a) Schematic view of a typical three-tower plant using open cycle wet gas cooling and heating on regeneration in that order

(b) Schematic view showing open cycle wet gas heating and cooling on regeneration in that order

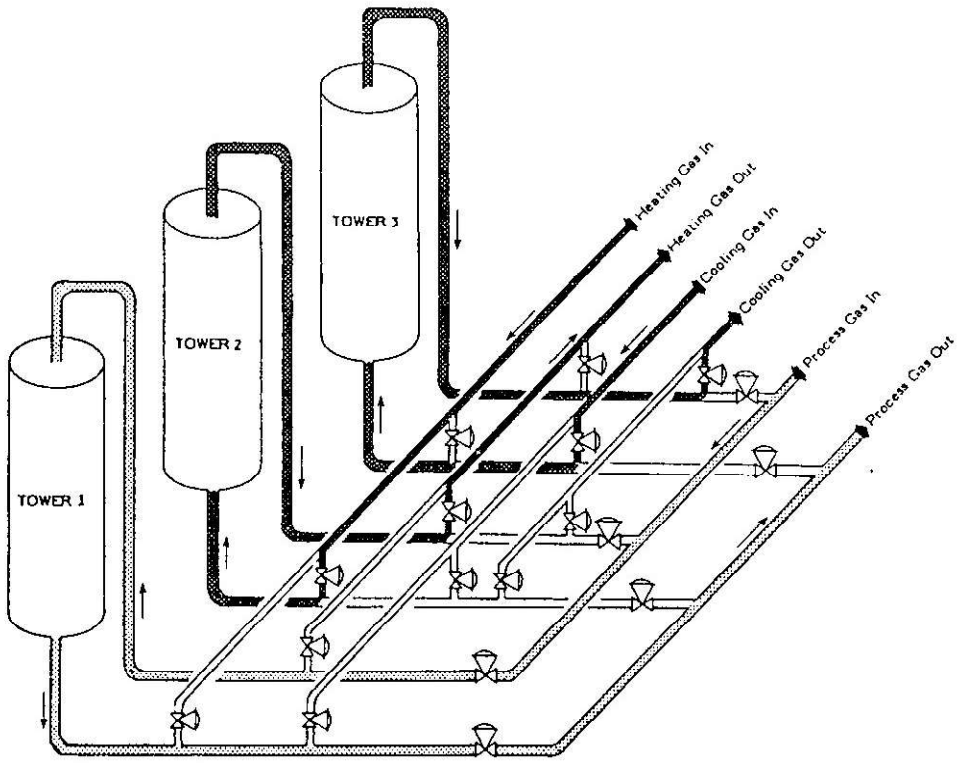
Figure 19.2 Two Possible Configurations of a Three-Tower Plant



(a) Schematic view showing open cycle wet gas heating and effluent gas cooling

(b) Schematic view of closed cycle regeneration using effluent gas cooling

Figure 19.3 Two Further Possible Configurations of a Three-Tower Plant



Pipe Manifold for 3-Tower Adsorber Plant
Tower 1 is Adsorbing, Tower 2 is Heating, and Tower 3 is Cooling

THE REGENERATION CYCLE

Figure 19.4 is a temperature-time plot of the type obtained from a dry desiccant plant. The specific plot is for a two-tower plant of the type shown in Figure 19.1 when using an 8-hour cycle.

At first, the entering gas loses its heat primarily to "heat up" the vessel contents (plus the vessel itself if no internal insulation is used). At about 120°C [248°F], the water will start vaporizing and the curve flattens, while most of the heat input goes into such vaporization. It is often assumed in design that all of the water desorbs at an average temperature of about 125°C [257°F], which is designated by point T_B.

Following desorption, the outlet bed temperature starts rising again. The process of heating is terminated when the desired outlet temperature is reached. In the simplest plants, the heater is simply by-passed and cool gas enters the bed to prepare it for switching to drying service. In this scheme, the gas used is near saturation. Pre-saturation of the bed with water will occur as the bed cools. Cooling should be terminated at 50-55°C [122-131°F] to minimize this problem. In more complex plants dry exit gas or some outside source is used for cooling to minimize pre-saturation. In low temperature plants, one of the dry, process streams may be used. The bed is used as a kind of regenerative heat exchanger.

When using cycle lengths above 4 hours, good regeneration usually can be obtained with a maximum exit gas temperature of 180-205°C [350-400°F] for silica gel and 275-300°C [530-570°F] for molecular sieve. The final heating is necessary to remove the "heel" from the bed – the heavy hydrocarbons and contaminants that do not vaporize at lower temperatures. The minimum temperature possible should be used to minimize heat load and fuel consumption. A good operator will find this optimum temperature by trial and error.

The nomenclature used in this figure will be used later when outlining a regeneration cycle calculation. Although Figure 19.4 is for an 8-hour cycle, the relative time for heating and cooling is indicative of any cycle above 4 hours in a gas dehydrator.

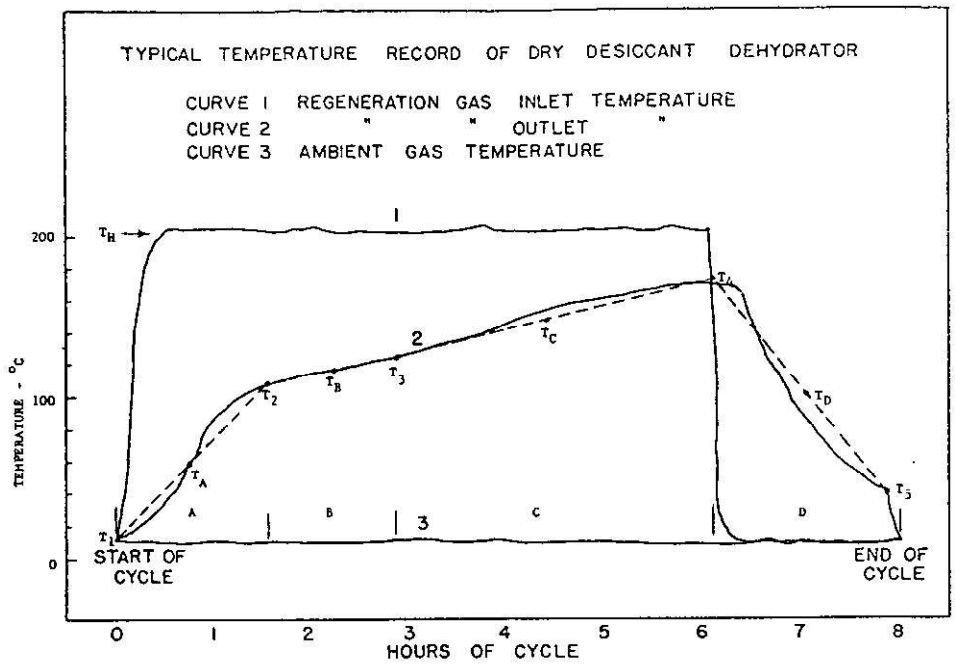


Figure 19.4 Temperature Curves for a Two-Tower Plant

Table 19.2 summarizes the characteristics and common regeneration practices in gas dehydration.

THE NATURE OF ADSORPTION

Figure 19.5(a) illustrates the basic behavior of an adsorbent bed in gas dehydration service. During normal operation in the drying (adsorbing) cycle, three separate zones exist in the bed: 1) equilibrium zone, 2) mass transfer zone (MTZ), and 3) active zone.

In the equilibrium zone the desiccant is saturated with water. It has reached its equilibrium water capacity based on inlet gas conditions and has no further capacity to adsorb water.

Virtually all of the mass transfer takes place in the MTZ. A concentration gradient exists across the MTZ. This is illustrated in Figure 19.5(b) for various times throughout the cycle. Curves 1-3 show the formation of the MTZ; curve 4 reflects the concentration gradient for the MTZ position in Figure 19.5(a). Curve 6 shows the concentration gradient at breakthrough. Notice the adsorbate bed saturation is 0% at the leading edge of the MTZ and 100% at the trailing edge.

The third zone is the active zone. In the active zone the desiccant has its full capacity for water and contains only that amount of residual water left from the regeneration cycle.

When the leading edge of the MTZ reaches the end of the bed, breakthrough occurs. If the adsorption process is allowed to continue, the water content of the outlet gas will increase following the traditional "S" curve. Breakthrough curves are illustrated in Figure 19.5(c) for three MTZ lengths.

Figure 19.5(d) shows the location of MTZ's in multicomponent adsorption typical of hydrocarbon and water adsorption on silica gel. As the gas enters a dry desiccant bed, all of the adsorbable components are adsorbed at different rates. After the process has proceeded for a very short period of time, a series of adsorption zones will appear. These zones represent the length of tower involved in the adsorption of any component. Behind the zone all of that component entering has been adsorbed on the bed. Ahead of the zone, the concentration of that compound is zero (unless some is left from a previous adsorption or on regeneration). These zones form and move down through the desiccant bed. Water would be the last zone

TABLE 19.2

Summary of the Operating Characteristics Dry Desiccant Dehydration

RECOMMENDED OPERATING RANGE:
At temperatures preferably below 50°C in order to utilize the higher desiccant capacity. The gas should enter the unit above its hydrate point. There seem to be no effective pressure limitations.

DESICCANT SERVICE:
Normally from three-five years in the absence of poisoning. Service limited by loss of capacity, dusting and breakage.

DEHYDRATION OBTAINED:
Essentially bone dry gas produced. Most units will give a –75 to –125°C [–103 to –193°F] dewpoint during the first part of the cycle.

LENGTH OF CYCLE:
Varies with water loading and gas rate, usually 8-24 hours.

REGENERATION:
Final regeneration temperature varies with type of desiccant, usually 175-300°C [347-572°F]. About 5 to 15 percent of the total gas stream used for regeneration. Normal eight hour cycle uses about six hours for heating, two hours for cooling in two tower plant.

ADVANTAGES:
1) Low exit dewpoint obtained. 2) Gives effective dewpoint depressions over a wide range of operating conditions. 3) Compact, particularly the smaller units. 4) Relatively low initial investment for small amounts of gas, such as for instruments, where "batch" or "semi-batch" operation is satisfactory. 5) Rated capacity may be increased if some wet gas is by-passed around the unit and recombines with dry gas, where the unit gives an exit dewpoint lower than that needed or specified.

DISADVANTAGES:
1) High initial investment. 2) Desiccant sensitive to poisoning, particularly from heavy oils, which frequently requires expensive desiccant replacement. 3) Rated capacity of the unit declines with pressure. 4) Pressure drop is higher than with liquid desiccant systems. In compressed gas systems this increases the required compressor horsepower. 5) At flow rates below the rated capacity, the regeneration heat load is high in relation to the amount of gas processed.

Summary of Regeneration Practices

METHOD OF HEATING:
Usually part of the main stream is by-passed which is either returned to the system downstream or is recombined and dehydrated. Liquefied petroleum gases which have been vaporized or super-heated steam are also used.

REQUIRED TEMPERATURE:
In most instances 175-300°C [347-572°F] is recommended. Higher temperatures increase capacity but shorten effective life of desiccant. Majority of water is driven off at 125°C [257°F]. Gas temperature from heater usually 200-350°C [392-662°F].

DIRECTION OF GAS FLOW:
Usually countercurrent to main flow in vertical towers in long cycle units. Concurrent in short cycle units.

GAS FLOW RATE:
About 5 to 15 percent of main gas stream. Percentage varies with main gas flow rate and with design of unit. Flow rate must be sufficient to supply the necessary heat in time allotted, for regeneration.

WATER REMOVAL:
Where regeneration gas recombined with main gas, water from regeneration is removed by cooling with main gas stream or by water cooler. Maximum heat load occurs when bed reaches about 125°C [257°F], at which time most of water is coming off. Heat exchanger should be designed for this condition.

HEAT REQUIRED:
Heat of desorption of water plus sensible heat to bring water vapor, desiccant and container up to temperature.

TIME REQUIRED:
To bring exit regeneration gas up to desired temperature. Usually about 65-75 percent of total cycle time.

PRESSURE:
Full line pressure satisfactory.

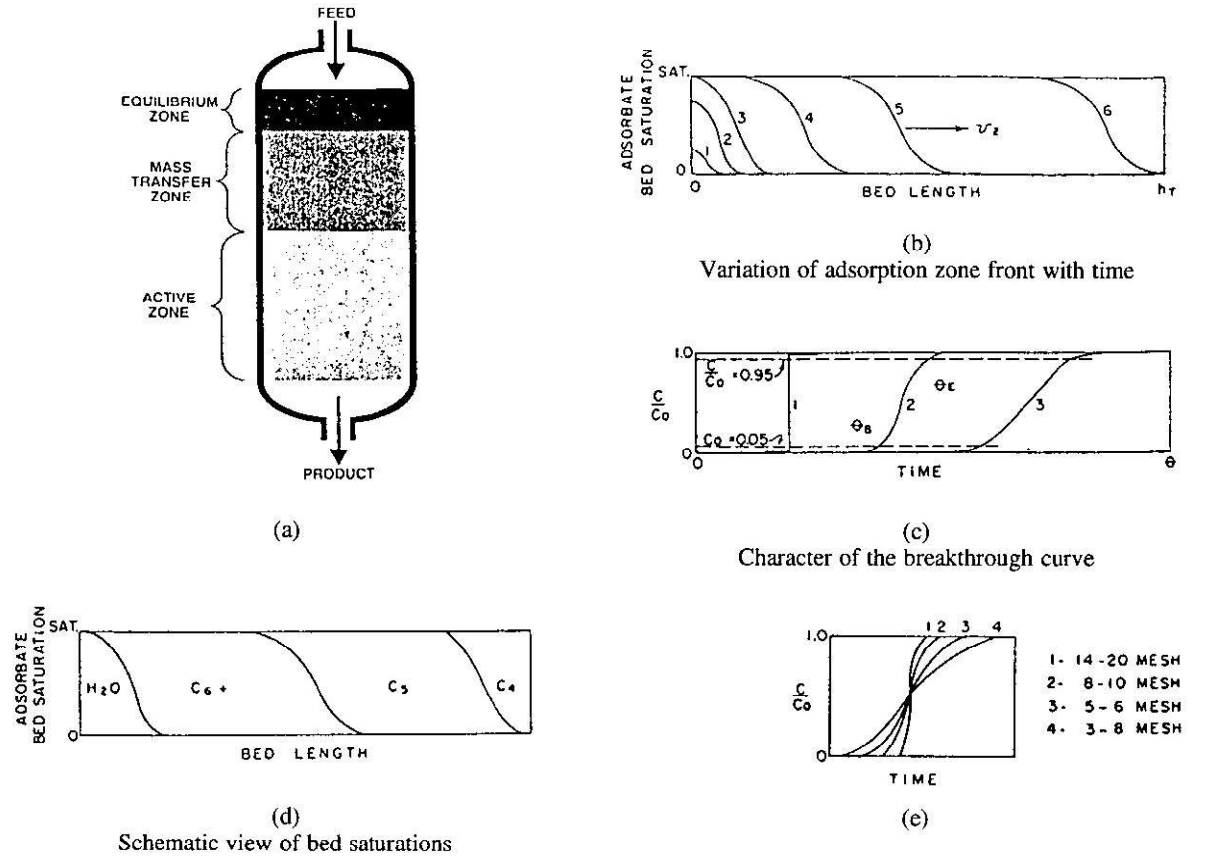


Figure 19.5 Schematic Portrayal of Adsorption Process

formed. On all materials except carbon it will displace the hydrocarbons if enough time is allowed to do so. If molecular sieve is used, adsorption of the C_4-C_6+ fractions will not occur because these molecules cannot fit in the desiccant structure.

100% of any component is adsorbed on the desiccant until the front of its zone reaches the outlet of the bed. When the back of its zone reaches the outlet of the bed, no more adsorption of that component will occur. It will furthermore be displaced almost entirely by the component in the zone following it down the bed if the cycle is continued. If the process continues long enough, no effective amount will remain on the bed.

With silica gel, at commercial flow rates and tower configurations usually employed, pentane will have a breakthrough time of from 12-20 minutes. Methane and ethane break out almost instantaneously. If the process cycle proceeds beyond 30-40 minutes, all but the heaviest hydrocarbons will have been displaced out of the bed. From this time on, primarily dehydration is taking place. thus, the performance of a given unit is dependent on the cycle length used.

For very short cycles both hydrocarbon adsorption and dehydration occur. The hydrocarbon recovery will substantially reduce dehydration costs charged to the unit or eliminate them. Such units may be used to simultaneously control water and hydrocarbon dewpoints at minimum cost. Their potential application is far greater than their use to date would indicate.

Part (e) shows the effect of desiccant size on the length of the zone. The steeper the zone, the sharper the separation, the better the process. Therefore, the desiccant used should always be the smallest compatible with the drop limitations. The smallest size will seldom be greater than 14 mesh (Tyler Screen Scale) in most commercial natural gas installations.

Other factors which affect the length of the MTZ include gas velocity – increasing velocity increases length – contaminants, water content and relative saturation of the inlet gas. Contaminants are particularly insidious because they can slow the mass transfer process (lengthen MTZ) by providing additional resistance.

The length of the MTZ has a significant effect on the useful capacity of the desiccant since the MTZ is left in the bed at the end of the adsorption cycle. Remember, the desiccant in the MTZ is only partially saturated with water!

THE PROCESS VARIABLES

The first step in planning and specification is to establish the waterload per 24 hours based on gas flow rate, P, T and water content. Also needed is the desired outlet water dewpoint (or water content). The unit will be sized by assuming all inlet water is removed regardless of the outlet dewpoint specified. All commercial desiccants are capable of producing water dewpoints below –60°C [–76°F].

The actual outlet dewpoint will depend on the desiccant chosen and design of the unit. With designs used to date, the following dewpoints are achievable:

Desiccant	Outlet Dewpoint
Alumina	–73°C [–100°F]
Silica Gel	–60°C [–76°F]
Molecular Sieves	–90°C [–130°F]

Slightly lower dewpoints than these have been reported in some instances.

To achieve these low dewpoints, the drying cycle must be such that the MTZ never reaches the end of the bed. So-called *short cycle* units are sometimes used in this application. Heavier hydrocarbons are recovered as well as producing very low exit water dewpoints.

Once the water load is fixed it is simply necessary to expose the gas to enough active desiccant to adsorb it. There are an infinite number of cycle length-number of tower combinations to accomplish this. Which combination is optimum?

Optimization considerations include: (1) Cycle time, (2) Allowable gas flow rate, (3) Desiccant capacity, (4) Required outlet water dewpoint, (5) Total amount of water to be removed, (6) Dynamic adsorption performance of the desiccant tower, (7) Regeneration requirements and (8) Pressure drop limitations. These are not independent variables. Consequently, some have to be fixed for the purpose of a calculation. True optimization will require repeating the calculation several times to obtain the best combination of variables.

In making these calculations one must assume a particular desiccant in order to have capacities and physical properties for use in the calculation.

Desiccant Capacity

The capacity of a desiccant for water is expressed normally in mass of water adsorbed per mass of desiccant. There are three capacity terms used.

Static Equilibrium Capacity – the water capacity of new, virgin desiccant as determined in an equilibrium cell with no fluid flow.

Dynamic Equilibrium Capacity – the water capacity of new, virgin desiccant where the fluid is flowing through the desiccant at a commercial rate.

Useful Capacity – the design capacity that recognizes loss of desiccant capacity with time as determined by experience and economic considerations and the fact that all of the desiccant bed never can be fully utilized.

The static equilibrium capacity has no direct use in design although it shows the effect of P, T and gas composition on capacity. As later calculations will illustrate, dynamic and useful capacity are used directly in calculations. Dynamic capacity typically is 40-60% of static capacity.

All desiccants degrade in service. Figure 19.6 is a typical curve for silica gel. Other desiccants will have the same shaped curves in normal service, although the values will vary.

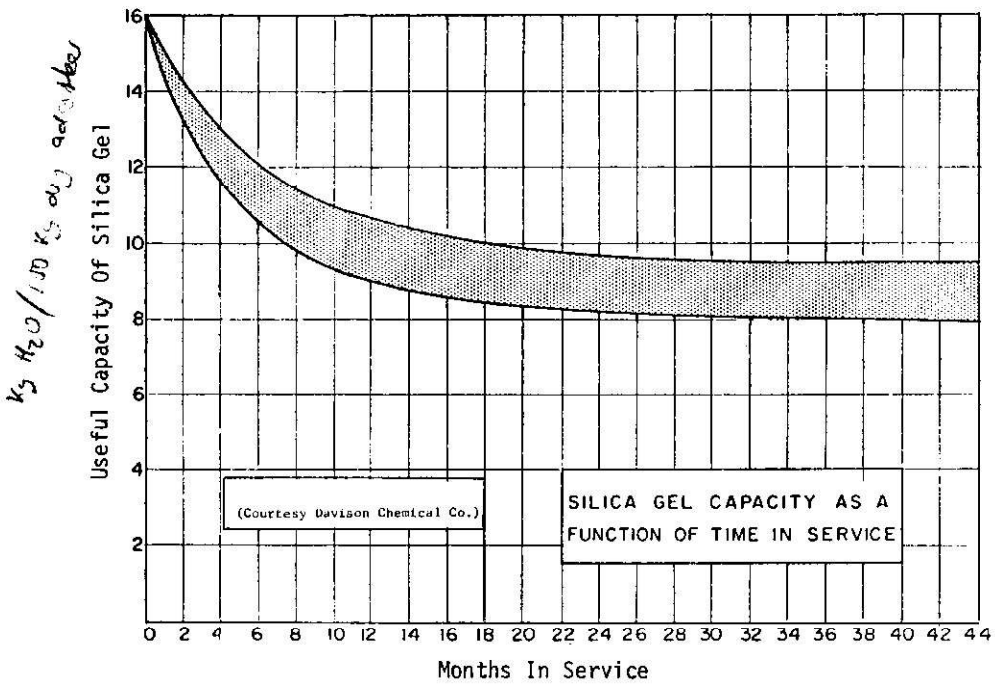


Figure 19.6 Silica Gel Capacity as a Function of Time in Service

Normal degradation occurs through loss of effective surface area on repeated regeneration. This loss is rapid at first and then becomes more gradual as the desiccant "matures." Abnormal degradation occurs primarily through blockage of the small capillary or lattice openings which control access to the interior surface area. Heavy oils, amines, glycols, corrosion inhibitors and the like, which cannot be removed by regeneration, can reduce the capacity to uneconomic levels in short periods of time. There is no room for wishful thinking. If these contaminants are present ahead of the unit, provision to handle them must be made just ahead of the unit. An ordinary separator will help, but filter separation or a "guard bed" of spent desiccant or some packing material is usually desirable.

Water is always a problem. Salt water entering will evaporate and fill the bed with salt. With the gels this water will cause bead breakage unless a guard section is provided at the inlet. The only good solution is to let no liquid water enter the bed.

The useful capacity used should be such that economic desiccant life will be obtained. For normal service the following are commonly specified as useful capacity:

Bauxite – 4-6 kg water per 100 kg of desiccant.	Gels – 7-9 kg water per 100 kg of desiccant.
Alumina – 4-7 kg water per 100 kg of desiccant.	Molecular Sieves – 9-12 kg water per 100 kg of desiccant.

In normal service, outlet dewpoints will be below –60°C [–76°F] for silica gel and –90°C [–130°F] for mol sieve until water zone breakthrough. Where lower dewpoints are needed, as in cryogenic plants, the overall effective capacity might be lower because the adsorptive driving force is so low at the exit end of the bed.

When applying the foregoing design capacities to water removal in natural gas service, it is customary to assume that the gas enters saturated and *all* water will be removed. This introduces a slight safety factor in most cases. Most natural gas is saturated as it leaves the reservoir, but subsequent pressure and temperature changes alter this. The relative saturation (RS) of the entering gas has a calculable effect on the desiccant performance, particularly silica gel and alumina.

4A and 5A molecular sieves tend to degrade slower because their pore size is such that heavy hydrocarbon molecules are excluded from the interior. However, a heavy external coating will still compromise their performance.

Most of the contamination occurs near the inlet. Sometimes the desiccant tower is designed so that this portion of the bed may be replaced more frequently than the total bed.

A form of degradation can occur if liquid water enters the bed. Some desiccants explode in the presence of liquid water. The *fines* thus produced increase pressure drop, reduce effective capacity, and may get into the pipeline and cause damage to rotating machinery downstream. A layer of water resistant desiccant may thus be placed on top of the bed to minimize this problem. The most positive solution is effective inlet scrubbing.

For pipeline service where outlet dewpoints are relatively high, it is desirable to continue the cycle until the water front reaches the end of the bed. Upon regeneration the steam formed helps clean the desiccant. Thus, cycle length may be variable with desiccant age and gas flow rate. For this reason, outlet dewpoint control of cycle time is preferable to mere time cycle control although the latter is simpler and cheaper. At worst, a dewpoint recorder should be placed on the outlet so that one can adjust performance or obtain critical data for troubleshooting functions.

ADSORBER SIZING EQUATIONS

For a given set of gas flow conditions, water loading, cycle length and tower configuration, one can size the desiccant bed. It must have enough area to meet velocity limitations, enough mass (surface) to hold the water adsorbed, and possess enough length so that the MTZ has not passed through the desiccant bed in the cycle length chosen.

The true dynamics of the adsorption process are difficult to simulate. The calculation procedure that follows is, however, a good approximation for estimation of dehydration behavior.

Desiccant Capacity

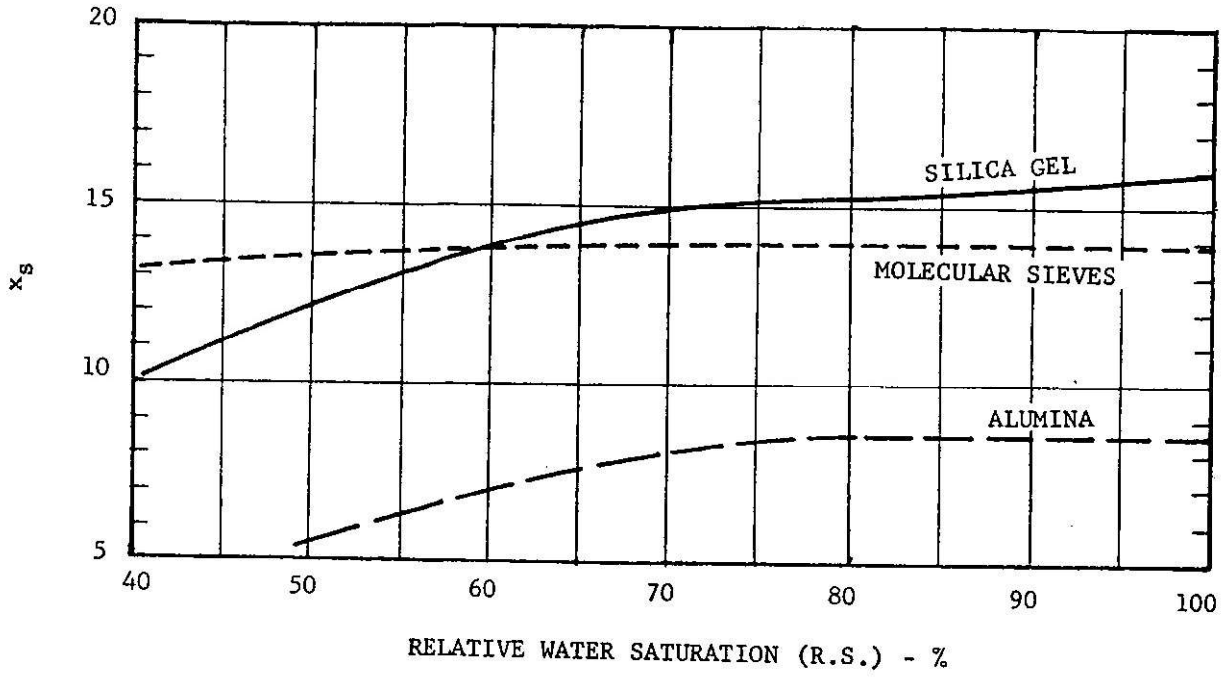
$$(x)\,(h_B) = (x_s)\,(h_B) - (0.45)\,(h_Z)\,(x_s) \qquad (19.1)$$

Where:
- x = maximum desiccant useful capacity (U.C.), kg water per 100 kg desiccant
- x_s = dynamic capacity at saturation (U.C.), kg water per 100 kg desiccant
- h_Z = MTZ length
- h_B = bed length (or length of bed to front of adsorption zone)

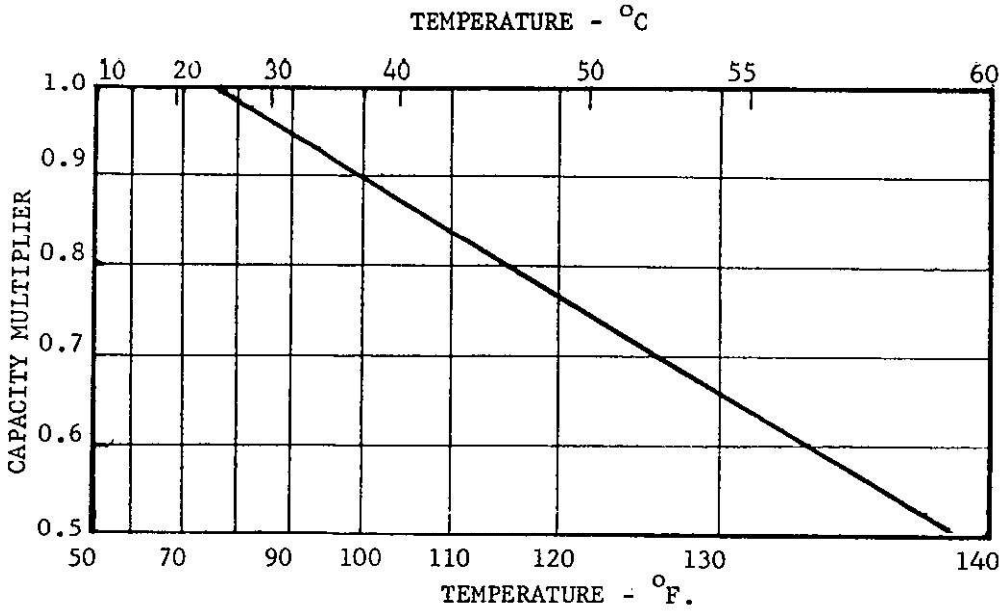
(Values of x's and h's may be in metric or English units so long as consistent).

The dynamic capacity "x_s" must reflect desiccant condition and other such factors. It is the effective capacity of the desiccant -- for water – *behind* the adsorption zone. Since desiccant degrades in service, the value used must reflect a capacity at some future time to optimize desiccant replacement cost.

Figure 19.7(a) may be used to predict "x_s" in Equation 19.1 as a function of relative saturation. Remember ... the relative gas saturation is fixed by the last pressure and temperature at which liquid water was present – the last separator producing any water or the reservoir. If any water is drained off the inlet



(a)



(b)

Figure 19.7 **Effect of Relative Saturation and Temperature on the Dynamic Capacity of Desiccants**

scrubber, the inlet gas is saturated. If not, the *saturated* water content at the previous contact divided by that at the dehydrator give the R.S. value as a *fraction*.

The values in Figure 19.7(a) are lower then the theoretical numbers published for air. They are for natural gas and reflect the competition of the hydrocarbons for adsorption surface and expected dynamic saturation after a short time use in an actual plant – with normal degradation only.

For *gels* and *aluminas*, the values in Figure 19.7(a) must be corrected for temperature. No temperature correction is needed for *molecular* sieves in the temperature range shown. The value from Figure 19.7(b) is multiplied by that in Figure 19.7(a) to obtain the "x_s" for use in Equation 19.1.

The "x" obtained from Equation 19.1 will be the useful capacity of virgin, activated desiccant. This is greater than the useful capacity after degradation as shown in Figure 19.6. In effect, Equation 19.1 simply corrects for that amount of bed unused because of zone length.

MTZ Length

The MTZ length depends on gas analysis, gas flow rate, relative saturation of the water in the gas and the loading capability of the desiccant. Pressure has only a small effect, particularly above 2.1 MPa [300 psia].

The numerical value of 0.45 in Equation 19.1 is an average number based on test. It is a function of MTZ but only varies from 0.40-0.52 in a wide range of applications. The value used is the mode of the distribution curve for most services.

For silica gel, the MTZ length may be estimated from the equation

$$h_Z = A\left[\frac{q^{0.7895}}{v_g^{0.5506}\,(R.S.)^{0.2646}}\right] \qquad (19.2)$$

			Metric	English
Where:	A	= constant	141	375
	h_Z	= MTZ length	cm	in.
	q	= water loading	$kg/h{\cdot}m^2$	$lb/(hr\text{-}ft^2)$
	v_g	= superficial velocity	m/min	ft/min
	R.S.	= percent relative saturation of inlet gas	dimensionless	

(The superficial velocity is based on bed diameter)

The values of "h_Z" from Equation 19.2 are those quoted from Reference 19.3 for air drying. The values, however, are useful for natural gas drying. Reference 19.8 represents a slightly more complex approach.

In natural gas service, when using Equation 19.2, the following multipliers are suggested for alumina and molecular sieves:

Alumina – 0.8 times h_Z for gel

Molecular Sieve – 0.6 times h_Z for gel

Shorter zones are obtained with these materials because they have less capacity for hydrocarbon. As noted in Table 19.1, 3A or 4A sieve will adsorb no heavier hydrocarbons.

Water Loading

$$q = 0.053\left[\frac{(\text{Flowrate})\,(W)}{d^2}\right] \tag{19.3}$$

			Metric	English
Where:	q	= water loading	kg/h·m^2	lb/hr-ft^2
	Flowrate	= gas rate	10^6 std m^3/d	MMscf/d
	d	= bed diameter	m	ft
	W	= water content	kg/10^6 std m^3	lb/MMscf

This is the water loading on a mass basis. Equation 19.3 is merely a conversion from water content per standard volume divided by bed cross-sectional area.

Breakthrough Time

$$\theta_B = \frac{(0.01)\,(x)\,(\rho_B)\,(h_B)}{q} \tag{19.4}$$

$$h_B = \frac{(127.3)\,(\text{wt of water adsorbed/cycle})}{(\rho_B)\,(d)^2\,(x)} \tag{19.5}$$

			Metric	English
Where:	wt water is expressed in		kg	lb
	q_B	= breakthrough time	h	hr
	ρ_B	= bulk density of desiccant	kg/m^3	lb/ft^3
	h_B	= bed length	m	ft
	q	= water loading	kg/(h·m^2)	lb/(hr-ft^2)

General Conversion Equations

$$w = \frac{(A)\,(v_g)\,(\gamma_g)\,(P)}{(T)\,(z)} \tag{19.6}$$

$$w = \frac{(B)\,(\text{Flowrate})\,(\text{MW Gas})}{d^2} \tag{19.7}$$

$$d = \left[\frac{(C)\,(\text{Flowrate})\,(z)\,(T)}{(P)\,(v_g)}\right]^{0.5} \tag{19.8}$$

$$v_g = \frac{(C)\,(\text{Flowrate})\,(z)\,(T)}{(P)\,(d^2)} \tag{19.9}$$

$$q = \frac{(E)\,(W)\,(P)\,(v_g)}{(T)\,(z)} \tag{19.10}$$

			Metric	English
Where:	A	= constant	209	162
	B	= constant	2214	140
	C	= constant	307	25
	E	= constant	0000 173	0.002 16
	w	= gas mass velocity	$kg/(h \cdot m^2)$	$lb/(hr\text{-}ft^2)$
	v_g	= superficial gas velocity	m/min	ft/min
	d	= bed diameter	m	ft
	P	= adsorber pressure	kPa	psia
	T	= inlet gas temperature	K	°R
	W	= water content	$kg/10^6$ std m^3	lb/MMscf
	q	= water loading	$kg/(h \cdot m^2)$	$lb/(hr\text{-}ft^2)$
	Flowrate	=	10^6 std m^3/d	MMscf/d
	z	= compressibility factor	dimensionless	
	g_g	= gas relative density	dimensionless	

Equation 19.10 is an algebraic combination of Equations 19.3 and 19.8.

Allowable Gas Flow Rate (Bed Area)

The main flow is downward through the bed, and high superficial velocities (based on bed cross-sectional area) may be used. Most designers, however, find that less "fines" and desiccant breakage occur if the rate does not exceed 1.0 to 1.5 times the maximum upflow velocity predicted by Ledoux[19.4] to prevent churning. Modifying his equation for downflow,

$$v_g = C\left(\frac{D_P}{\rho_g}\right)^{0.5} \qquad (19.11)$$

			Metric	English
Where:	v_g	= gas superficial velocity	m/min	ft/min
	ρ_g	= gas density	kg/m^3	lb/ft^3
	D_p	= particle diameter (average)	m	ft
	C	= constant	1200	540

The particle diameter, D_p, is found from the mesh size of the desiccant used. Alumina and bauxite are granular materials; the gels are somewhat spherical. Their size is determined by screening through a series of screens bearing a *mesh size*. Different scales are used. The most common is the Tyler Screen Scale. The table below shows the common mesh sizes used for most desiccants.

Tyler Mesh	Screen Opening	
	mm	inches
3	6.680	0.263
4	4.699	0.185
5	3.962	0.156
6	3.327	0.131
7	2.794	0.110
8	2.362	0.093
9	1.981	0.078
10	1.651	0.065
12	1.397	0.055
14	1.168	0.046

The U.S. scale is very similar to the Tyler Scale. A typical gel will have a size like 3-8 mesh or 4-8 mesh. The first number is the size of screen all particles pass through; the second number is the size opening all particles are retained on. The size distribution is never uniform but for calculation purposes an average size for the range may be used for D_p.

Molecular sieves are supplied in spherical and in pellet form, as well as a powder. Pellets 1.59 mm and 3.18 mm [1/16 and 1/8 in.] are available in most grades. Comparable sphere sizes are marketed by some vendors.

Equation 19.11 is conservative for gels and sieves which tend to produce less "fines" than granular materials with sharp edges. For a typical 4-8 mesh gel this equation produces the following superficial velocities at a temperature of 27°C.

Pressure		Gas Velocity	
MPa	psia	m/min	ft/min
2.6	400	12-16	40-54
3.4	500	11-15	37-49
4.1	600	10-13	33-44
4.8	700	9-13	31-41
5.5	800	8-12	27-38
6.2	900	8-11	26-35
6.9	1000	8-10	25-33
7.6	1100	7-10	24-32
8.3	1200	7-9	23-31

Velocities up to 18 m/min [60 ft/min] have been used successfully in some installations. The velocity affects both diameter and length of the bed. As it increases, diameter decreases and length increases. The length requirement for a given diameter is fixed by two factors – total desiccant needed to handle the water load and the effect of v_g on zone front velocity. Cycle length must be adjusted for given tower dimensions to satisfy both criteria.

An alternative method for determining superficial velocity in a mol sieve bed uses the method of Ergun[19.14] which relates ΔP to v_g, μ, ρ and desiccant size.

$$\frac{\Delta P}{L} = B\,\mu\,v_g + C\,\rho_g\,v_g^2 \qquad (19.12)$$

			Metric	English
Where:	$\Delta P/L$	= pressure drop/length	kPa/m	psi/ft
	μ	= gas viscosity	cp	cp
	ρ_g	= gas density	kg/m^3	lbm/ft^3
	v_g	= superficial gas velocity	m/min	ft/min

Constants for Equation 19.12 are:

Particle Type	Metric		English	
	B	C	B	C
1/8" bead	4.16	0.00135	0.0560	0.0000889
1/8" extrudate	5.36	0.00189	0.0722	0.000124
1/16" bead	11.3	0.00207	0.152	0.000136
1/16" extrudate	17.7	0.00319	0.238	0.000210

Most designs are based on a $\Delta P/L$ of about 7-10 kPa/m [0.31-0.44 psi/ft].

ADSORBER SIZING CALCULATION

The equations in the previous section serve as the basis for a calculation based on a given *cycle length, number of vessels and their configuration*, and a given desiccant.

1. Calculate the total water load for the cycle length for which the ensuing calculation applies.
2. Divide (1) by the number of towers on stream in parallel to find water load per cycle per tower.
3. Establish useful capacity "x" from Equations 19.1 and 19.2, and Figure 19.7, or by a company standard.
4. Multiply water load per cycle per tower by the number of cycles a tower operates before regeneration and divide the result by "x" to find the *total mass* of desiccant needed per tower.
5. Divide mass in (4) by desiccant bulk density to find *volume* of desiccant required per tower.
6. Calculate minimum bed diameter by one of two methods:
    a. Calculate allowable superficial gas velocity from Equation 19.11, 19.12, or company specification.
7. Determine breakthrough time from Equation 19.4.
8. Determine minimum bed length from Equation 19.5.
9. Check θ_B from Equation 19.4 to see if cycle length chosen is satisfactory. If not, adjust and repeat Steps 1-6. (Note that "q" is independent of cycle length.)
10. Use the results of the above for regeneration calculations.

A similar approach may be used to check an existing tower or a bid proposed by a vendor.

Example 19.1: 0.27×10^6 std m^3 [10 MMscf/d] of a 0.6 relative density natural gas is to be dehydrated. The wet gas enters saturated at 6.9 MPa [1000 psia] and 38°C [100°F]. The vendor proposes a unit composed of 2-76 cm [30 in.] O.D. towers containing silica gel beds 4.57 m [15 ft] in length. After allowing for shell and internal insulation thickness, the bed diameter is 64.8 cm [25.5 in.]. Does this meet company criteria including a gas superficial velocity not exceeding 9.15 m/min [30 ft/min]? The water content of the inlet gas is 1021 kg 10^6 std m^3 [61 lb/MMscf]. z = 0.88 and bulk density of gel is 721 kg/m^3.

Water absorbed = (0.27)(1021)/3 = 91.9 kg/cycle

From Equation 19.9,
$$v_g = \frac{(307)(0.27)(0.88)(311)}{(6900)(0.648)^2} = 7.83 \text{ m/min}$$

From Equation 19.3,
$$q = \frac{(0.054)(0.27)(1021)}{0.648^2} = 35.45 \text{ kg/h·m}^2$$

From Equation 19.2,
$$h_Z = 141\left(\frac{35.45^{0.7895}}{7.83^{0.5506}(100)^{0.2646}}\right) = 225 \text{ cm} = 2.25 \text{ m}$$

From Figure 19.7,
$$x_s = (16)(0.9) = 14.4$$

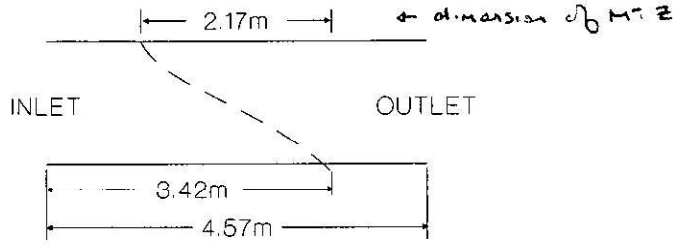
From Equation 19.1,
$$x = \frac{14.4\,[4.57 - (0.45)(2.25)]}{4.57} = 11.2 \text{ kg } H_2O/100 \text{ kg gel}$$

Example 19.1 (Cont'd.):

From Equation 19.5, $$h_B = \frac{(127.4)(91.9)}{(721)(0.648)^2(11.3)} = 3.42 \text{ m}$$

From Equation 19.4, $$\theta_B = \frac{(0.01)(11.3)(721)(4.57)}{35.45} = 10.5 \text{ hours}$$

This calculation shows the following situation:



When the desiccant is *new*, about 1.15 m of the bed will be below the front of the water zone when dehydration is discontinued about 2.5 hours before the zone front reaches the end of the bed. Thus, this unit will be able to easily produce pipeline specification gas initially, with a safety factor.

In the absence of abnormal contamination, how long can it do so? There are several approaches one can take. One can resolve Equation 19.4, for $\theta_B = 8$ hours, and find equivalent x. In the example, this x = 8.6. From Figure 19.4, the service life will be at least 24 months, and probably longer.

Some prefer to fix "x" based on experience and then use this value to fix h_B as total bed length from Equation 19.5, and then adjust cycle time from Equation 19.4 so that the two are compatible. Since any compatible combination of variables is satisfactory, various designs may be satisfactory.

I must emphasize that this is an approximate calculation. It is reliable enough though that if a proposed unit appears unsatisfactory when thus analyzed, further conversations with the vendor are indicated.

These equations are specifically for silica gel but may be used also for alumina and molecular sieves for dehydration of natural gas. The zone length, h_z, will be shorter, however, since both alumina or 4A and 5A sieve have a limited capacity for hydrocarbons. If hydrocarbons are already on the surface it lengthens the transfer zone length. As noted previously,

Alumina – h_z is 0.8 times that of silica gel.

4A or 5A sieve – h_z is 0.6 times that of silica gel.

All other variables may be estimated satisfactorily from the equations shown.

You may have noticed that the water loading calculation assumes all of the entering water vapor is removed from the bed. This is done because the exit water content is very low in a properly operating unit. It also varies somewhat with time. Thus, this assumption is convenient and introduces a small safety factor into the calculation.

REGENERATION AND COOLING CALCULATIONS

The problem is to supply enough carrier gas and heat to desorb the adsorbed components and then cool down the bed in the cycle time available. For a two-tower plant, both heating and cooling must be accomplished in the cycle time. With a three-tower system, with one tower drying at a time, twice the cycle length is available. For multiple towers (beyond two), the time depends on the switching pattern used.

The curve shapes of Figure 19.4 are typical of plant operations although the absolute and relative times shown vary with the installation. Curve 1 is the temperature of the gas to the bed being conditioned. Temperature "T_H" is the outlet gas temperature from the heater. Curve 2 is the outlet temperature of the regeneration gas from the bed. The difference in temperature between Curves 1 and 2 fixes the available heat energy available for transfer to the desiccant bed.

Temperature "T_4" is the maximum regeneration temperature. It will vary from 175-300°C [347-572°F]. The lowest temperature possible is recommended. "T_H" should be at least 19°C [34°F] higher than "T_4" and 38°C [68°F] is often desirable. In no case though is a value of "T_H" higher than 315°C be recommended.

The total heat load is that necessary to heat the vessel and its contents to "T_4" plus the *heat of desorption* of *all* adsorbed components. The adsorbed components are water, hydrocarbons and contaminants. The heat of desorption is the latent heat of vaporization plus that energy necessary to break the wetting forces. It is a function of concentration.

For gels the concentration of hydrocarbons ahead of the water front will be about 7-10 kg of hydrocarbon per 100 kg desiccant. Behind it, the concentration will fall to about 1-2 kg per 100 kg. Since the front will vary with water load and desiccant condition at the end of the adsorption process – which varies with time in an unknown way – it is normally satisfactory to assume that the hydrocarbon mass to be desorbed is about 10% of the water adsorbed, for cycles longer than four hours. For shorter cycles, a detailed hydrocarbon analysis is recommended. For sieves, hydrocarbon adsorption will be neglible.

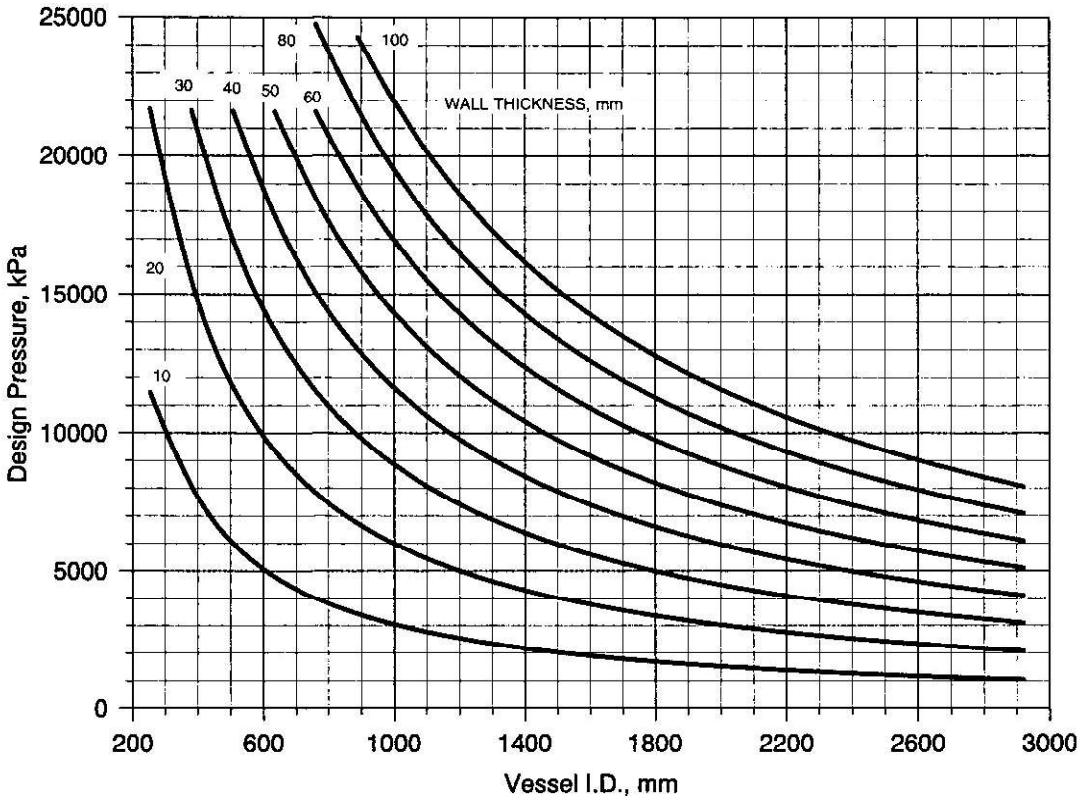
The total regeneration cycle in Figure 19.4 is divided into four parts – A, B, C and D. Temperature "T_H" and regeneration gas flow rate govern the time for each. Total regeneration time cannot be greater than the time available which in turn is fixed by number of towers and θ_B for the drying tower(s). Almost all of the hydrocarbon will be removed in Interval A; almost all water in Interval B. From test, $T_2 \cong 110°C$ [230°F], $T_3 \cong 127°C$ [260°F] and $T_B \cong 116°C$ [240°F]. Temperature "T_1" is that of the entering wet gas.

The sensible heat load will include the desiccant, those adsorbed liquids not yet desorbed, the steel vessel, retaining screens, and support balls. A "guard bed" installed to protect gel from liquid water would be added to the desiccant weight.

Steel Shell

The heat required for the steel shell will depend on whether internal or external insulation is used. Internal insulation is of two types: (1) a steel "can" inside the shell that provides a stagnant gas space between the bed and shell or (2) cast or sprayed internal insulation. With internal insulation the bed diameter usually is about 15 cm [6 in.] less than the shell I.D..

Internal insulation is a requirement on towers operating on cycles less than several hours. It may be desirable on longer cycle units to save on fuel costs. The shell sensible heat load is about 0.50-0.75 that of an externally insulated tower.



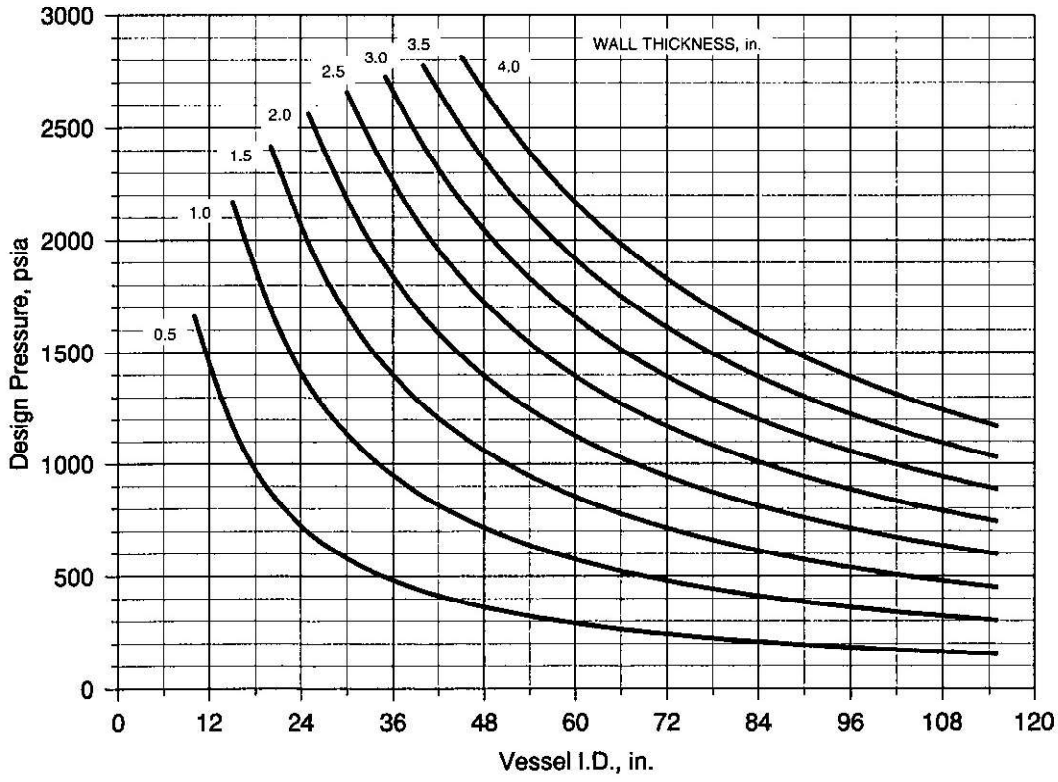


Figure 19.8 Approximate Pressure Vessel Wall Thickness

The approximate thickness of shell is shown in Figure 19.8. The diameter should be the nearest commercial size available that will allow a desiccant bed diameter at least as large as that calculated. The mass of the shell and heads may be estimated by Equation 19.13.

$$m = A\ h\ d\ t \qquad (19.13)$$

			Metric	English
Where:	m	= mass	kg	lbm
	h	= vessel length (HS – HS)	m	ft
	d	= vessel I.D.	mm	in.
	t	= shell thickness	mm	in.
	A	= weight factor	0.0347	15
	HS – HS	= head seam to head seam		

Heat Factors

The following values are suitable for the procedure below.

Heat Capacity, C_p

Steel – 0.50 kJ/(kg·K) [0.12 Btu/(lbm-°F)]

Liquid Water = 4.19 kJ/(kg·K) [1.0 Btu/(lbm-°F)]

Desiccant – from table on page 368

The heat of desorption is larger than the latent heat because of the forces holding the adsorbate to the adsorbent.

Heat of Desorption

Water on molecular sieves – 4187 kJ/kg [1800 Btu/lbm]

Water on alumina and gel – 3256 kJ/kg [1400 Btu/lbm]

Adsorbed hydrocarbon – 465 kJ/kg [200 Btu/lbm]

Heating from T_1 and T_2 (Interval A) -

The total heat load is the sum of the following:

1. (Wt. desiccant)$(C_p)(T_2 - T_1)$
2. (Wt. hydrocarbon)$(C_p)(T_A - T_1)$
3. (Wt. vessel shell)$(C_p)(T_2 - T_1)$*
4. (Wt. inert balls)$(C_p)(T_2 - T_1)$
5. (Wt. hydrocarbons)(heat of desorption)
6. (Wt. water)$(C_p)(T_2 - T_1)$

*With internal insulation multiply shell weight by 0.70.

If "m" is the regeneration gas mass flow rate, the available energy to supply the above needs is:

$$(m)(C_p)(T_H - T_A)(\theta_A) \quad \text{or} \quad (m)(\Delta h)(\theta_A) \qquad (19.14)$$

Heating from T_2 to T_3 (Interval B) -

Total heat is found as follows:

1. (Wt. desiccant)$(C_p)(T_3 - T_2)$
2. (Wt. water)$(C_p)(T_B - T_2)$
3. (Wt. water)(Ht. of adsorption)
4. (Wt. inert balls)$(C_p)(T_3 - T_2)$
5. Vessel load – same procedure as Interval A, with new temperatures.

The total available energy is found from the equation

$$(m)(C_p)(T_H - T_B)(\theta_B) \quad \text{or} \quad (m)(\Delta h)(\theta_B) \tag{19.15}$$

Heating from T_3 and T_4 (Internal C) -

This step merely is for the purpose of removing the "heel" from the bed – a final clean-up of heavier components. The total heat load is then

1. (Wt. desiccant)$(C_p)(T_4 - T_3)$
2. (Wt. inert balls)$(C_p)(T_4 - T_3)$
3. Vessel heat load consistent with previous intervals.

Available heating

$$(m)(C_p)(T_H - T_C)(\theta_C) \quad \text{or} \quad (m)(\Delta h)(\theta_C) \tag{19.16}$$

Cooling from T_4 and T_5 (Interval D) -

Temperature "T_5" is normally not less than 50-55°C [122-131°F] to minimize presaturation of the desiccant. The coolant is presumed to be gas at temperature "T1."

1. (Wt. of tower and contents)$(C_p)(T_4 - T_5)$

The cooling available is

$$(m)(C_p)(T_D - T_1)(\theta_D) \quad \text{or} \quad (m)(\Delta h)(\theta_D) \tag{19.17}$$

assuming cooling gas rate is equal to the regeneration gas rate.

For each interval, as well as the entire cycle, energy available for heating and cooling must equal the load. One has four equations containing "m" and "θ," the total value of each equation (from the corresponding heat load) and the fact that $\theta_A + \theta_B + \theta_C + \theta_D$ must not exceed the time available. For a given cycle time, a solution for "m" is possible.

Normally, the maximum heat load occurs in Interval B. As a first try it might be assumed that "m" is about 10% of the main gas flow rate.

During the desorption of water (Interval B) the combination of gas flow rate and its water capacity must be such that the gas can hold the water desorbed in time θ. If it is assumed that the water comes off at an average temperature of 116°C [241°F], the saturated water content of the gas at this temperature and regeneration pressure fixes the total amount of water vapor the gas can hold.

From a material balance

$$\text{Mass of water adsorbed/cycle} = \frac{18\ m}{MW\ Gas}(\theta)\ (y_B - y_1) \tag{19.18}$$

Where: θ = time for water desorption, hours
yB = mole fr. of water in saturated gas at TB
y1 = mole fr. of water in entering wet gas (or dry gas when used for regeneration)

The time for water desorption is about 16-17% of the total cycle length for cycles of 4 hours or longer. This may be used to estimate a value of "m" from Interval B, the most critical interval of the cycle.

The regeneration gas rate fixed by Equation 19.18 is a minimum rate and will normally be less than "m" required to meet total regeneration heat needs.

Heater Load

$$Q = (m)(C_p)(T_H - T_1) = m \Delta h \quad (19.19)$$

Where:
- m = regeneration gas rate
- C_p = gas heat capacity
- T_H = heater outlet temperature
- T_1 = heater inlet temperature
- Δh = gas enthalpy change at unit from T_1 to T_H

Do not skimp on heater size! A unit at least 25% higher than that calculated should be used. In this service a heater thermal efficiency of 70% is appropriate to find fuel consumption.

Condenser Load

One needs to calculate the condenser load for all three intervals to find the highest load. It will normally occur in interval B for long cycle units. The latent heats of water and hydrocarbons may be estimated in Chapter 8. Knowing the time for the interval and assuming the desorption is uniform during it, one can find the latent heat load. To this one must add the gas sensible heat load. The normal temperature approach will be 16-20°C [29-38°F] for air cooling and 8-10°C [15-18°F] for water cooling.

Summary

The above heat balance must be applied for every cycle length and configuration used in adsorber tower sizing. From this one can develop an array of information useful for planning and decision purposes.

The actual unit will possess a diameter and length different than that calculated to conform to commercially available steel sizes and fabrication economics.

HYDROCARBON RECOVERY

The basic mechanism for hydrocarbon recovery is similar but more complex than dehydration. One is faced with describing multiple zone behavior.

In a dehydrator, the purpose of the condenser is just to remove the desorbed liquids from the gas stream. In the short cycle plant, condenser operation has a critical effect on recovery. The adsorption bed simply serves to concentrate the recoverable components so that condensation is more efficient. The temperature and pressure of condensation is a critical parameter governing plant economics. A carbon plant with a refrigerated condenser is capable of good ethane recovery in some instances. A gel plant with ambient condensation is limited to some butane recovery and 75-90% of the pentanes. There are many alternatives in between.

Consider that the hydrocarbon deposited on the bed is picked by 10-15% as much regeneration gas. The net effect is to make the gas 6-10 times richer in condensable hydrocarbons, thus making recovery easier. A refrigerated condenser may be used to further enhance recovery but the condensation temperature should exceed the hydrate temperature. In some cases enough liquid may be recovered to reduce simultaneous dehydration cost below that of glycol.

Ambient cooling plants have been used primarily on lean gas streams where other methods of processing were not economically attractive. The untapped potential for hydrocarbon dewpoint control and as an adjunct to refrigeration appears large particularly at higher pressures. The biggest obstacle to more widespread use of the process would appear to be the rather unimaginative design methods used to date.

Process Characteristics

The capacity of most desiccants is about the same for hydrocarbons as for water. Activated carbon, of course, has no effective capacity for water.

Figure 19.9 shows the equilibrium capacity of silica gel for various hydrocarbons in a two component gas where the second component is methane. The figure shows both static equilibrium (from cell tests) and dynamic equilibrium (from flow tests). It is apparent that capacity is not affected very much by flow.

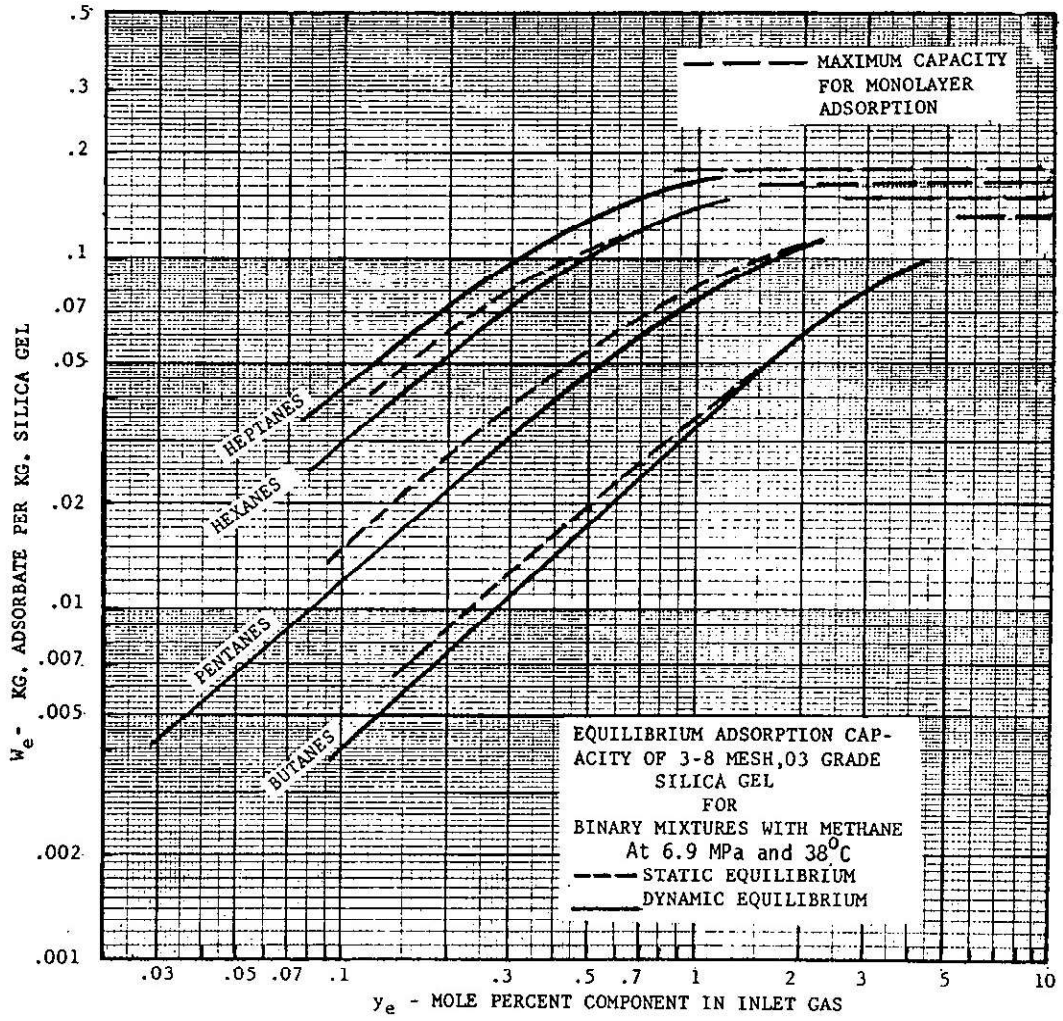


Figure 19.9 Hydrocarbon Equilibrium on Silica Gel

Notice that all curves are approaching the monolayer capacity of the gel. The monolayer capacity is found by assuming that only one layer of molecules is held to the solid surface. Knowing both surface area and molecule size, one may compute the capacity. This same characteristic has been found for all gels, aluminas and molecular sieves. This means that ultimate capacity for any component is fixed by surface area – provided that the component is small enough to enter the interior of the adsorbing particle.

Actual capacity for any component is fixed by the zone movement previously described, bed geometry, equilibrium capacity and gas flow rate. The surface of the adsorbent is always occupied by some molecule. As the zone of a given component progresses down the bed it must displace the molecules already there. The rate of displacement depends on their relative wettability.

Theoretically, the zone for any component cannot move any faster than it can completely displace the materials ahead of it. In actual practice, at commercial flow rates, the zone tends to "over-run" said displacement. Therefore, true chromatographic separation does not occur. This is illustrated in Figure 19.10.

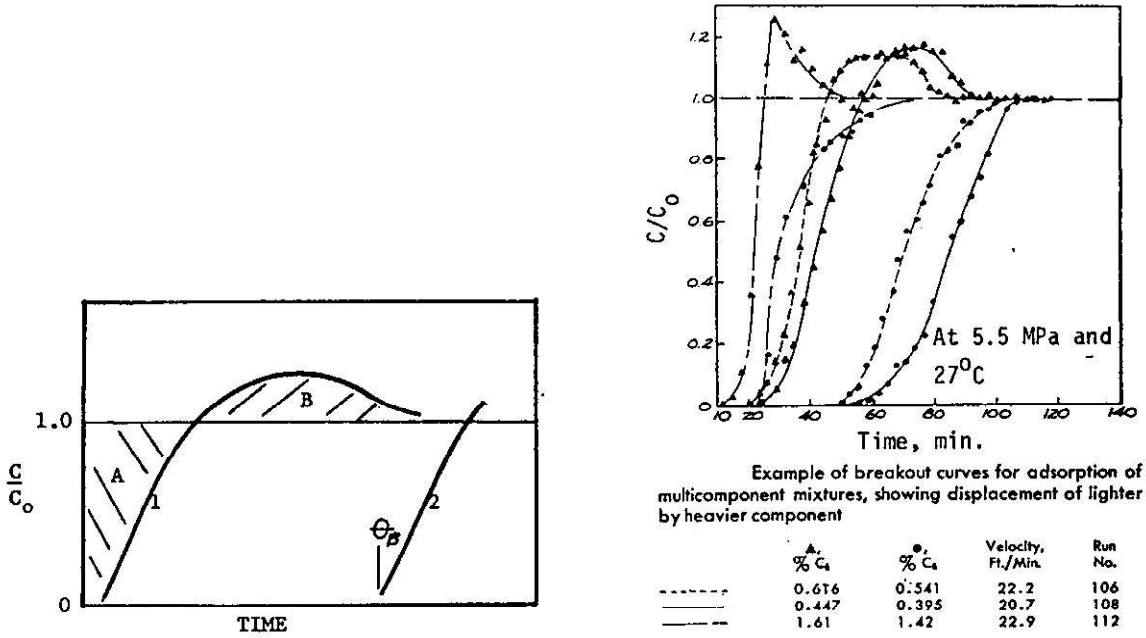


Figure 19.10 Illustration of the Adsorption/Desorption Process

As shown in Part (a), once the front of a given zone reaches the outlet of the bed the ratio of outlet to inlet concentration (C/C_o) starts to increase. When this ratio reaches unity, all primary adsorption ceases for that component. Desorption now begins because the zone behind it is replacing the material adsorbed. The concentration ratio rises above unity but again *approaches* unity when this next zone starts breaking out the end of the bed. This process continues until the cycle is terminated.

Area A is representative of the amount of Component 1 adsorbed and Area B of that amount desorbed *by the next zone*. The latter is smaller than the former. At times θ_B for Component 2 (Area A – Area B)/Area A is generally about 0.35-0.40. Thus, immediate displacement has not occurred.

This is shown by the following test on a field unit.

	Time, min.	Outlet mol %, C		
		C_3	iC_5	nC_5
Inlet Mol% (C_0)	–	1.020	0.120	0.085
	2	0.804	0.031	0.012
	12	0.976	0.074	0.031
	22	0.938	0.075	0.043
	32	0.962	0.077	0.065
	42	0.970	0.155	0.130
	52	0.952	0.109	0.102

Even if one recognizes the 6-10% error in sampling and analysis, no sharp separation has occurred. The propane has broken through in less than two minutes. This is not a very efficient plant because even

good pentanes recovery is not obtained early in the cycle. Beyond this point, the exit stream is being *enriched.*

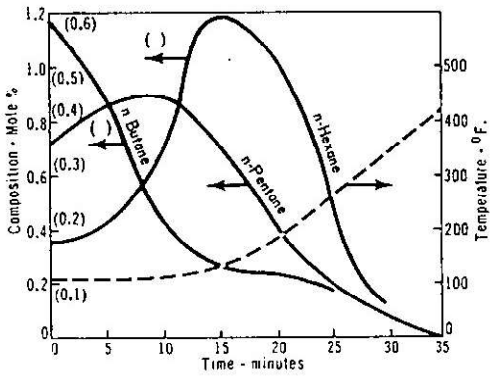
If liquid recovery is the goal, some net amount of component is available even after its zone passes from the tower. The recovery will simply be less. If hydrocarbon dewpoint control is the goal, such enrichment is probably intolerable for components heavier than the butanes. In such case, the iso-pentane θ_B represents maximum cycle time. For these reasons, liquid recovery plants tend to use longer cycles than dewpoint control plants since the loss of efficiency is not so apparent. Unfortunately, the bulk of the recovery plants I have examined use cycle times too long for most efficient recovery. Recovery is not limited by the process but by the way it is applied.

Part (b) of Figure 19.10 shows the adsorption-desorption process for a test run. The gas in question contained methane, ethane, negligible propane and butanes, and the amounts of pentanes and hexanes shown. There was no heavier component present to displace the hexanes. Water content was negligible.

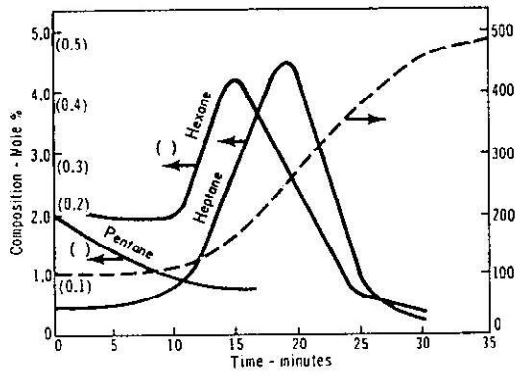
With activated carbon the zones tend to move slower. For one thing, water does not promote displacement. Basically though, the zone speed is lower because of the greater affinity for the lighter hydrocarbons.

Regeneration and Recovery

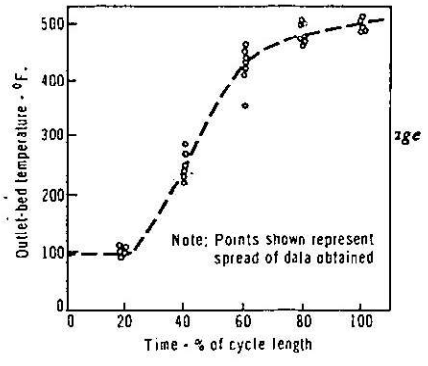
Figure 19.11 summarizes the regeneration behavior of a short cycle plant. Notice that the materials do not desorb at a constant rate. The pentanes and lighter start desorbing almost immediately. The hexanes and heavier concentration in the exit gas peak after a finite time.



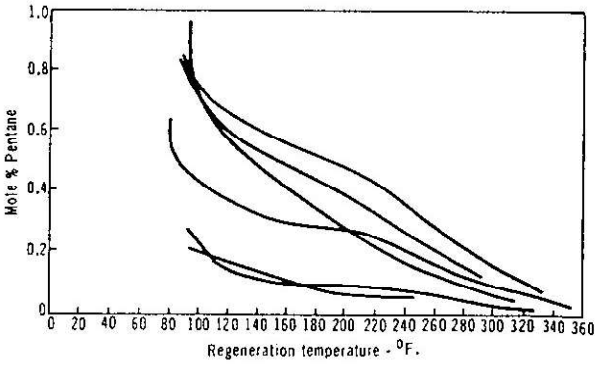
With butane, pentane, hexane



With pentane, hexane, heptane



Outlet bed temperature produces characteristic curve



Characteristic pentane content of regeneration gas

Figure 19.11 Typical Regeneration for Hydrocarbon Adsorbers

Obviously, the composition of the stream to the condenser varies continually with time. For this reason a series of flash calculations must be made with time to accurately represent the liquid recovery to be expected. The minimum necessary amount of regeneration gas should be used to enhance the concentration of recoverable components in the condenser. The use of refrigeration will likewise enhance recovery. Even at refrigeration levels as high as 16-20°C [60-68°F], marked recovery efficiency may be obtained.

General Specification

Proper detailed design is complicated enough that a computer is necessary. A design method will not be outlined herein although the principles governing it have been. It is sufficient to say that the general empirical methods to date fail to utilize the full potential of the adsorption process.

Most obvious problems stem from improper specification. A liquid recovery guarantee is useful for planning purposes but is more likely to be a basis for controversy than a measure of plant performance.

I recommend the following minimum specifications:

1. Gas flow limited by the rate previously discussed for dehydration (to promote desiccant life).
2. Cycle length should be fixed by the following considerations:
    a. Not less than 15 minutes for gas containing pentanes and heavier.
    b. Breakthrough time for the component for which recovery is desired or which must be removed for dewpoint control.
3. Bed length should be at least 15 feet.
4. Regeneration should be to at least 230°C [446°F] and preferably 260°C [500°F] when processing gases containing pentanes and heavier.
5. The alternative of using refrigeration instead of ambient cooling in the condenser should be considered.

Items 1-4 are not independent; each affects the other. If the cycle length is less than 15 minutes it is almost impossible to remove the "heel" properly, which ultimately affects the economics adversely. If this 15 minutes is greater than the breakthrough time for key component, some compromise is needed. Breakthrough time depends on gas velocity and bed length (for a given gas composition and adsorbent. Economics and/or process needs will govern the compromise. As a matter of information – so one may make an intelligent decision – it is wise to also specify that the vendor furnish you with adsorption efficiency as well as condenser recovery. Adsorption efficiency is simply that fraction of the component entering during the proposed cycle length that is retained on the adsorbent. This enables you to not only compare the relative merit of competitive bids but to make necessary changes prior to purchase. Any design approach that uses an overall method of calculation from inlet gas to stock tank may yield a workable plant but seldom an optimum one.

The adsorbent bed may contain more than one adsorbent. Such composite bed will behave like two towers in series and should be treated as such.

LIQUID DEHYDRATION

The gels, alumina and molecular sieves may be used to dry hydrocarbon liquids. The flow sheet is similar to that for gas. Some larger plants are designed so that the flow may be reversed to "loosen" the bed if it has been compacted or to free the retaining screens of sediment. This provision is seldom needed for fractionated liquids. If there is any possibility of free liquid water being present, a free water knockout should be provided.

The primary difference is in the regeneration cycle. Several systems are commonly used to provide regeneration:

1. Gas
2. Steam (closed)
3. Closed Vapor

Table 19.3 summarizes these processes. The gas system may use superheated steam, natural gas, flue gas or any inert gas. If steam is indicated, the closed system is normally recommended. Even super-heated steam tends to rehydrate the desiccant. With alumina a monohydrate is formed which is less efficient than the trihydrate.

TABLE 19.3
Comparison of Various Regeneration Practices

Method	Advantage	Disadvantages	Common Usage
Open Steam	1. Low initial cost 2. Simple in design	1. Usually shows highest operating cost. 2. Only sensible heat may be utilized. 3. Tendency to rehydrate desiccant beds. 4. Requires cheap source of steam.	General service where steam is available at low cost. In conjunction with refineries and gasoline plants for relative nonvolatile liquids.
Closed Steam	1. Low operating cost. 2. Either saturated or superheated steam may be used. 3. Little safety hazard. 4. No contamination of product.	1. High initial cost. 2. Requires cheap source of steam.	Same as above.
Natural Gas, Flue Gas, etc.	1. Uses readily available material. 2. Low operating cost. 3. Simple construction. 4. Readily adaptable to automatic control.	1. Has higher operating cost than closed steam system. 2. Introduces some additional safety hazard. 3. Requires compressor if high pressure gas not available.	Field locations, Product Pipe lines, Non-Volatile Liquids.
Closed Vapor	1. Simple operation. 2. Low cost of operation. 3. Minimizes loss of expensive volatile liquids. 4. No contamination of product.	1. Control of system more critical. 2. Requires pumping equipment. 3. Requires efficient condensation of exit regeneration gas.	With volatile liquids such as propane, butane, etc. Where composition of feed is substantially constant.

The gas is heated to 160°C [320°F] in a heater in the normal manner.

A closed stream system is recommended over the open stream system when steam is to be used. The initial cost of imbedding steam coils is greater but so is the efficiency. The latent heat of saturated steam may be utilized. Contamination of the *hold-up stock* in the drying tower at the end of the cycle is also minimized. When drying volatile material such as propane and butane, they may be vaporized for use as regeneration gas. The hold-up stock is normally used for this purpose.

Design Considerations

The solubility of water in sweet hydrocarbons is shown in Figure 19.12. Notice that it is far more soluble in many unsaturated and aromatic hydrocarbons than in the normal paraffins. Knowledge of composition is thus very important. The presence of sulfur compounds enhances water solubility. If no data are available for the specific liquid, a *weight fraction* relationship may be used to estimate liquid mixture water content.

Most contracts specify that the dried liquid show a negative result to the Cobalt Bromide test, which is equivalent to a water content of 15-30 ppm. This is virtually bone dry for ppm is weight percent times 10 000. In design, one assumes all incoming water is removed.

Liquid velocity should be 1-2 m/min. This will fix tower diameter. Tower length will usually be shorter than for gas. An (L/D) ratio of 2-3:1 is common. As little as three seconds contact time is commonly provided. Some operators require a minimum bed length of 1.5 meters.

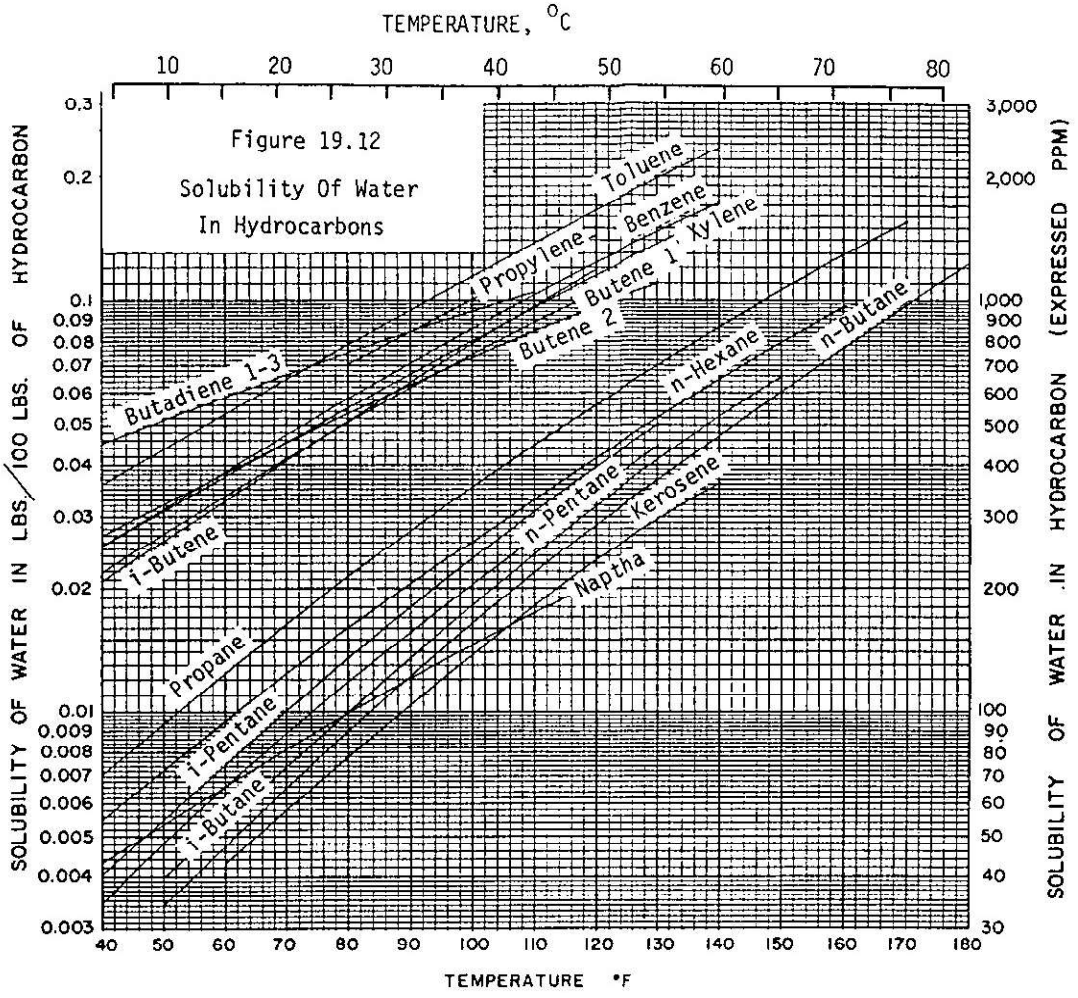


Figure 19.12 Solubility of Water In Hydrocarbons

Activated alumina has been used quite widely for liquid drying since it is relatively inexpensive and tower costs are minimized at low pressure. An effective capacity of 4-5 kg of water per 100 kg alumina is common. This is equivalent to that in gas service, as is the capacity of gels and sieves.

A 3A sieve is useful for drying liquids where contaminants are present, for the opening size is too small to admit these contaminants to the interior particle surface. Olefins, for example, may "tie-up" the available surface and reduce water capacity when using alumina.

Molecular sieves may be used also to both dry and sweeten liquids as discussed in a later section.

GAS AND LIQUID SWEETENING

Molecular sieves are widely used for sweetening gases and liquids. Carbon dioxide and sulfur compounds are co-adsorbed with water.

Figure 19.13 is a basic, simple flow sheet for a sweetening unit. The process is much like that for water alone except for handling the regeneration gas. Burning the flare gas as shown may be in conflict with environmental standards. As an alternative, the regeneration gas may be treated first by an amine type

sweetening process after which it is dehydrated using glycol. The effluent gas from the dehydrator is then co-mingled with the effluent gas from the molecular sieve beds. Thus, no gas is flared.

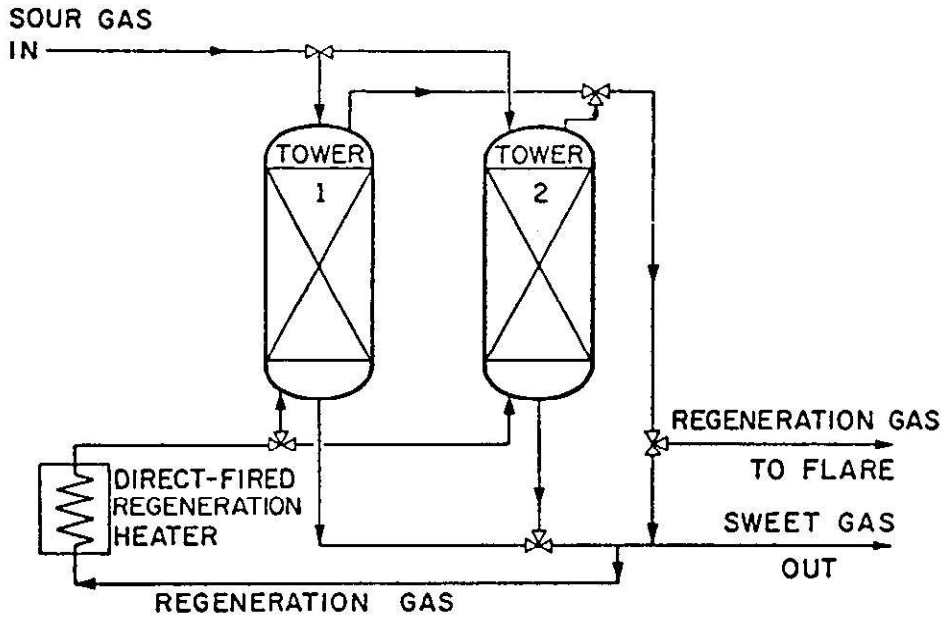


Figure 19.13 Flow Diagram for Basic Molecular Sieve Drying and Sweetening Process

A closed cycle process known as the EFCO system is shown in Figure 19.14. It is also designed to reduce the problem of flaring sour gas.

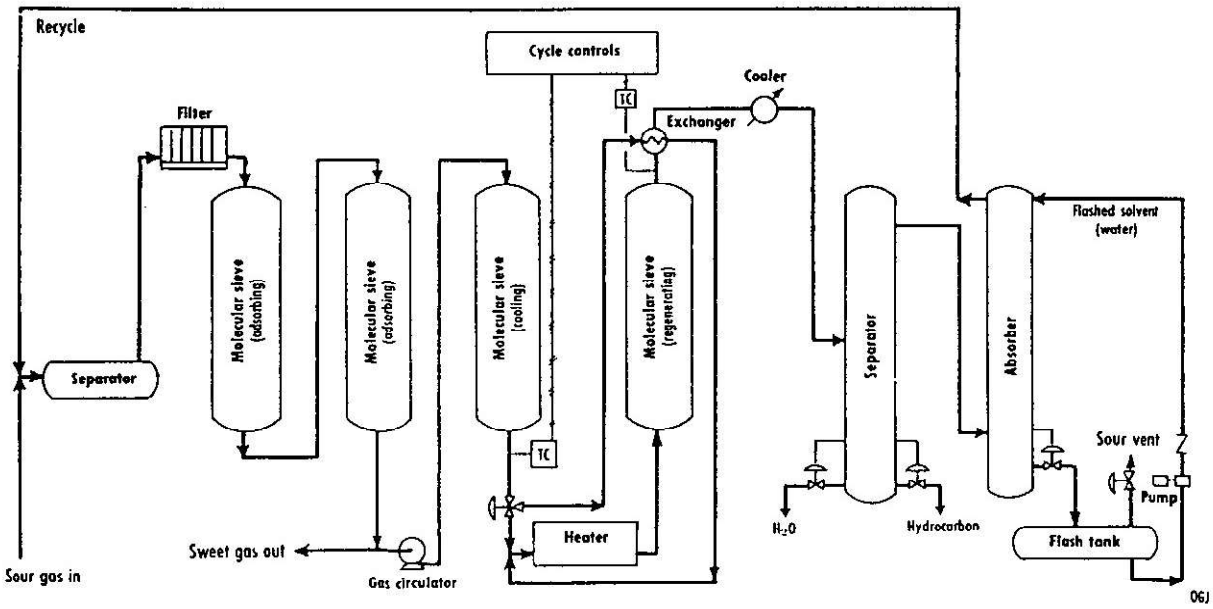


Figure 19.14 Flow Diagram for the EFCO Process

With sour gases the major use of molecular sieves is to selectively remove H_2S and other sulfur compounds from gases containing large amounts of CO_2. Most processes like the amines are non-selective. One must remove all of the CO_2 to meet sulfur specifications. This is not economical. Only that amount of CO_2 should be removed to meet heating value or Wobbe number specifications. Sieves have an affinity for CO_2 but it is greater for polar molecules like H_2O and H_2S. The cycle can be adjusted so that the amount of CO_2 removed, if any, can be controlled.

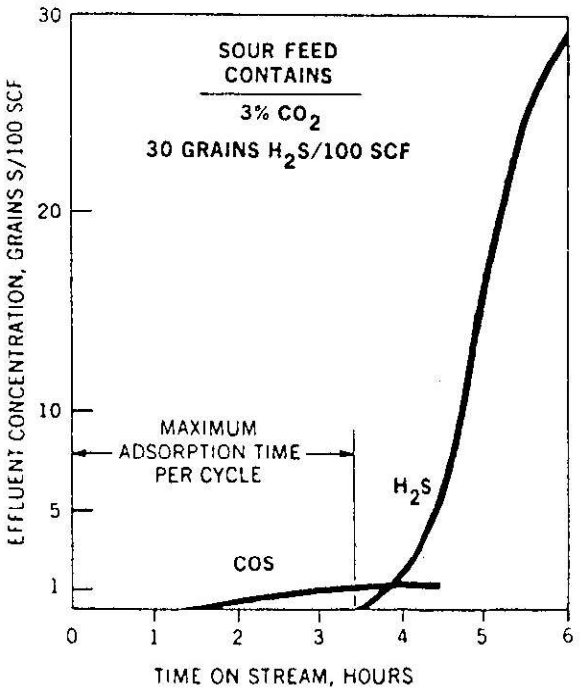
Sieves also can be used for removal of mercaptans and other heavier sulfur compounds. In prepurification of gases for LNG plants, water, H_2S and CO_2 can be reduced to acceptable levels.

Use of 13X sieve for the simultaneous drying and sweetening of propane and butane has been increasing. This replaces drying first, and then sweetening, by a process like caustic wash.

One problem that can occur is the conversion of H_2S to carbonyl sulfide (COS) in the bed. This is the result of the equation

$$H_2S + CO_2 \rightleftarrows COS + H_2O$$

The equilibrium constant for the reaction to the right increases with temperature. The figure following shows how COS forms with time. This is important for on occasions the effluent has been sweet in H_2S but contained too much COS.



In the presence of water the COS is hydrolyzed back to H_2S. Obviously, water vapor thus tends to keep COS from forming.

Further details about all sweetening processes are shown in Volume 4, "Gas and Liquid Sweetening," a companion book in the Campbell Petroleum Series.

Rather obviously, molecular sieves are the most versatile of the commercial desiccants now available. They also are much more expensive. Proper choice of desiccant for maximum economic benefit is not routine. Arbitrarily using molecular sieves, regardless of cost, is not the automatic answer. One must look at all factors. In addition to the initial cost, molecular sieves also have a higher heat of desorption which thus increases heat loads for regeneration.

Either alumina or gel may be suitable in a given case for either gas or liquid drying alone. For liquid drying, alumina may be the most economical if the liquid is already sweet. The lower capacity is offset by the lower water loading, which results in reasonable size towers.

Where suitable, gel is a commonly used material for the drying of sweet gases. It may be used for sour gases but the co-adsorption of heavy or aromatic hydrocarbons may lead to regeneration problems. For the drying of sweet gas or recovery of the pentanes plus, gel may prove to be a suitable economic compromise between cost and performance. In drying sour gases where the pH of the adsorbed water is less the 5.0, the proper choice is acid resistant molecular sieves.

Somewhat by default, molecular sieves will probably be the choice for

1. Drying fluids at a temperature above about 50°C.
2. Drying liquids when heavy hydrocarbons and/or aromatics are present which can reduce the capacity of alumina gels for ethane, propane and butane.
3. Co-adsorption of water and sulfur compounds.
4. Selective adsorption of H_2S from high CO_2 gases.
5. Acid gases when the pH of the adsorbed water is less than 5.0.
6. Outlet dewpoints less than –73°C.

By careful selection of the desiccant and optimum design of the system, dry desiccant can prove to be economically attractive when compared to the use of glycol or hydrate inhibition.

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