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.

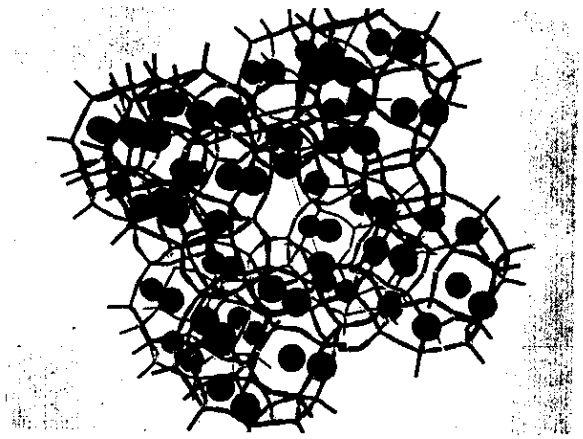
Alumina is a hydrated form of aluminum oxide (Al_2O_3). When manufactured it is essentially iron free. In its natural state (bauxite) it contains varying amounts of iron. It is *activated* by driving off part of the hydrated water adsorbed on the surface. $Al_2O_3 \cdot 3H_2O$ the hydrated version would 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.

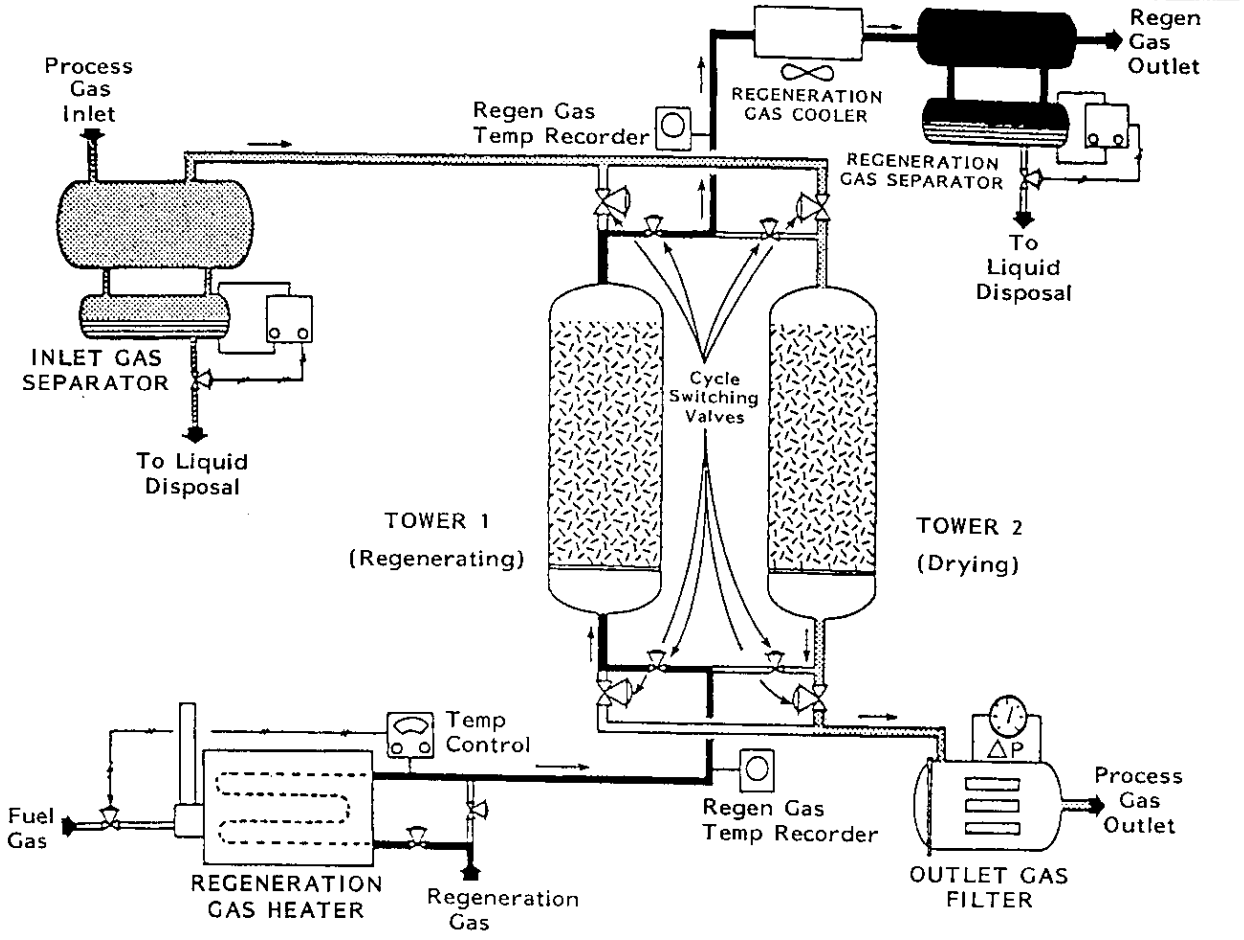
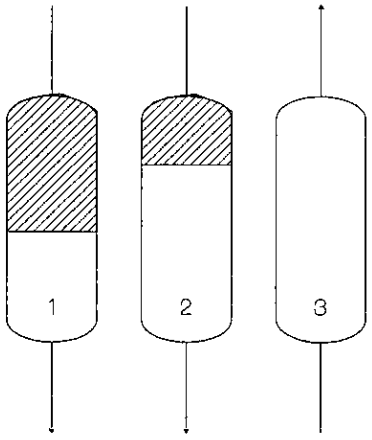


Figure 19.1 Flow Sheet of a Basic Two-Tower Dry Desiccant Unit

(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.

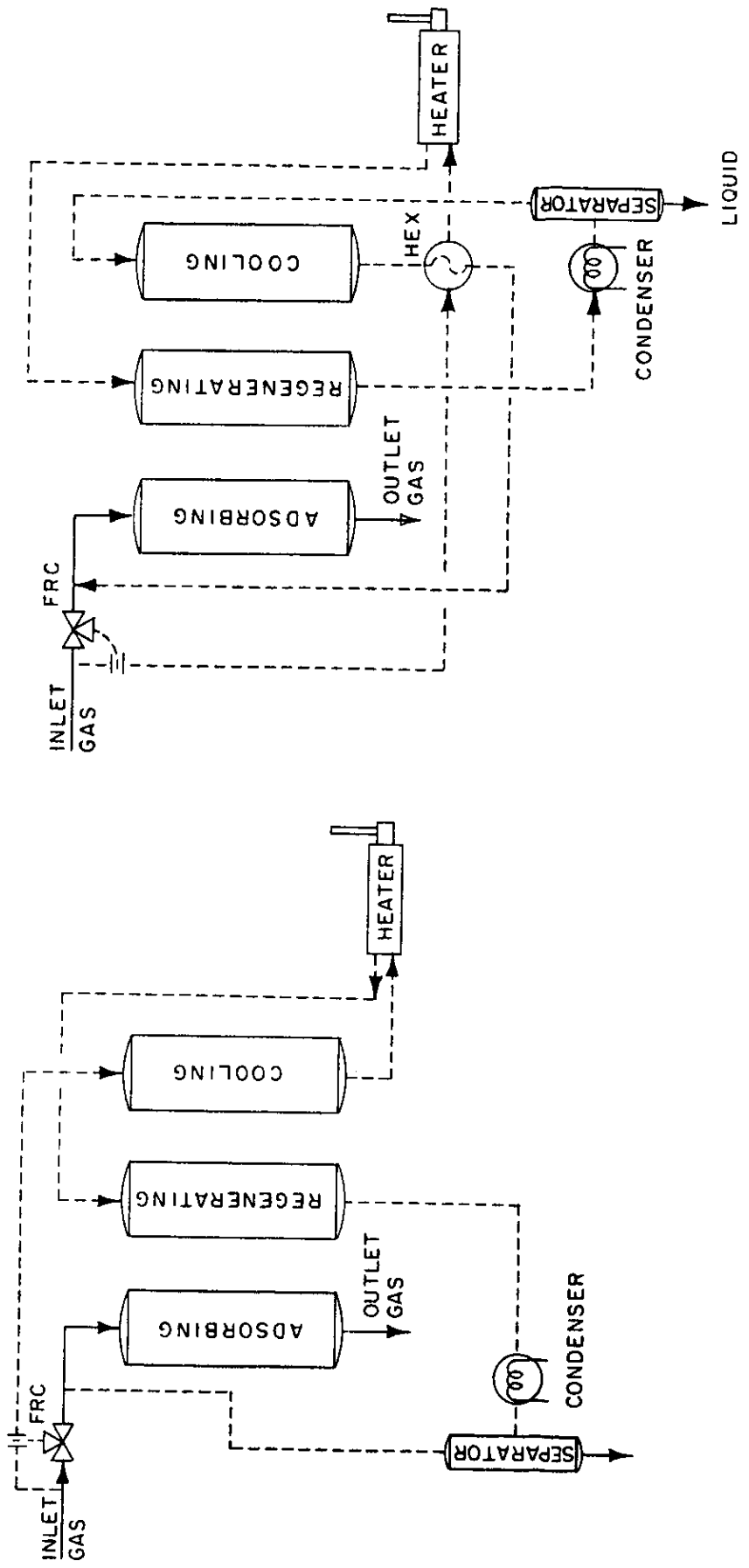
Shown on page 376 is a piping manifold for a three tower plant using a general configuration like that shown in Figure 19.2 and 19.3. Two-way valves are shown. Three-way valves are sometimes used, but are not recommended. This illustrates the basic type of layout required. It is important that the valves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

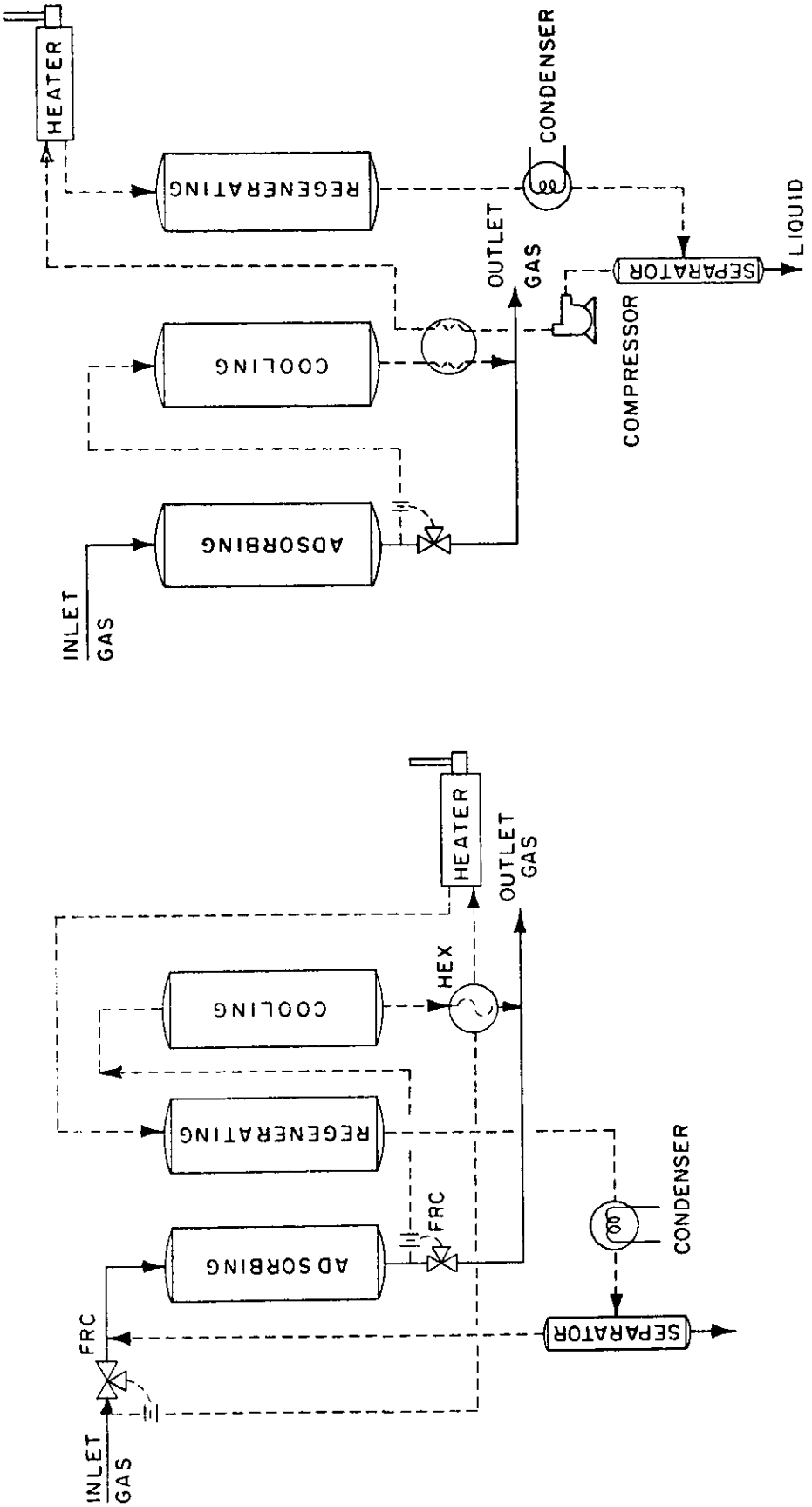
A more detailed discussion of desiccant plants and their operations is available in Reference 19.1.



(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

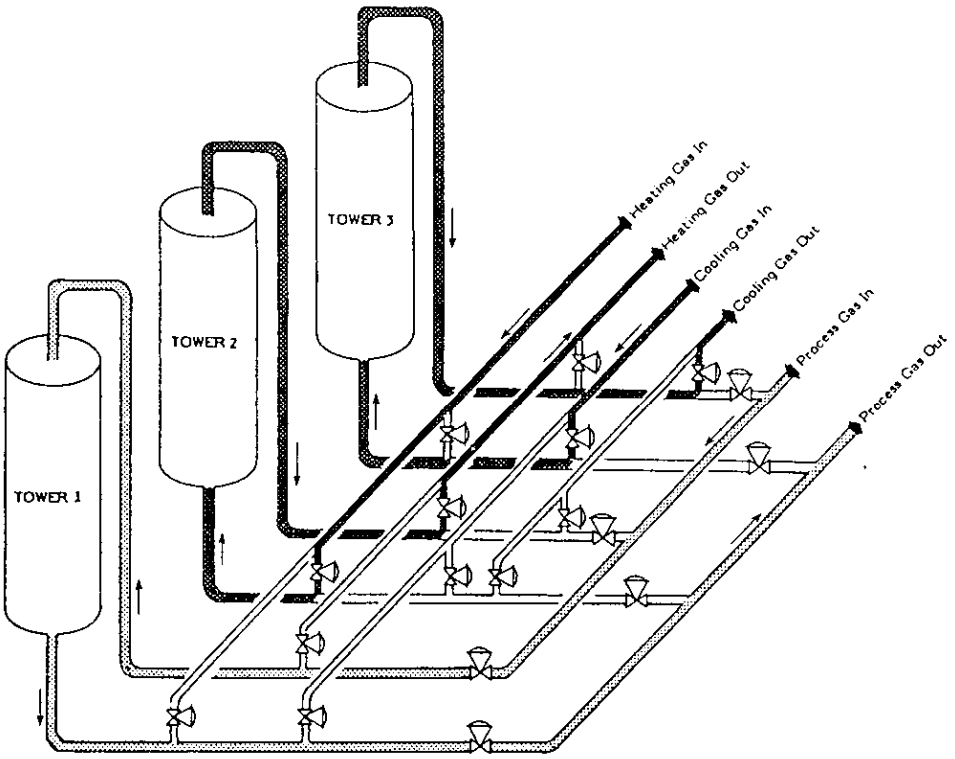
Figure 19.2 Two Possible Configurations of a Three-Tower Plant



(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.

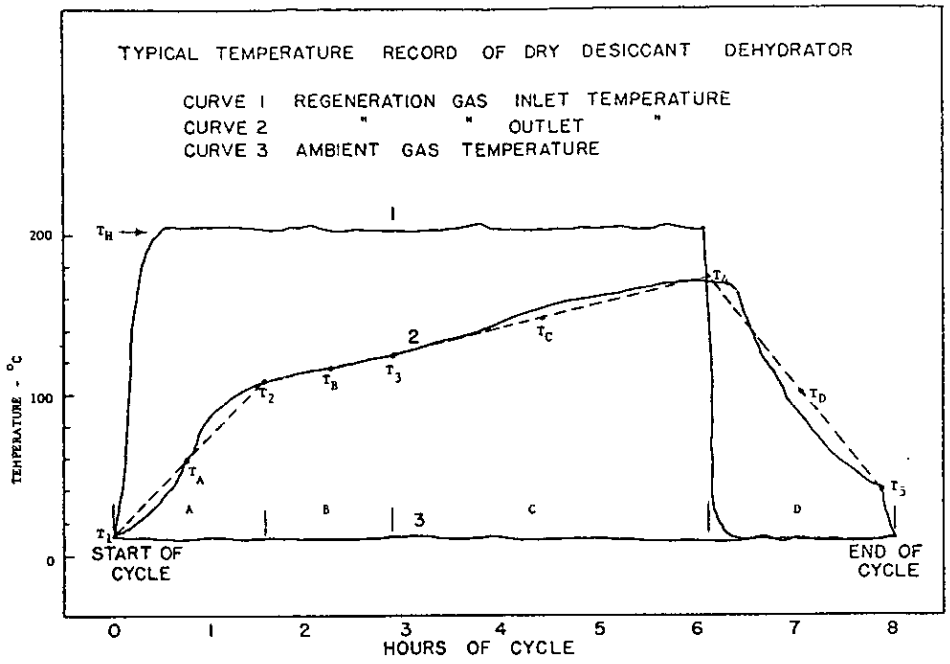


Figure 19.4 Temperature Curves for a Two-Tower Plant

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 horesepower. 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.

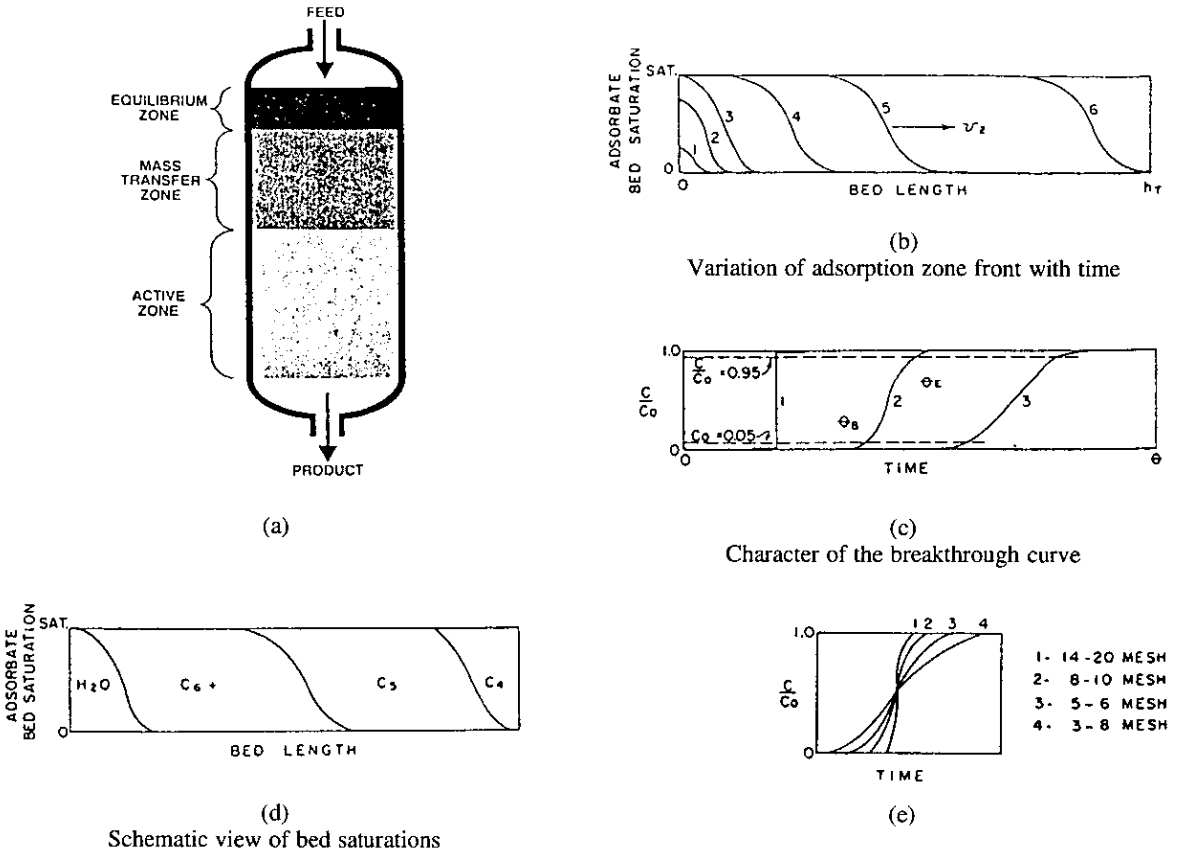


Figure 19.5 Schematic Portrayal of Adsorption Process

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.

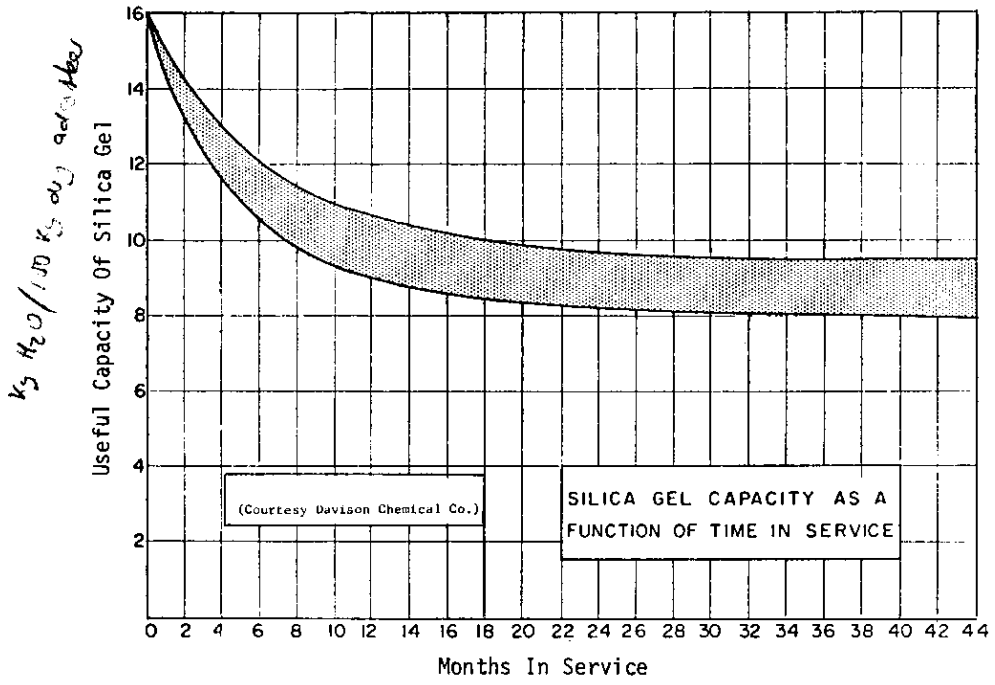


Figure 19.6 Silica Gel Capacity as a Function of Time in Service

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

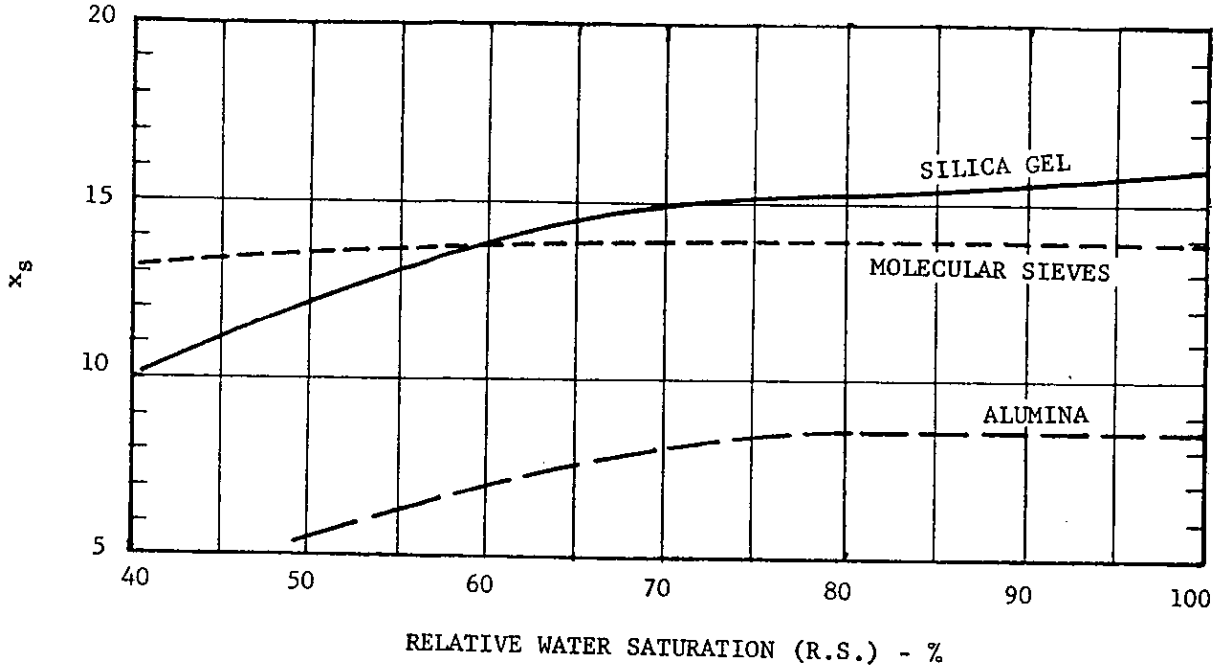
$$(x)\,(h_B) = (x_s)\,(h_B) - (0.45)\,(h_Z)\,(x_s) \qquad (19.1)$$

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)

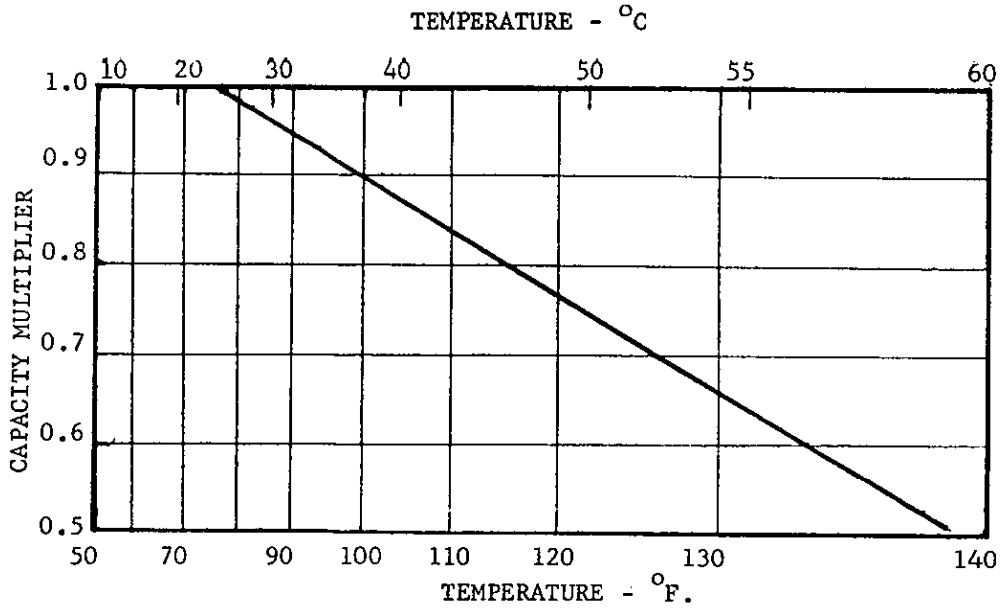
(Values of x's and h's may be in metric or English units so long as consistent).

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,
$$x_s = (16)(0.9) = 14.4$$

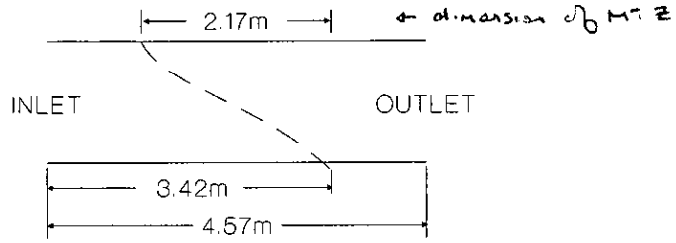
From Equation 19.1,
$$x = \frac{14.4\,[4.57 - (0.45)(2.25)]}{4.57} = 11.2 \text{ kg } H_2O/100 \text{ kg gel}$$

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 θ_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.

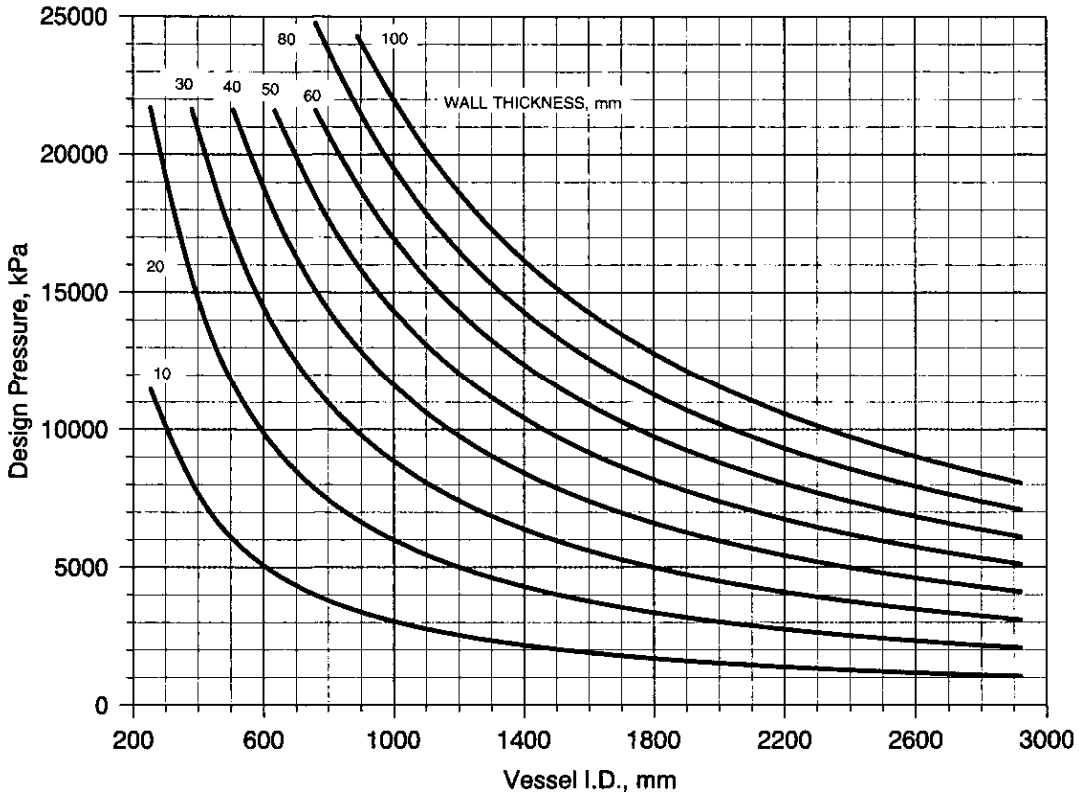
The total regeneration cycle in Figure 19.4 is divided into four parts – A, B, C and D. Temperature "T_H" and regeneration gas flow rate govern the time for each. Total regeneration time cannot be greater than the time available which in turn is fixed by number of towers and θ_B for the drying tower(s). 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.



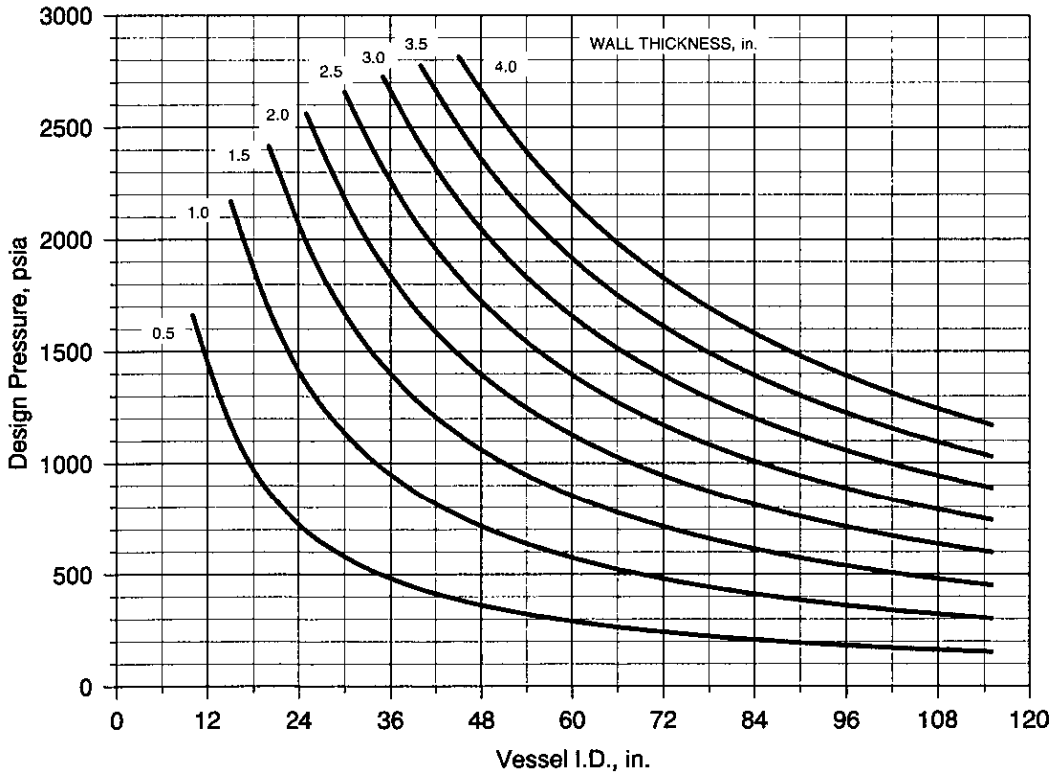


Figure 19.8 Approximate Pressure Vessel Wall Thickness

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

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

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.

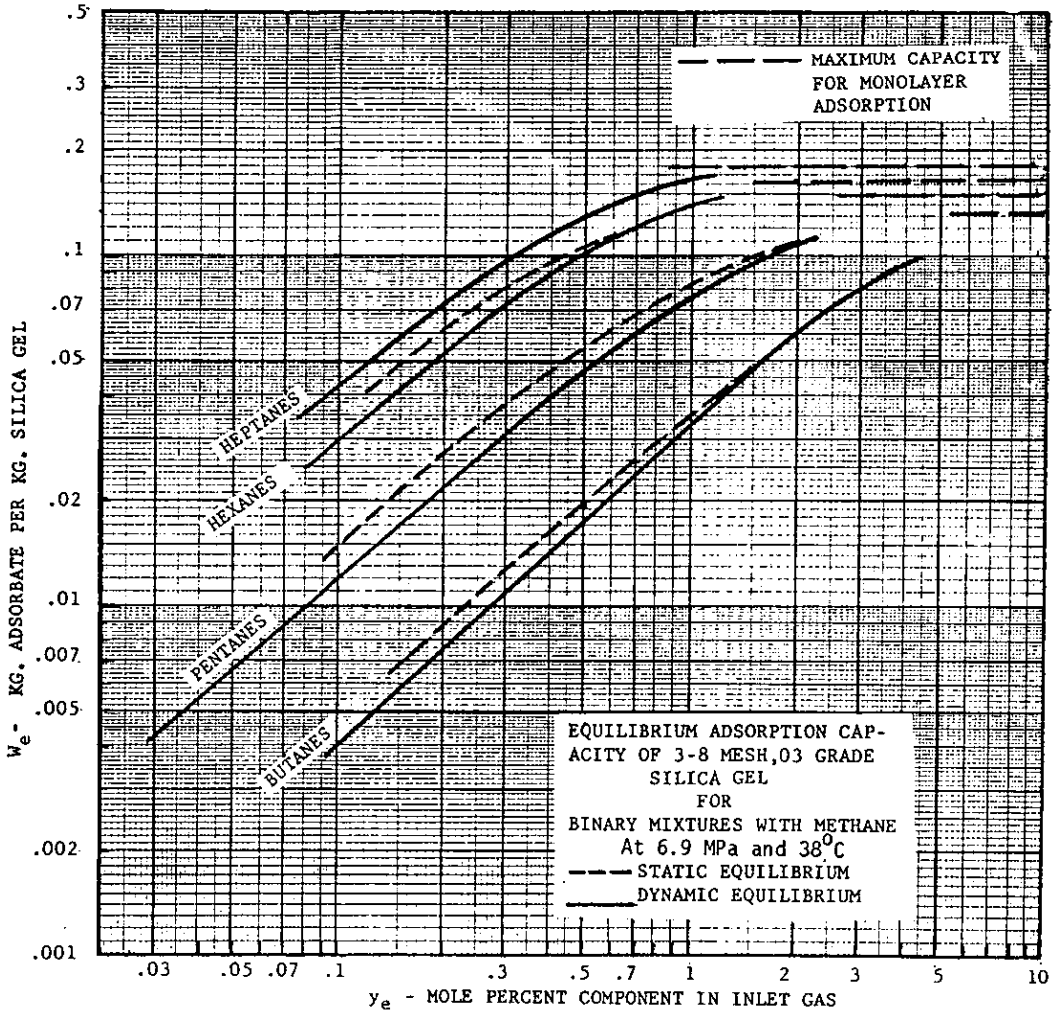
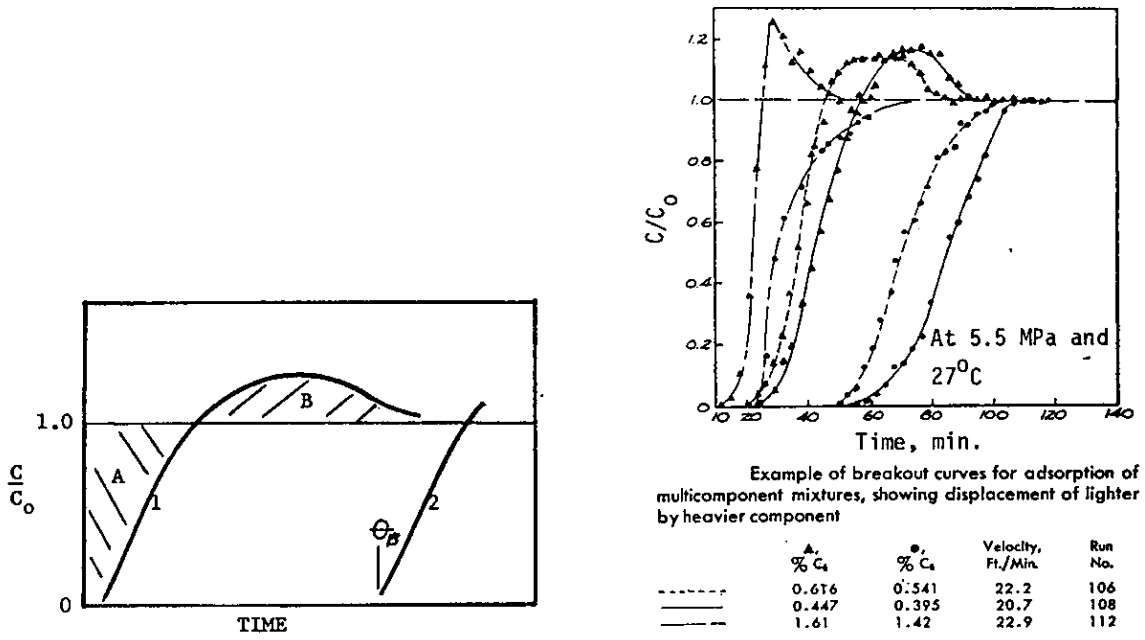


Figure 19.9 Hydrocarbon Equilibrium on Silica Gel

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.



Example of breakout curves for adsorption of multicomponent mixtures, showing displacement of lighter by heavier component

	A, % C_4	B, % C_4	Velocity, Ft./Min.	Run No.
-------	0.676	0.541	22.2	106
———	0.447	0.395	20.7	108
——— --	1.61	1.42	22.9	112

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_0) 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.*

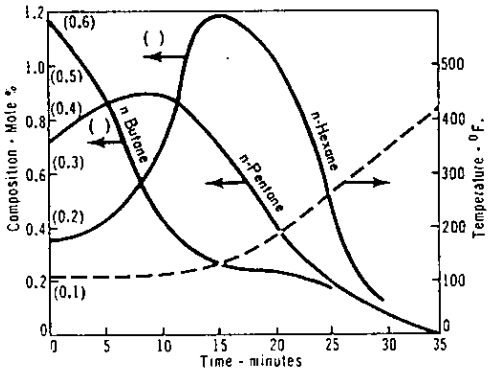
If liquid recovery is the goal, some net amount of component is available even after its zone passes from the tower. The recovery will simply be less. If hydrocarbon dewpoint control is the goal, such enrichment is probably intolerable for components heavier than the butanes. In such case, the iso-pentane 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.

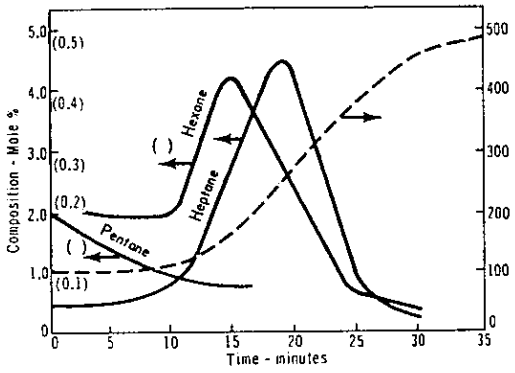
With activated carbon the zones tend to move slower. For one thing, water does not promote displacement. Basically though, the zone speed is lower because of the greater affinity for the lighter hydrocarbons.

Regeneration and Recovery

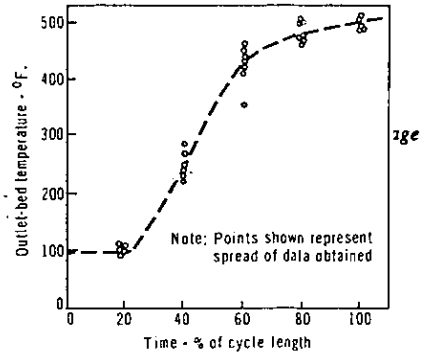
Figure 19.11 summarizes the regeneration behavior of a short cycle plant. Notice that the materials do not desorb at a constant rate. The pentanes and lighter start desorbing almost immediately. The hexanes and heavier concentration in the exit gas peak after a finite time.



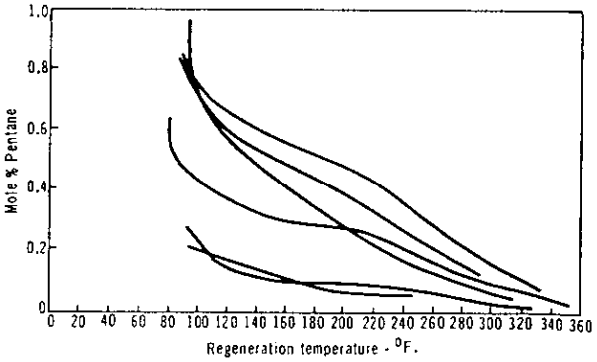
With butane, pentane, hexane



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.

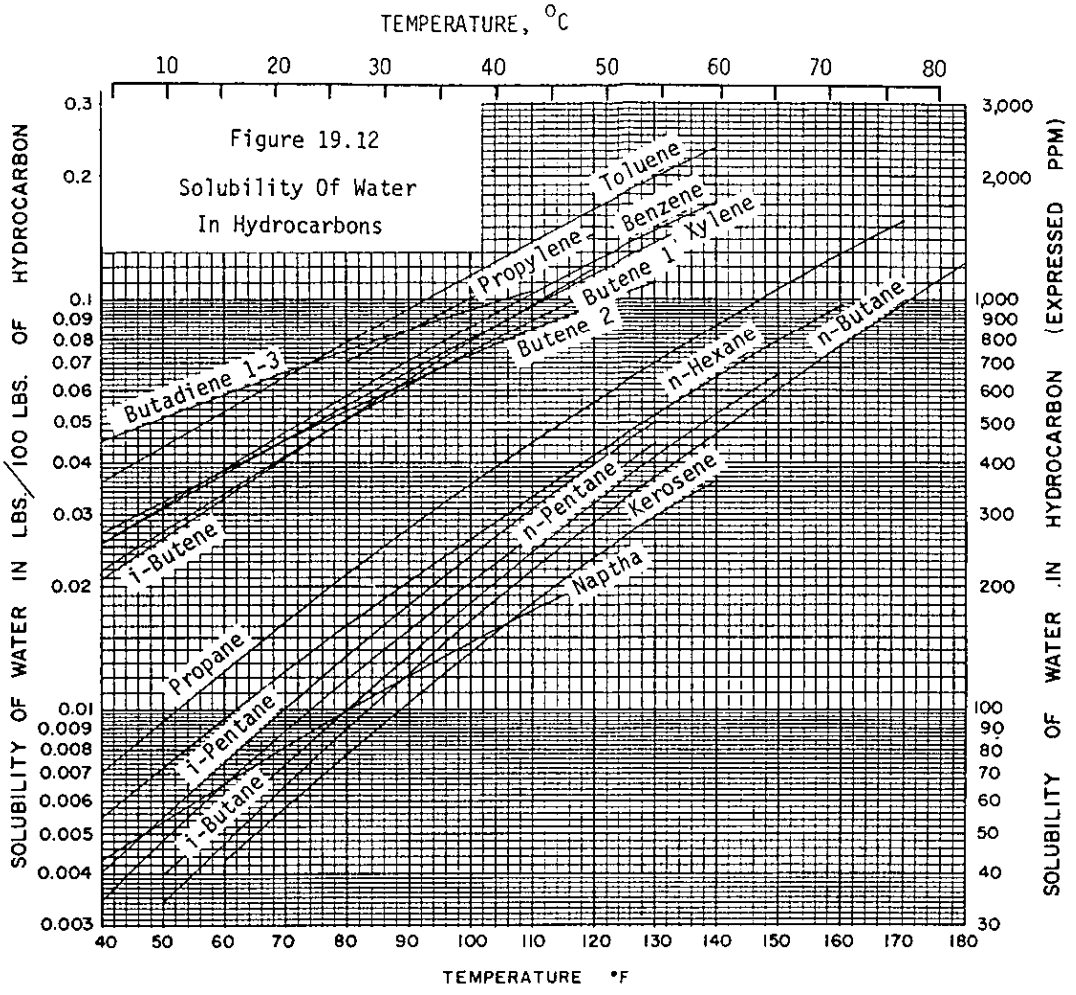


Figure 19.12 Solubility of Water In Hydrocarbons

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.

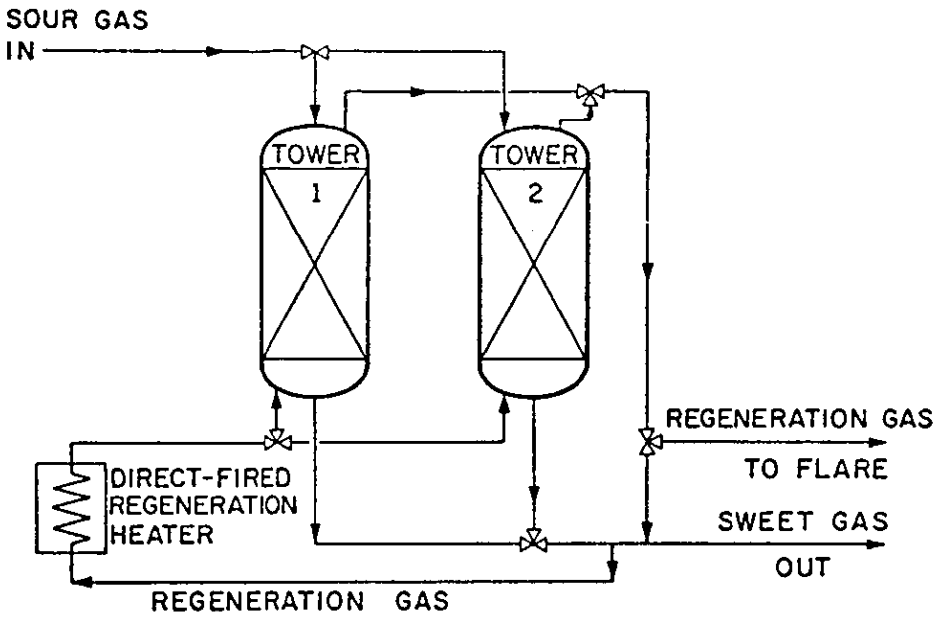


Figure 19.13 Flow Diagram for Basic Molecular Sieve Drying and Sweetening Process

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.

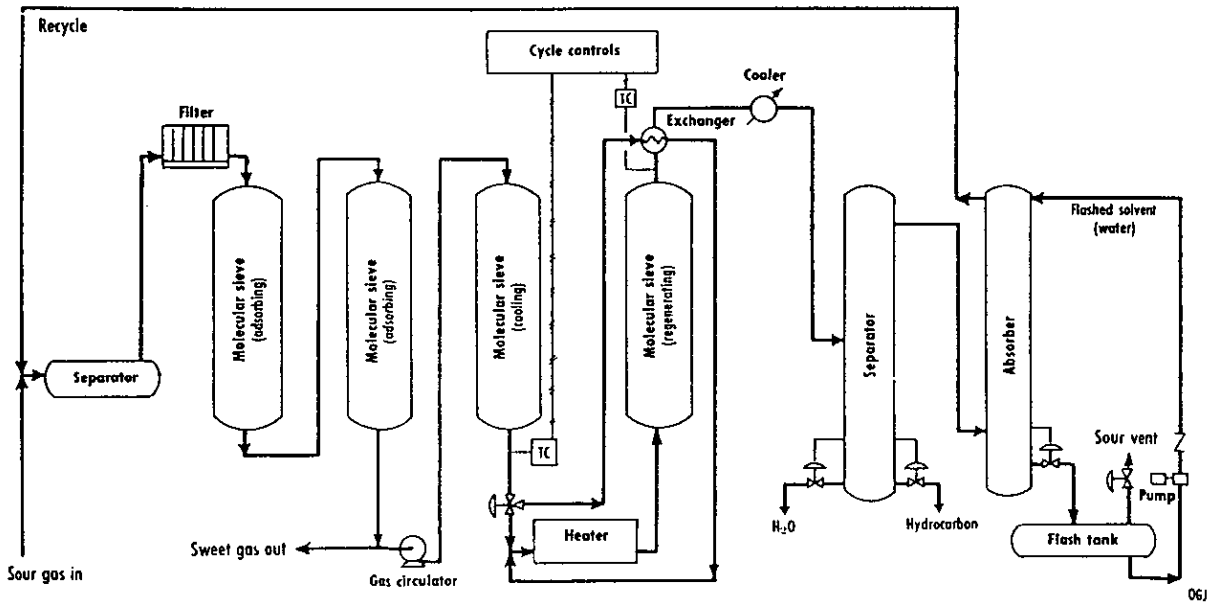


Figure 19.14 Flow Diagram for the EFCO Process

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.

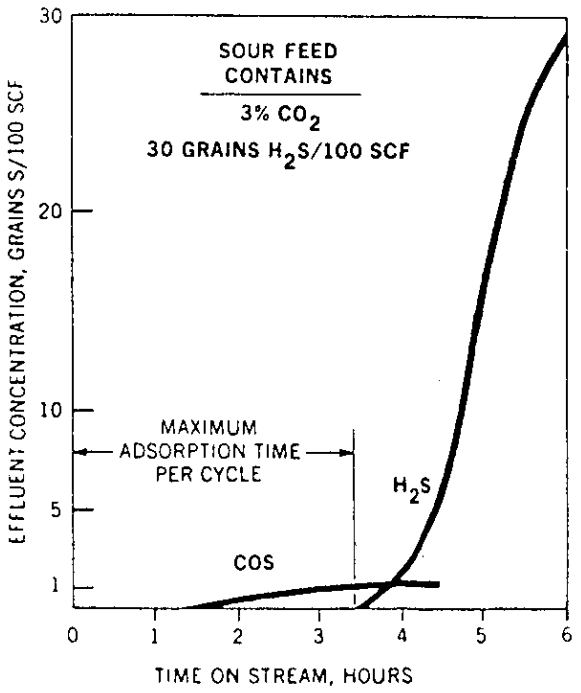
Sieves also can be used for removal of mercaptans and other heavier sulfur compounds. In prepurification of gases for LNG plants, water, H_2S and CO_2 can be reduced to acceptable levels.

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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