DESICCANTS

1. Introduction

Many substances take up (sorb) water from their surroundings by one or more of a number of different physical or chemical mechanisms. Many common materials have an affinity for water, such as wood, paper, natural fibers, polymers, solvents, or salts. Some materials have sufficient capacity for water or efficiency for drying as well as appropriate physical and chemical properties that they are classed as drying agents, or desiccants. These substances are widely used for removing water from gases, liquids, and solids. Desiccants may be liquids or solids. They may be used repetitively by regenerating the desiccant after use to return it to its active state, or they may be used only once. If the desiccant is used only once, it may last the life of the article being dried or may be discarded when spent. Drying agents are used either in a static (batchwise) or dynamic (continuous or semicontinuous) mode. Their use may be further classified as open system, if fluid flows through the system, or closed system if it does not. Examples of the industrial uses of desiccants, designated as dynamic or static and open- or closed-system applications, are given in Table 1. The list is not all inclusive and ignores various laboratory uses.

Desiccants have varied fundamental characteristics in terms of water capacity and the rate of water sorption. The degree of water removal achieved, or efficiency, is usually given in terms of the water content remaining in the substance that has been dried. This water content can be expressed in several ways, such as humidity ratio, relative humidity (at atmospheric pressure only), relative saturation (at elevated pressure or in liquids), dew point (used at any temperature), ice or frost point (used below 0°C), or parts per million (ppm) by weight or volume. The effectiveness of any drying agent can be measured in terms of its water capacity. In static applications, this capacity is usually the true equilibrium capacity. In dynamic systems, the rate of water removal must be taken into account. Usually, to allow for mass-transfer zones, an additional amount of drying agent is used. In these instances the dynamic capacity, also termed breakthrough capacity, falls short of the true equilibrium capacity (1).

2. Mechanism

The drying mechanisms of desiccants may be classified as follows: Class 1: chemical reaction, which forms either a new compound or a hydrate; Class 2: physical absorption with constant relative humidity or vapor pressure (solid + water + saturated solution); Class 3: physical absorption with variable relative humidity or vapor pressure (solid or liquid + water + diluted solution); and Class 4: physical adsorption.

These mechanisms are characterized by the relative magnitudes of the heats of reaction, solution, or adsorption (see ADSORPTION, GAS SEPARATION). All useful drying mechanisms are exothermic. Phosphorus pentoxide is a Class 1 drying

Table 1. **Applications of Desiccants**

Industry	Application	Classification
compressed air	prevent freeze-up and corrosion in air-actuated components	dynamic, open
air separation	prevent ice formation in heat exchangers before cryogenic distillation	dynamic, open
natural gas	prevent corrosion and hydrate formation in pipelines, remove water before cryogenic hydrocarbon recovery, dry liquefied petroleum gas (LPG) to prevent freeze-ups during vaporization	dynamic, open
petrochemical	remove moisture before low temperature fractionation, remove moisture during the rejuvenation or burnoff of spent catalysts, prevent side reactions during catalytic refining	dynamic, open
chemical	remove water that is a diluent or contaminant of some finished product, remove water prior to or during polymerization reactions, prevent caking and corrosion	static or dynamic, closed or open
storage and shipping	prevent food deterioration and corrosion of equipment by relative humidity control	static or dynamic, closed or open
moisture vapor control	lower the dew point in sealed spaces where condensation could occur	static, closed
vapor compression refrigeration	remove moisture from circulating refrigerants	dynamic, closed
space cooling	dry air to permit cooling by evaporation of water	dynamic, open
dehumidification	dry ambient air for air conditioning or for storage, manufacture, or drying of moisture-sensitive parts or materials	dynamic, open
corrosion control	reduce the dew point in automobile exhaust systems during cool down to reduce internal cold condensate corrosion	static, semiclosed
absorption refrigeration	cyclic absorption and stripping of water with liquid desiccants to produce chilled water for air conditioning[a] and process cooling	dynamic, open

[a] See AIR CONDITIONING.

agent that reacts with water to form a polyphosphoric acid (2):

$$x\mathrm{P_2O_5} + (x+1)\ \mathrm{H_2O(g)} \longrightarrow \mathrm{HO} \left(\mathrm{HPO_3} \right)_{2x} \mathrm{H} \qquad \Delta H = 109.5\ \mathrm{kJ/mol}\ (26.17\ \mathrm{kcal/mol}) \tag{1}$$

Class 1 drying agents (and zeolites, which are Class 4 desiccants) liberate the largest amounts of heat and should be used with appropriate care. Calcium chloride is a Class 1 drying agent that reacts with water to form a hydrate:

$$\mathrm{CaCl_2} + \mathrm{H_2O(g)} \longrightarrow \mathrm{CaCl_2 \cdot H_2O} \qquad \Delta H = 70\ \mathrm{kJ/mol}\ (16.7\ \mathrm{kcal/mol}) \tag{2}$$

The more highly complexed hydrates of calcium chloride ($CaCl_2 \cdot H_2O$ where $n > 2$) may also exhibit the characteristics of a Class 2 drying agent, because the hydrated species can physically absorb additional water to form a saturated solution. The term absorption is used to describe the phenomenon that occurs when a gas or vapor penetrates the solid structure to produce a saturated solution:

$$CaCl_2 \cdot 6\,H_2O + nH_2O\,(g) \longrightarrow \text{saturated solution} \qquad (3)$$

Because calcium chloride has a number of hydrates, the one that is in equilibrium with a saturated solution is a function of the temperature. In this case, the solid is dissolved as it absorbs water to form the saturated solution, and three phases are present: solid, saturated solution, and vapor. Systems having these three phases, or two solids and a vapor phase, have a constant vapor pressure at a given temperature. Therefore, Class 2 drying agents can be used to maintain a constant relative humidity.

Ethylene glycol is an example of a Class 3 drying agent. Because the solution produced is not saturated with water in its useful composition range, only two phases, solution and vapor, exist:

$$\text{ethylene glycol} + nH_2O\,(g) \longrightarrow \text{dilute solution} \qquad (4)$$

For this system, the vapor pressure is a function of both temperature and the concentration of water in the dilute solution.

Molecular sieve zeolites are an example of a Class 4 drying agent (see MOLECULAR SIEVES). Water is removed by physical adsorption, but at no time does the adsorbent change phase or dissolve.

$$\text{molecular sieve adsorbent} + H_2O\,(g) \longrightarrow H_2O\,(\text{adsorbed}) \qquad (5)$$

Adsorption (qv) is a phenomenon in which molecules in a fluid phase spontaneously concentrate on a solid surface without any chemical change. The adsorbed molecules are bound to the surface by interactions varying from weak to relatively strong between the solid and gas, similar to condensation (van der Waals) forces. Because adsorption is a surface phenomenon, all practical adsorbents possess large surface areas relative to their mass.

Desiccants can lose water capacity and drying efficiency by taking up moisture during storage. They should therefore be analyzed before use. If necessary, the materials should be reactivated (regenerated) before putting them in service.

3. Water Analysis

Hand in hand with desiccants goes the analysis for low levels of water (moisture). There are a number of proven methods, ranging from color change indicators to electronic hygrometers to the wet chemical and Coulometric Karl Fischer titration methods. The method chosen depends on the phase being analyzed, the precision needed, and convenience.

Color change indicators are chemicals often impregnated into a paper substrate or a solid desiccant itself. The indicator typically changes color at a fixed value of the relative saturation of the fluid in contact with it. For example, cobalt chloride changes from blue when dry to pink when wet. However, color change indicators are relatively imprecise.

Hygrometers are instruments capable of continuous on-line measurement of water in gases. Some hygrometers also work in liquids and saturated vapors. Hygrometers are particularly useful for continuous analysis in a flowing stream, such as dried air in a heating, ventilating, and air conditioning (HVAC) system. Some can be placed directly in the flowing stream while others must be installed outside the stream and exposed to a continuous sample of the fluid.

For analysis of water in a solid or a static liquid or gas sample, the standard technique is the Karl Fischer method. A liquid sample can be added directly to the solution in the KF reaction vessel, and a gas sample can be bubbled through the solution to extract the water. Solid samples are generally analyzed by heating them to a temperature appropriate to desorb the water in a drying oven or tube furnace purged with very dry nitrogen. The purge gas and volatiles, including water, are bubbled through the Karl Fischer extracting solution. The extracted water is then titrated with Karl Fischer reagent and the volume of reagent used is proportional to the mass of water evolved. The Coulometric Karl Fischer instrument generates the reagent electrochemically as needed directly in the titrating vessel and is capable of high precision at very low water concentrations. Several ASTM test methods are based on the Karl Fischer chemistry (3,4).

4. Compatibility

Desiccants must be chemically compatible with the material being dried. Ideally, the desiccant and the material should not react because such a reaction may produce harmful or undesirable by-products. For example, in the refrigeration and air conditioning industry, ozone-safe alternative refrigerants had to be tested to replace the chlorofluorocarbons in vapor compression refrigeration systems. The desiccants that keep these fluids dry must not react appreciably with the refrigerants or lubricants in the systems. Compatibility tests were conducted in which the desiccant and fluid were contacted under pressure often in the presence of system materials, such as lubricants and metals (5). The mixture was aged for various periods, typically 7 days or more, at temperatures above those expected at the desiccant location in the refrigeration system to increase the reaction rates. Following the exposure, the desiccant was analyzed for degradation products and retention of water capacity and physical properties.

5. Static Drying

Many liquids are dried batchwise rather than continuously. The drying agent is added to the liquid and sufficient time is allowed to dry the product. The liquid is then separated from the drying agent by filtration, decantation, or distillation.

Drying agents employing Class 1 or 2 mechanisms are generally used for these applications.

5.1. Desiccants Used in Static Drying. The most commonly used desiccants are discussed in this section; activated alumina, silica gel, and molecular sieves, which are discussed later under dynamic, solid drying agents, are also widely used in static or batch-drying situations.

Barium Oxide. This compound [1304-28-5] (Class 1, nonregenerative) is used primarily as a laboratory drying agent (6). It is the only drying agent that continues to dry even at red heat. Barium oxide is relatively expensive and cannot be regenerated by conventional methods. Therefore, it is not used extensively in commercial applications (see BARIUM COMPOUNDS).

Calcium Chloride. Calcium chloride, [10043-52-4], $CaCl_2$, (Class 1 or 2, regenerative), can be either a solid or liquid drying agent (6). Its principal advantage is that its cost is low enough to permit discarding after use in small units. Commercial anhydrous calcium chloride is available in a range of compositions from $CaCl_2 \cdot 0.05H_2O$ to $CaCl_2 \cdot 0.25H_2O$. Figure 1 is a phase diagram for calcium chloride (see CALCIUM COMPOUNDS SURVEY).

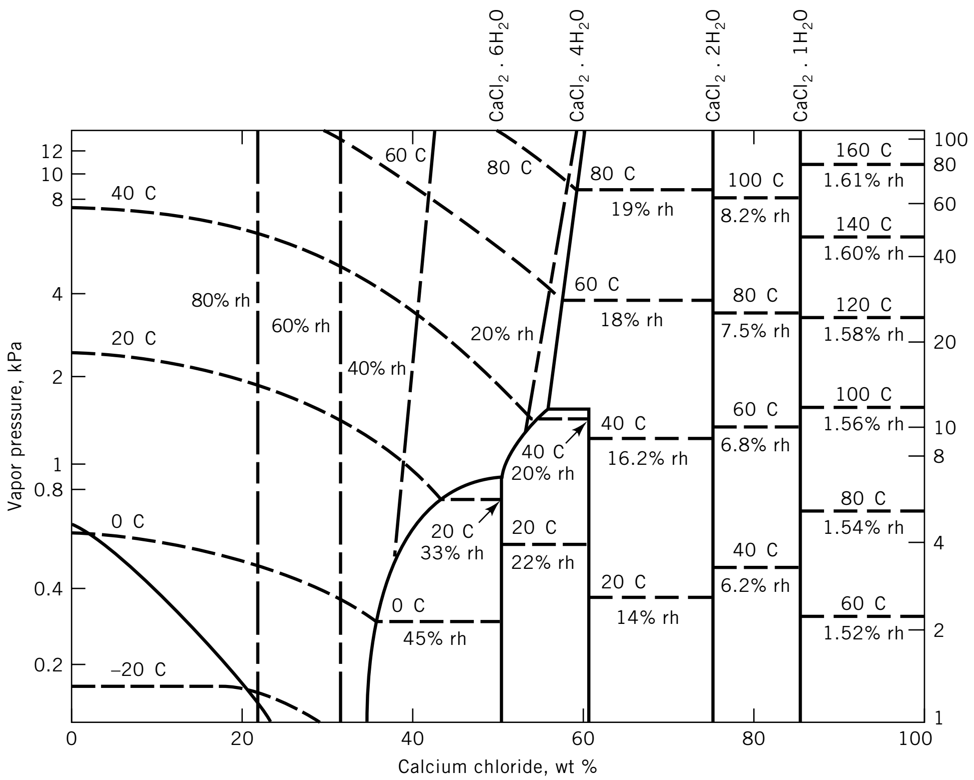

Fig. 1. Vapor pressure and relative humidity over $CaCl_2$ solutions and solids. The straight horizontal lines in the right-hand portion represent two solid phases and a gas phase for vertical line intersections. In addition, a solid phase, saturated solution, and a vapor phase occur in the regions between the vertical lines. The lower left-hand corner shows the ice solution line. The region in between, with skewed isothermal lines, represents unsaturated solutions; the vapor pressure varies as a function of temperature.

Calcium Oxide. Also called lime or quicklime (6,7), calcium oxide [1305-78-8] (Class 1, nonregenerative), is relatively inexpensive. It is prepared by roasting calcium carbonate (limestone) and is available in a soft and a hard form according to the way in which it was burned. For desiccant service, soft-burned lime should always be used. Calcium oxide is most commonly used to dehydrate liquids and is most efficient when it can be heated to speed the reaction rate. The reaction product is calcium hydroxide, which crumbles as it picks up moisture.

Calcium Sulfate. Calcium sulfate [7778-18-9] (Class 1, regenerative) is sold under the trade name Drierite (6,8). It occurs in nature in the anhydrous form, $CaSO_4$, and in the hydrated form, $CaSO_4 \cdot 2\,H_2O$, commonly known as gypsum. When prepared properly, small capillaries form within the granules and increase the somewhat low water capacity of the material by sorbing additional moisture. The first stages of water removal occur by adsorption and a chemical reaction to form a hemihydrate [10034-76-1], $CaSO_4 \cdot 1/2H_2O$. The material can be regenerated repeatedly by heating to $\sim$200°C. However, above 300°C, it loses some of its desiccating power. Calcium sulfate is used extensively because it is chemically inert to most materials, reusable, and inexpensive.

Clays. Montmorillonite clay (Class 4, regenerative) is a calcium magnesium alumino-silicate mineral. It is a heat-activated solid adsorbent used as a desiccant in packaging applications (see CLAYS), where it conforms to military specification MIL-464E.

Metal Halides. Of the metal halides, calcium bromide [7789-41-5], $CaBr_2$, zinc chloride [7646-85-7] $ZnCl_2$, $CaCl_2$, and lithium chloride [7447-41-8] LiCl, (Class 1, nonregenerative) are the most effective for water removal (6). All are available in the form of deliquescent crystals. The hydrates of LiCl are $LiCl \cdot nH_2O$, where $n = 1$, 2, or 3. Lithium chloride solutions are more stable in air and less corrosive than the other metal halides. The high solubility of lithium carbonate [554-13-2], Li_2CO_3, usually eliminates scale formation problems (see LITHIUM AND LITHIUM COMPOUNDS).

Perchlorates. The three common perchlorates (Class 1, nonregenerative) used as drying agents are barium perchlorate [13465-95-7], $Ba(ClO_4)_2$, lithium perchlorate [7791-03-9], $LiClO_4$, and magnesium perchlorate [10034-81-8] $Mg(ClO_4)_2$. The last is the most efficient with drying action above 100°C. Even the higher hydrate form has good drying capacity. Perchlorates are strong oxidizing agents and should never be used in the presence of organic compounds because the mixture is highly explosive. For this reason, perchlorates are usually not regenerated (seeCHLORINE OXYGEN ACIDS AND SALTS).

Phosphorus Pentoxide. This compound, P_2O_5, (Class 1, nonregenerative) is made by burning phosphorus in dry air. It removes water first by adsorption, followed by the formation of several forms of phosphoric acid (2). Phosphorus pentoxide [1314-56-3] has a high vapor pressure and should only be used below 100°C. Its main drawback is that as moisture is taken up, the surface of the granules becomes wetted and further moisture removal is impeded. For this reason, phosphorus pentoxide is sometimes mixed with an inert material (see PHOSPHORIC ACIDS AND PHOSPHATES).

Sodium and Potassium Hydroxides. Sodium hydroxide [1310-73-2] and potassium hydroxide [1310-58-3] (Class 1, nonregenerative) are commonly used

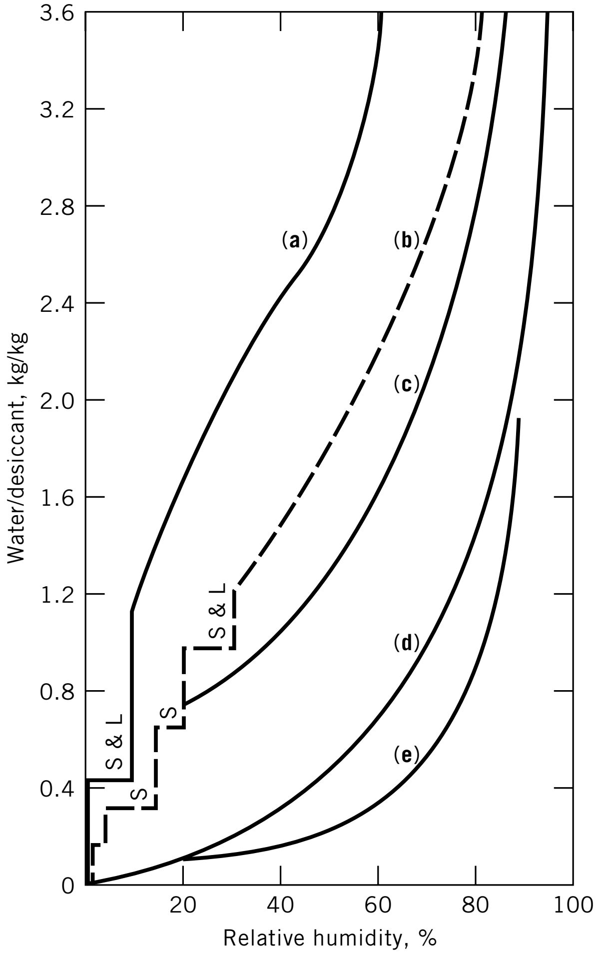

Fig. 2. Drying capacity of selected drying agents in liquid form. (**a**) represents lithium chloride; (**b**) calcium chloride; (**c**) sulfuric acid; (**d**) glycerol; (**e**) triethylene glycol. S is solid, L is liquid.

when moisture and carbon dioxide or hydrogen sulfide must be removed simultaneously (6). Fused sticks or solutions of the alkali hydroxides are frequently used. These materials must be handled with care to prevent serious skin burns.

5.2. Capacity and Efficiency. Figure 2 shows the drying capacity of selected desiccants as a function of relative humidity. The higher capacity desiccants go through the various hydrate levels to yield fairly broad ranges of constant relative humidities as moisture is picked up. However, these compounds do not produce very low relative humidities or dew points. Figure 3 shows the water vapor pressure over several desiccants as a function of temperature. The addition of more desiccant lowers the vapor pressure. The best performance, or lowest dew point, occurs with excess drying agent. The minimum dew points attainable in air at room temperature and atmospheric pressure are given in Table 2 (9,10).

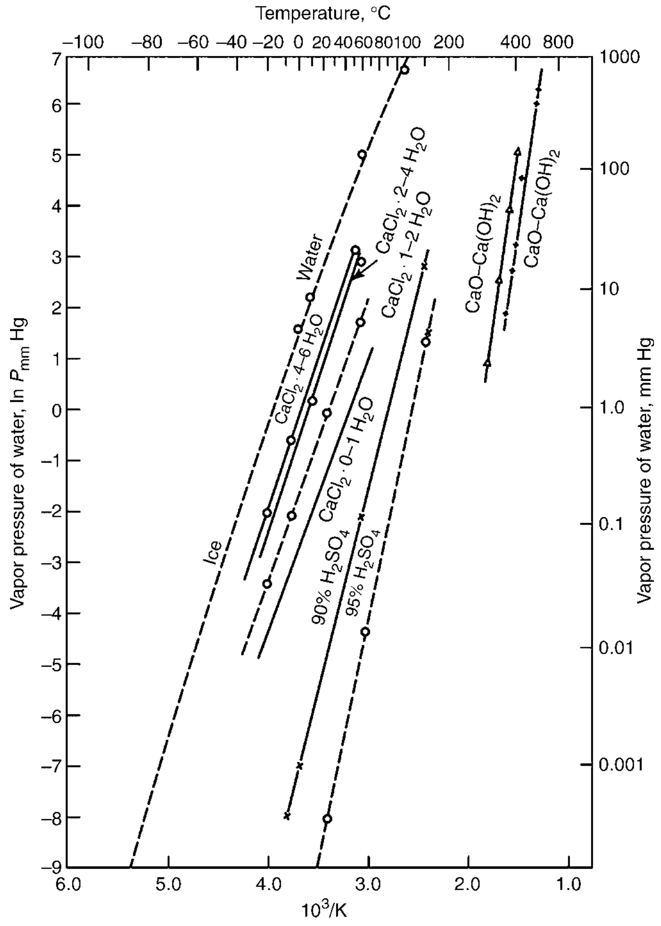

Fig. 3. Water vapor pressure over ice, water, and several desiccants.

The efficiency ranking of desiccants in drying air is not always the same as that observed in drying other materials. Other materials may interact with the desiccants to reduce drying effectiveness. From a study of the efficiency of some 25 desiccants for drying several families of laboratory solvents and reagents it was concluded that molecular sieves are the desiccants of choice in most cases (11–19).

5.3. Closed-System Drying. Equilibrium capacity is the principal consideration in the design of closed nonregenerative, relatively static drying systems. The total amount of moisture to be removed must first be calculated from the volume of the system and the initial water concentration. Depending on the final moisture content desired, a drying agent can be selected based on its compatibility with the material to be dried and its ability to produce the final dew point. The equilibrium capacity of the drying agent must be determined at the system temperature and the final water concentration. The initial water content of the desiccant (the residual water) should be subtracted from the equilibrium water capacity to get a useful equilibrium water capacity for the

Table 2. **Performance of Chemical Desiccants in Drying Air at Room Temperature**

Substance	Minimum humidity[a]	Minimum dew point at 101.3 kPa,[b] °C
P_2O_5	0.0193	−98
BaO	0.503	−80.5
KOH fused	1.546	−73
CaO	2.32	−70.5
H_2SO_4	2.32	−70.5
$CaSO_4$ anhyd.	3.87	−67
Al_2O_3	3.87	−67
KOH sticks	10.83	−60
NaOH fused	123.7	−40
$CaBr_2$	139.2	−39
$CaCl_2$ fused	262.9	−33
NaOH sticks	618.6	−25
$Ba(ClO_4)_2$	634.0	−24.5
$ZnCl_2$	657.2	−24
$ZnBr_2$	896.9	−21
$CaCl_2$ granular	1159.8	−18

[a] mg H_2O/kg dry air.

[b] To convert kPa to mm Hg, multiply by 7.5.

desiccant. An amount of drying agent must be used so that the total amount of water to be removed does not exceed the predetermined useful equilibrium water capacity of the agent. The agent and the material are then placed in intimate contact. After sufficient time, the system comes into equilibrium with the drying agent.

Although equilibrium capacity is the prime concern, few of these closed systems are truly static. Even closed systems have dynamic features or other nonsteady-state aspects, such as temperature fluctuations, moisture ingression, and drydown rates.

Closed systems are usually nonregenerative: The desiccant charge is designed for the life of the system or is replaceable. Often in a nominally closed (static) drying system, the total amount of moisture to be removed consists of both the water initially in the system and that which leaks into the system over its lifetime. In multipane (insulating glass) windows, eg, molecular sieve desiccant is used to keep the air (or gas-filled) space dry to prevent condensation in cold weather. The glass panes are typically separated by an aluminum spacer, which is a hollow channel partially filled with the desiccant. The glass and spacer are joined and sealed with organic sealants. Although a small amount of desiccant is required to dry the gas initially sealed into the space, a much larger amount is typically used to adsorb moisture that is slowly transmitted into the space from the outside. The transmission of water vapor through the sealant is driven by the difference in water partial pressure between the desiccated space and the ambient air. Thus to specify the mass of desiccant needed requires knowledge of the moisture vapor transmission rate and specification of the design life of the unit as well as the moisture content of the gas initially sealed into the space. Because the system likely is nonisothermal, the analysis of a closed-desiccant system requires knowledge of the temperature of the desiccant as well as the dew point (ice point) or water concentration (partial pressure) specification. Indeed, the whole system may undergo periodic temperature transients that may complicate the analysis. For example, in dual-pane windows the desiccant temperature is approximately the average of the indoor and outdoor temperatures after a night of cooling. However, after a day in the sun, the desiccant temperature becomes much warmer than the outdoor temperature. When the sun sets, the outdoor pane cools quickly while the desiccant is still quite warm. The appropriate desiccant for such an application must have sufficient water capacity and produce satisfactory dew points at the highest temperatures experienced by the desiccant.

Another aspect to consider in the design of closed-drying systems is the drydown time. The drydown time is the period required for the system to dry down from its initial water concentration (or partial pressure) to a concentration that approaches equilibrium with the desiccant. During this time, the system is not fully protected from the negative effects of the moisture that the desiccant is designed to remove. In such a system, the instantaneous drying rate is proportional to the water content at any time (20).

The drying rate is represented by differential equation (eq. 6) where h is mass transfer coefficient $1/(\mathrm{h} \cdot \mathrm{cm}^2)$; A, specific surface area of desiccant beads, cm^2/g; m, mass of desiccant, g; C, concentration by weight of water in the fluid being dried; C', concentration of water at the surface of the desiccant, ie, concentration of water in the fluid that would be in equilibrium with the instantaneous loading on the desiccant, ppm; and $t = \text{time}$, h.

$$\frac{dC}{dt} = -hAm\,(C - C') \tag{6}$$

If C' is approximately constant during the initial drydown period, as it is in many closed-system applications, then the water concentration decays exponentially with time. The rate equation can be integrated to give the relationship between water concentration and time:

$$\frac{C}{C_0} = \exp\left[-hAM\,(t - t_0)\right] \tag{7}$$

where C_0 is the water concentration at the initial time t_0.

If required, the drydown can be hastened by increasing desiccant mass, particle surface area, or mass-transfer coefficient. The mass-transfer coefficient can be altered to some extent by the design of the desiccant container.

Because a material balance on water must be satisfied during the drydown as well as afterward, the path from the initial concentration to equilibrium can be represented graphically by a material balance line and an equilibrium curve. The coordinates of the starting point on the material balance line are the initial water contents of the fluid to be dried and the desiccant. The slope of the line is the ratio of fluid mass to desiccant mass. The line terminates at its intersection with the equilibrium curve (Fig. 4).

An interesting and novel use of a solid desiccant, the reduction of cold condensate corrosion in automotive exhaust systems, illustrates a hybrid closed–open system. Internal corrosion occurs in mufflers when the water vapor in

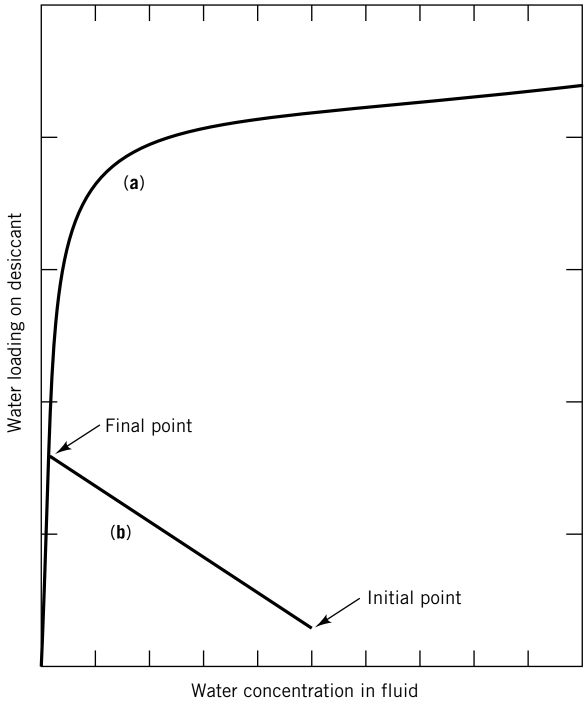

Fig. 4. Drydown path to equilibrium in a closed system. (**a**) represents the equilibrium curve and (**b**) the material balance line.

the exhaust condenses after the engine is turned off and the muffler cools. Carbon dioxide dissolves in the condensate to form an acidic soup. In an essentially closed static drying step, an acid- and heat-resistant desiccant located in the muffler adsorbs water vapor from the exhaust gas as it cools to prevent formation of corrosive acidic condensate. When the engine is restarted, the system becomes open, and the desiccant is regenerated by the hot exhaust gas to be ready for the next cooldown step (21).

6. Dynamic Drying

Continuous drying is employed when drying a volume of gas or liquid in a batchwise fashion is not practical. When a solid, dynamic desiccant is used, the fluid stream is passed over a fixed bed of the drying agent, which must have the physical properties to allow the fluid to pass readily through. When liquid desiccants are used, the drying is usually achieved by countercurrent contact of the gas (flowing up) against the liquid (flowing down). The desiccants are usually regenerable.

6.1. Liquid Desiccants. Glycols and sulfuric acid are the principal examples.

Sulfuric Acid. Sulfuric acid, H_2SO_4 [7664-93-9] (Class 3, regenerative), is used extensively throughout the chemical industry to dry acidic and corrosive

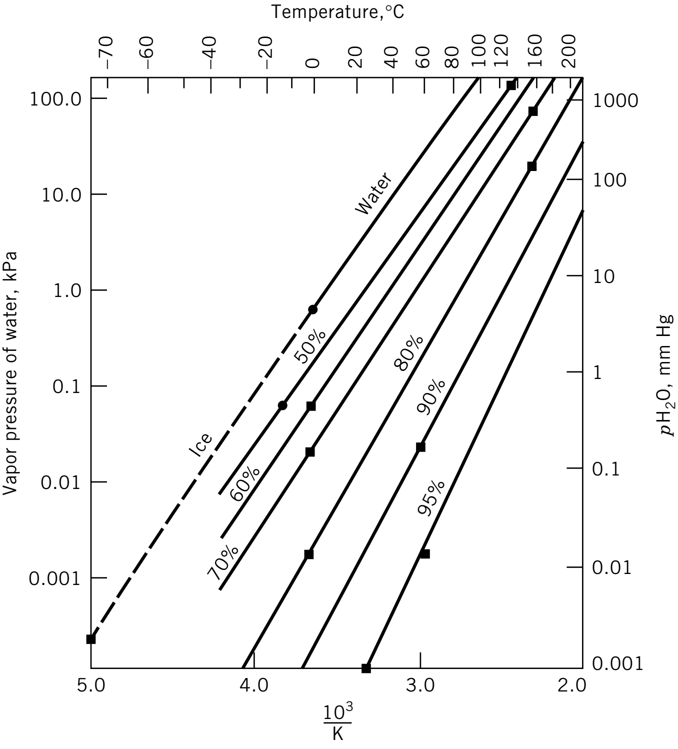

Fig. 5. Vapor pressure of water over sulfuric acid solutions. Percentage of H_2SO_4 noted on each curve.

gases. It has good capacity and drying capability as illustrated by the vapor pressure curves in Figure 5. At 25°C, the dew point attainable in gases dried with 95% sulfuric acid is less than −75°C.

Sulfuric acid is used in circulating towers like those depicted in Figure 6; the gas flows countercurrent to the acid. The spent acid is removed from the primary contactor at a 50% H_2SO_4 content and may be used for chemical manufacturing or recycled after reconcentration. The makeup, or recycled, acid is usually introduced at 93% H_2SO_4 (sp gr 1.84, 66° Bé or higher) because this moisture content establishes the final moisture level of the dried product gas. Sulfuric acid is highly corrosive, and protective clothing and eye protection must be provided.

Glycerol, Glycol, and Other Polyhydric Alcohols. These alcohols (Class 3, regenerative) are widely used to dry gases (22,23). However, they can only produce dew points in the range of −15 to 0°C (see ANTIFREEZES AND DEICING FLUIDS). They have somewhat lower capacity than sulfuric acid (Fig. 2) but are effective when either injected or employed in a multistage contactor to achieve dew point depression.

Ethylene glycol [107-21-1] , diethylene glycol [111-46-6], and triethylene glycol [112-27-6] are used extensively in the natural gas industry to inhibit hydrate formation (24,25). Diethylene glycol (DEG) is the most widely used.

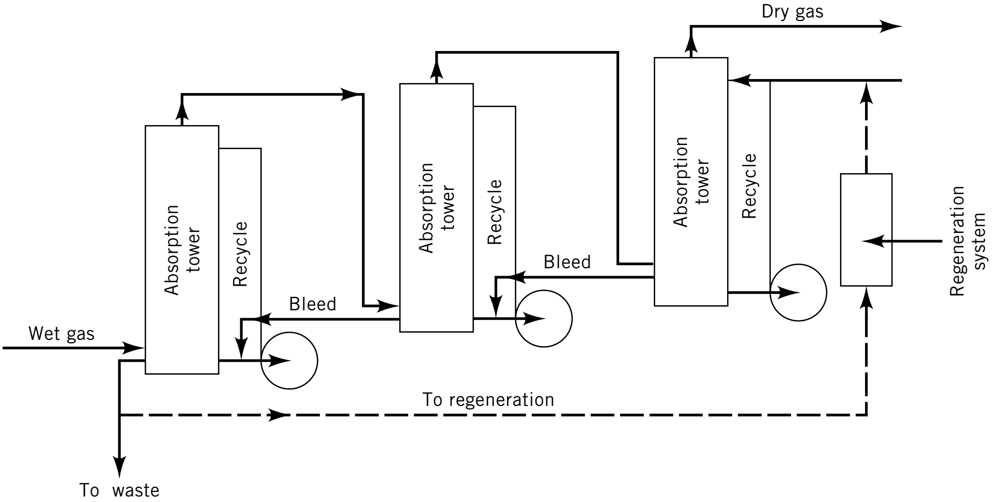

Fig. 6. Continuous sulfuric acid drying system.

The dew point that can be achieved in the treated gas (26,27,28) is a function of the percentage of glycol present and the contact temperature (Fig. 7). The principal advantages of glycol dehydration are low cost, ease of regeneration, and minimal losses of the drying agent caused by solubility or vapor pressure during subsequent recovery or reclamation.

A typical flow diagram of a glycol dehydration plant is shown in Figure 8. The absorber, or gas–liquid contactor, operates with glycol flowing downward, countercurrent to the gas stream. The regenerator, or stripping column, operates at low pressures to keep the column temperature below the decomposition temperature of the glycol. The regenerated glycol is then recirculated to the absorber (see ALCOHOLS, POLYHYDRIC; GLYCEROL; GLYCOLS, ETHYLENE GLYCOL AND OLIGOMERS).

6.2. Solid Desiccants. The solid desiccants used in dynamic applications fall into a class called adsorbents (see ADSORPTION). Because they are used in large packed beds through which the gas or liquid to be treated is passed, the adsorbents are formed into solid shapes that allow them to withstand the static (fluid plus solid head) and dynamic (pressure drop) forces imposed on them. The most common shapes are granules, extruded pellets, and beads (spheres).

Activated Alumina. This material (Class 4, regenerative) is made by the calcination of an alumina gel or aluminum oxide trihydrate [21645-51-2], $Al_2O_3 \cdot 3H_2O$, into various crystalline phases of transition aluminas (29). Depending on the manufacturing procedure and starting material, the final product has different degrees of specific surface and pore volume. Table 3 lists the physical properties of a typical Grade A activated alumina.

The water removal mechanism is adsorption, which is the mechanism for all Class 4 drying agents. The capacity of such materials is often shown in the form of adsorption isotherms as depicted in Figures 9**a** and 9**b**. The initial adsorption mechanism at low concentrations of water is believed to occur by monolayer coverage of water on the adsorption sites. As more water is adsorbed,

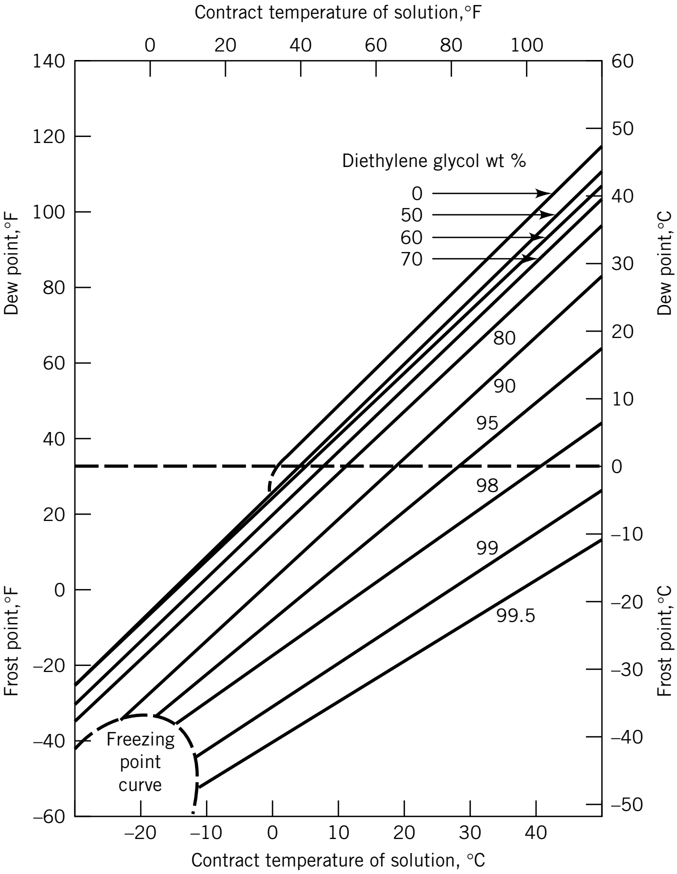

Fig. 7. Dew points of aqueous diethylene glycol solutions.

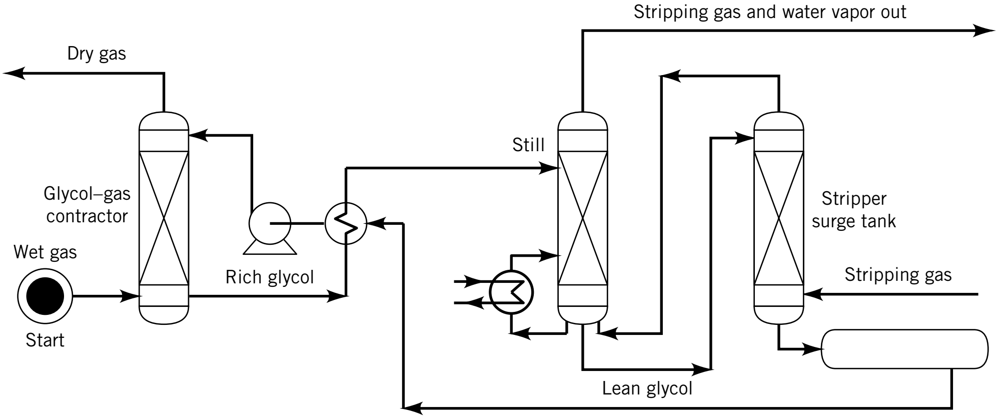

Fig. 8. Natural gas diethylene glycol dehydration system.

Table 3. **Physical Properties of Solid Adsorbents**

Property	Grade A activated alumina	Silica gel	Type 4A molecular sieve
surface area, m^2/g	320	832	750
bulk density, kg/m^3	800	720	670
maximum heat of adsorption, J/g H_2O^a	~1395	~930	~4180
specific heat, J/(kg · K)[a]	1005	921	1046
reactivation temperature, °C	150–315	125–275	200–315
pore volume, % of total	~50	~55	~48
pore size, nm	1–7.5	1–40	0.42
pore volume, $cm^3/100$ g	40	43	28.9

[a] To convert J to cal, divide by 4.184.

successive layers are added until condensation or capillary action takes place at water saturation levels $\gtrsim 70\%$ relative humidity. At saturation, all the pores are filled; and the total amount of water adsorbed, expressed as a liquid, represents the pore volume of the adsorbent.

In regenerating activated alumina, heating to a temperature of 150–200°C is sufficient to recover nearly all of the initial water capacity. This regeneration is usually accomplished by passing a heated gas through the adsorbent bed.

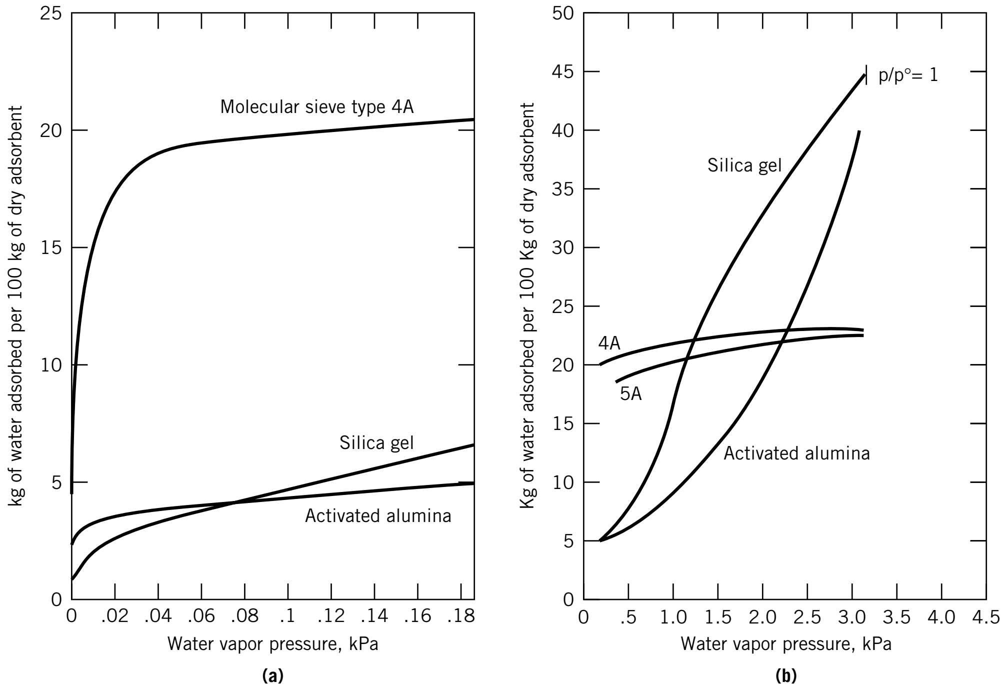

Fig. 9. Water adsorption isotherms for activated alumina, molecular sieves, and silica gel at 25°C (to convert kPa to mm Hg, multiply by 7.5). 4A and 5A designate molecular sieves.

Unless the surface is fouled by the gas or liquid being dried, the life of activated alumina is good and usually depends on the number of regeneration cycles (see ALUMINA, ACTIVATED).

Silica Gel. This material [7631-86-9] (Class 4, regenerative) is made by dehydration of high purity silica hydrogel (30). The final product is high in purity (99.7% SiO_2), which contributes to its chemical inertness. The typical physical properties are listed in Table 3. The pore size of silica gel has the broadest range of the three primary solid desiccants. Therefore, it can adsorb larger molecules in addition to water (critical diameter = 0.265 nm). The average pore diameter is ~2.5 nm.

The capacity of silica gel is shown in Figures 9**a** and 9**b**, and the shape of the isotherm is similar to activated alumina. At saturation ($p/p^\circ = 1.0$), silica gel, which takes up 40 kg H_2O/100 kg of adsorbent, has the highest capacity of the desiccants shown. However, some high capacity silica gels tend to shatter in the presence of liquid water. When liquid water may be present, a lower capacity, water-resistant silica gel must be used.

The normal regeneration temperature for silica gel is 175°C. In hydrocarbon service, higher temperatures (225–275°C) are recommended to desorb heavy hydrocarbons, which tend to foul the adsorbent during prolonged use (see SILICON COMPOUNDS, AMORPHOUS SILICA).

Molecular Sieves. Molecular sieve desiccants (Class 4, regenerative) are members of a class of materials called zeolites (31). Although some occur in nature, commercial molecular sieve zeolites are usually synthetic (see MOLECULAR SIEVES). They are crystalline framework aluminosilicates containing alkali metal cations. The structure extends in three dimensions by a network of AlO_4 and SiO_4 tetrahedra linked to one another by the sharing of oxygen atoms. Molecular sieves possess the high porosity that is characteristic of all adsorbents. In addition, the ordered crystalline structure of the molecular sieve provides pores of a constant size. In contrast, the pores in activated alumina and silica gel are nonuniform in size, as shown in Table 3. Silica gel is an amorphous material with no crystal structure. The pore structure in activated alumina is not contained within the alumina crystals but is formed by the spaces between randomly agglomerated crystals.

The pore size of molecular sieves can be enlarged or diminished by appropriate cation exchange. Many commercial types are available with pore openings ranging from 0.3 to ~1.0 nm. For example, type 3A (the potassium form of zeolite A) has a nominal pore opening of 0.3 nm (3 Å) and type 4A (sodium form) has a nominal 0.4 nm opening. Type 5A (calcium form) with a 0.5-nm opening and type 13X (sodium form of zeolite X) with an 0.85-nm opening are also available.

All these forms adsorb water molecules. The constant size and adjustable pore opening permit the exclusion of many other gaseous and liquid molecules from the internal pore structure, hence the name molecular sieve. This feature provides unique advantages in certain applications. Fouling of the adsorption surface by compounds with high molecular weights can be prevented by excluding them. Molecular sieves with larger pores can also be used simultaneously to dry and purify process streams, eg, by the adsorption of carbon dioxide or sulfur compounds in addition to water.

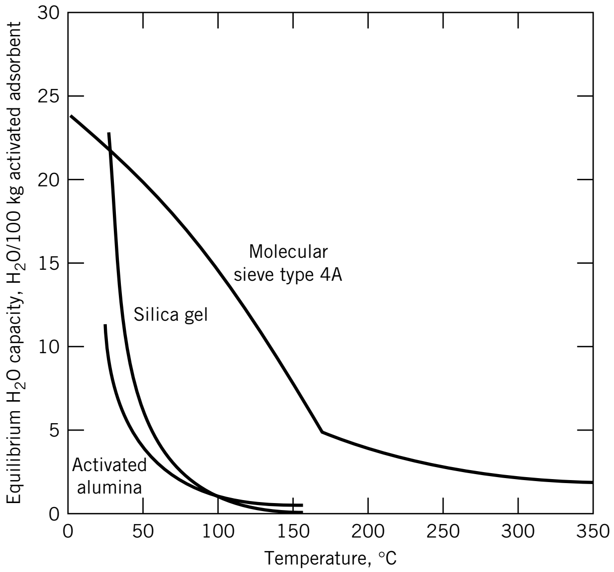

Fig. 10. Adsorbent isobars (p_{H_2O} = 1.38 kPa). To convert kPa to atm, divide by 101.3.

Because of their ordered structure, molecular sieves have high capacity at low water concentrations and do not exhibit a capillary condensation pore-filling mechanism at high water concentrations. The desiccating properties of the material are still good at elevated temperatures (Fig. 10). A dew point of −75°C can be obtained in a gas dried at 90°C with a molecular sieve that adsorbs water to the level of 1 wt%. In normal operations at ambient temperature, dew points of less than −100°C have been measured.

Molecular sieves are also inert to most fluids and are physically stable when wetted with water. Strong inorganic acids or alkalies and temperatures >700°C should be avoided. Mildly acidic streams can be dried with a molecular sieve of an acid-resistant type (32).

7. Design of Dynamic Adsorption Drying Systems

Adsorbent drying systems are typically operated in a regenerative mode with an adsorption half-cycle to remove water from the process stream and a desorption half-cycle to remove water from the adsorbent and to prepare it for another adsorption half-cycle (10,33,34). Usually, two beds are employed to allow for continuous processing. In most cases, some residual water remains on the adsorbent after the desorption half-cycle because complete removal is not economically practical. At cyclic steady state the amounts of water removed during the adsorption and desorption half-cycles is the same. Divided by the adsorbent weight, this amount is termed the differential loading, which is the working capacity available for dehydration.

The two most common types of drying systems operate on either a pressure-swing cycle or a thermal-swing cycle to take advantage of the difference in water

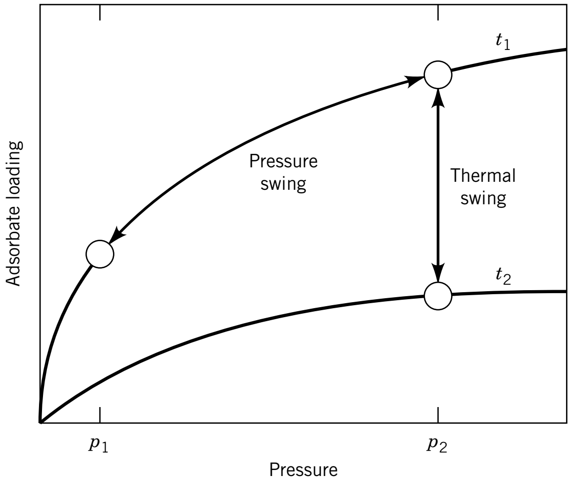

Fig. 11. Schematic illustration of the thermal-swing and pressure-swing cycles. In thermal swing, the differential loading, Δx, is given by $\Delta x_t = x_{t1} - x_{t2}$ at p_2; in pressure swing: $\Delta x_p = x_{p2} - x_{p1}$ at t_1.

loading on the desiccant with changes in pressure or temperature (Fig. 11) (31). A pressure-swing cycle uses a high pressure adsorption step and a low pressure desorption step and does not require an elevated temperature for regeneration. However, some amount of thermal energy can be added, if desired, during the desorption half-cycle to increase the desorption efficiency. This type of system operates with small differential water loadings. Therefore, short adsorption and desorption times are used (1–60 min). Higher effluent dew points are characteristic of this type of dehydration operation. A thermal-swing cycle requires an elevated temperature during the desorption step. Depressurization can also be used during this step to improve regeneration efficiency. This type of cycle operates with the highest differential loadings, and longer cycle times are normally used (4–24 h). If low dew points are required, a thermal-swing cycle should be employed.

In many cases a two-bed dehydrator system, with one bed on adsorption and the other on regeneration, can process all the fluid to be dried. Figure 12 is a schematic of a simple two-bed natural gas dehydrator; the same scheme can be used to dry air. Natural gas is first passed through a gas–liquid separator to ensure single-phase operation. The gas passes downflow through a molecular sieve drying tower (28). The dried product natural gas may then be sent for further processing, eg, cryogenic hydrocarbon recovery of liquefied petroleum gas (LPG) condensates. The residue or lean gas from the cold section of such a plant is commonly used for regeneration. The gas is heated and passed through the exhausted adsorbent bed (Tower B) with the flow countercurrent to the gas drying step. Tower B is then cooled to feed temperature by flowing gas around the heater directly to the bed. The spent regeneration gas then passes through a cooler, and liquid water is removed before it is returned to the pipeline. Depending on the process conditions, the amount of regeneration gas required

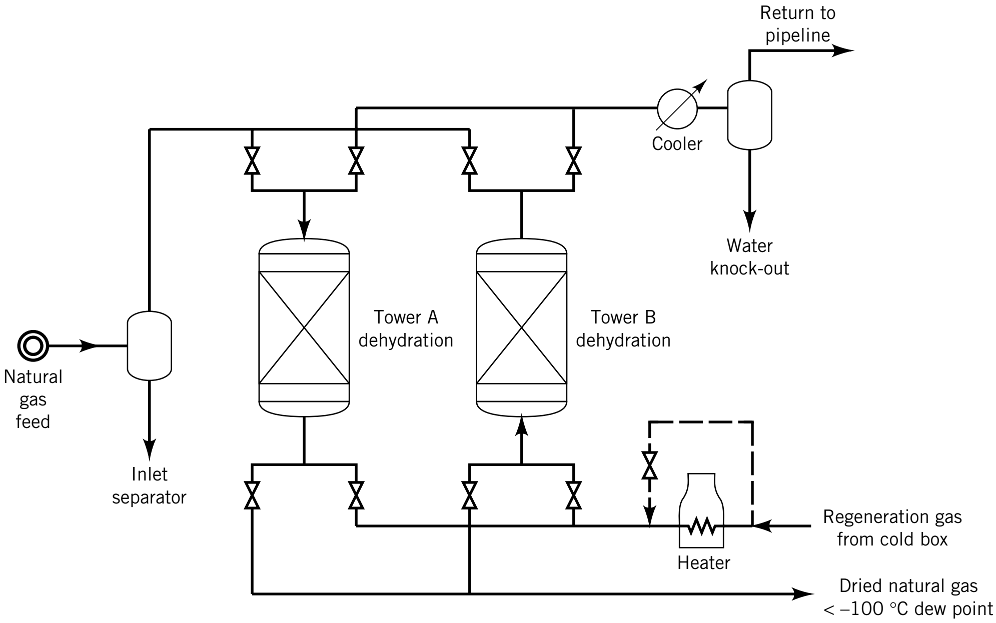

Fig. 12. Molecular sieve natural gas dehydrator.

is ~5–10% of the total amount of gas dried (see Cryogenics; Gas, natural; Liquefied petroleum gas).

Single-bed systems can also be used if the demand for drying is intermittent. For example, pressure-swing air dryers installed on heavy trucks usually employ a single desiccant bed to dry compressed air for operating the brakes. When the pressure in the primary air storage reservoir in the system reaches a set point, a blowdown to atmospheric pressure and a purge of the dryer bed using air from a purge reservoir take place (35,36). A single-bed, thermal-swing system can also be used for drying intermittent flows. Very dry gas is often needed to regenerate or cool adsorbent beds for gas purification (see Adsorption, gas separation). A single-bed auxiliary dryer can be used for this purpose (37).

Three-bed solid adsorption systems are also used for drying gases. The three beds can be arranged so that two beds are drying and one is in regeneration or one bed is drying and two are in regeneration, one in heating and one in cooling. When two beds are used in drying, they can be in series flow, one bed in the "lead" position and the other in the "lag" or "trim" position, or they can be in parallel flow, where the adsorption fronts are staggered.

A growing application is the use of a rotating desiccant wheel for drying air in dehumidification systems (38–45). The wheel may consist of a packed bed or a rolled corrugated paper (or polymer) monolith with desiccant particles adhered to the surface. The packed bed consists of a cylinder that rotates on its axis through sectors for adsorption and thermal desorption. The bed is filled with granular or beaded desiccant particles in axial compartments or passages to reduce leakage from the adsorption sector to the heating sector and vice versa.

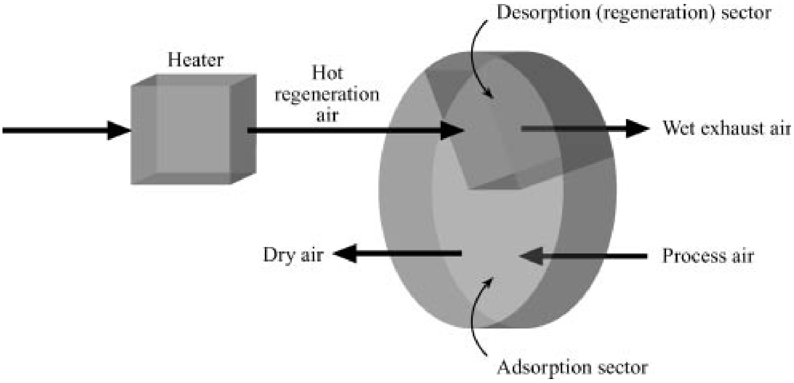

Fig. 13. Desiccant dehumidification wheel.

The ducting and housing around the bed are built with seals to minimize leakage between sectors at the wheel faces. Rotary beds and wheels operate continuously without the valve switching required in stationary packed beds. The desiccants used in wheels include silica gel, activated alumina, solid lithium chloride, molecular sieve types 4A or 13X, special zeolites, titanium silicate, and others.

The desiccant wheel can be used in two ways—for dehumidification and for energy exchange. As a dehumidification wheel, it adsorbs water from circulating moist air to produce low humidity air for a building. The regeneration air can be heated with natural gas, electricity, waste heat, or solar energy. The spent regeneration air is exhausted outside the building (Fig. 13).

As an energy exchange wheel, the wheel exchanges both sensible and latent heat with another air stream. This can be very useful for increasing fresh air in a building without losing excessive energy. Thus, in winter, humidity and sensible heat are recovered from the exhaust air and transferred to the make-up (incoming fresh) air as the wheel turns. In summer, humidity and sensible heat from the fresh make-up air are transferred to the exhaust air as the wheel turns (Fig. 14).

In designing a gas drying system, the engineer must often estimate the water content of the gas to be dried. If the gas is air at atmospheric pressure,

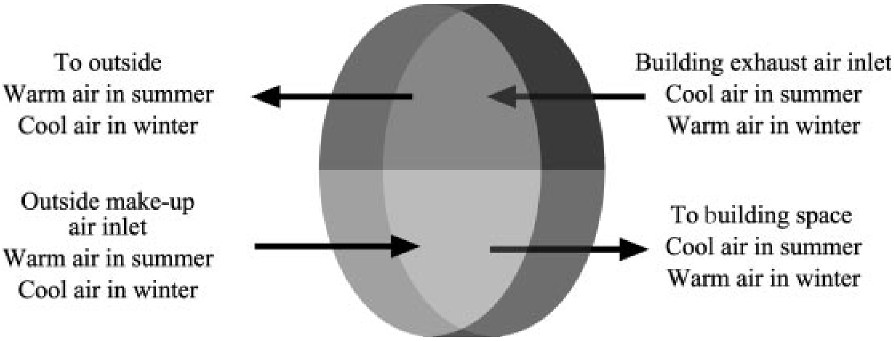

Fig. 14. Energy exchange wheel.

psychrometric charts are available to give the specific humidity (mass of water per mass of dry air) for given conditions of dry bulb temperature and relative humidity or wet bulb temperature (46,47). Often, however, the gas is under pressure and is known to be saturated with water under given temperature and pressure conditions. In this case, an estimate of the water content can be made by using the vapor pressure of water p° at the given temperature at total pressure π, as reported in the steam tables.

$$y = \frac{p^\circ}{\pi} \tag{8}$$

Although this estimate will sometimes be sufficient, it may well fail at higher pressures (48). Fortunately, several references are available that provide data and estimating procedures for high pressure hydrocarbons (C_1–C_4), natural gas, hydrogen, and nitrogen (49–65).

7.1. Adsorption Plots. Isotherm plots are the most common method of presenting adsorption data. An isotherm is a curve of constant temperature: The adsorbed water content of the adsorbent is plotted against the water partial pressure in equilibrium with the adsorbent. An isostere plot shows curves of constant adsorbed water content: The vapor pressure in equilibrium with the adsorbent is plotted against temperature. Figure 15 shows isosteres for the three primary

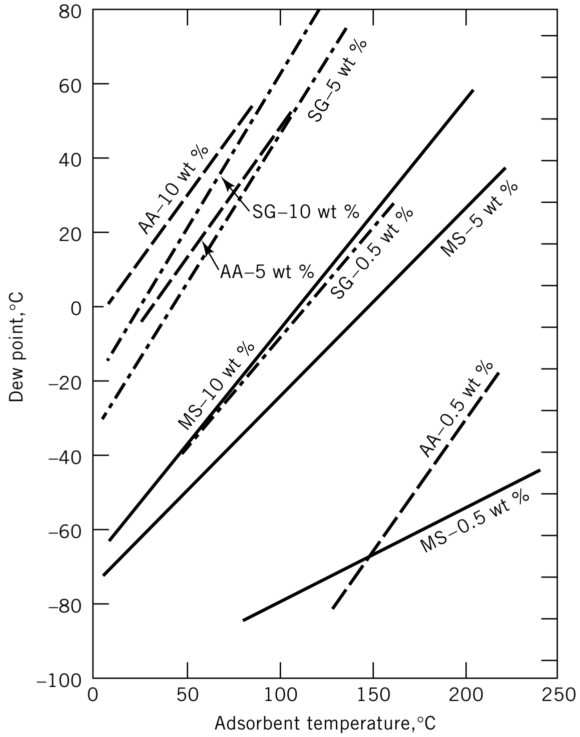

Fig. 15. Adsorbent isosteres for activated alumina (AA), silica gel (SG), and molecular sieves (MS).

adsorbents described previously. In this case, the dew points for the three adsorbents are plotted at 0.5, 5, and 10 kg H_2O/100 kg of adsorbent. At equilibrium and at a given adsorbed water content, the dew point that can be obtained in the treated fluid is a function only of the adsorbent temperature. The slopes of the isosteres indicate that the capacity of molecular sieves is less temperature sensitive than that of silica gel or activated alumina. In another type of isostere plot, the natural logarithm of the vapor pressure of water in equilibrium with the desiccant is plotted against the reciprocal of absolute temperature. The slopes of these isosteres are proportional to the isosteric heats of adsorption of water on the desiccant (see ADSORPTION, GAS SEPARATION).

7.2. Mass Transfer and Useful Capacity. The term useful capacity, also referred to earlier as breakthrough capacity, differs from the equilibrium capacity shown on Figures 9**a** and 9**b**. The useful capacity is a measure of the total moisture taken up by a packed bed of adsorbent at the point where moisture begins to appear in the effluent. Thus the drying process cycle must be stopped before the adsorbent is fully saturated. The portion of the bed that is not saturated to an equilibrium level is called the mass-transfer zone.

The parameters affecting the size and shape of a mass-transfer zone are adsorbent type, adsorption isotherm shape, flow rate, packed-bed depth, adsorbent particle size, physical properties of the carrier fluid, temperature, pressure, and the concentration of water in the carrier fluid. For example, as the particle size increases for a given fluid flow rate, the pressure drop decreases. However, as the particle size increases, the mass-transfer resistance increases, and the adsorbent takes longer to achieve its equilibrium water capacity. As a result, larger amounts of desiccant are required. Therefore, the optimal particle size is a compromise between pressure drop (energy consumption) and desiccant utilization. If conditions are chosen that are favorable to mass transfer, eg, small particle size, then the mass-transfer zone is small when compared to the total amount of packed bed employed in drying service. In this case, bed utilization is high and the breakthrough or useful capacity closely approaches the true equilibrium capacity. More often, conditions cannot be optimized on the basis of absorbent needs but are fixed by the needs of the drying process. This situation may dictate unfavorable mass-transfer conditions when pressure drop is limited or practical packed-bed diameters and depths must be employed. Bed utilization is then reduced and the breakthrough capacity falls short of the equilibrium capacity.

Figure 16 depicts the location of the water front in packed beds of adsorbents at a short but typical contact time for dehydration. The percentage of useful capacity as compared to equilibrium capacity is ~50% for activated alumina and silica gel and >90% for the molecular sieve. The reason for this difference in performance lies in the shape of the isotherm. Under the Brunauer classification, the molecular sieve has a type I isotherm shape, which is favorable for adsorption mass transfer (see ADSORPTION). This isotherm produces a self-sharpening adsorption front, or constant pattern behavior. Silica gel and activated alumina have non-type I isotherms, which are unfavorable for adsorption mass transfer. Their isotherms produce an expanding adsorption front or proportional pattern behavior. Thus the highest equilibrium capacity adsorbent may not always result in the highest useful capacity in a dynamic system. If higher moisture contents

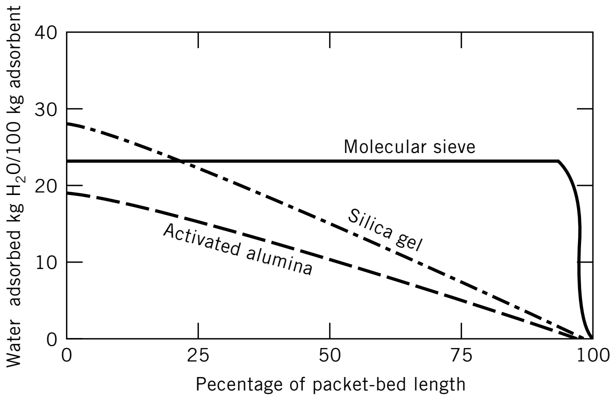

Fig. 16. Position of water front in packed bed of adsorbent during dynamic dehydration. Conditions: 50% rh; 10.2 cm/s air; particle size = ~0.167 cm; temperature = 25°C; contact time = 1.7s.

can be tolerated in the effluent, then a larger fraction of the mass-transfer zone can be allowed to leak through into the effluent stream. This technique improves bed utilization at the expense of an increase in the effluent dew point.

8. Economic Aspects

8.1. Cost-Effectiveness of Desiccants. The cost-effectiveness of a regenerable Class 4 (physical adsorption) desiccant is a function of the initial investment and the operating cost. The initial investment depends on the desiccant bed weight, which determines the costs of the desiccant and the desiccant vessel. The investment also includes other equipment costs, such as compressors or blowers for gas-phase systems, and regeneration equipment, such as regeneration compressor and heater. The principal operating costs are the energy costs associated with thermal-swing regeneration and compression costs associated with fluid pressure drop across the bed.

The required desiccant weight is a function of several factors: the water removal requirements (mass/time), the cycle time, the equilibrium loading of water on the desiccant at the feed conditions, the residual water loading on the desiccant after regeneration, and the size of the mass-transfer zone of the desiccant bed. These factors, in turn, depend on the flow rate, temperature, pressure, and water content of both the fluid being dried and the regeneration fluid (see ADSORPTION, GAS SEPARATION).

Shorter cycle times produce smaller bed sizes. The minimum cycle time is usually dictated by the minimum regeneration time required to heat and cool the bed. Systems of greater than two beds provide some flexibility in regeneration time but add to investment costs.

Operating costs consist of compression costs for drying gases and the energy costs for thermally regenerated systems. Labor is also a cost, although most systems are designed to run automatically with a minimum of operator attention. Compression costs are a function of bed size and design and desiccant particle

Table 4. **1997 Applications of Selected Desiccants in North America, Million Pounds**

	Molecular sieve	Activated alumina	Silica gel	Clay[a]	Lithium chloride
hydrocarbon processing	16	9.6	5.0		
insulating glass	19		1.0		
refrigeration	6.4	1.9			
packaging	3.2		6.5	17	
air drying[b]		9	1.6		0.5
polyurethane	5.7				
air brakes	2.9				

[a] Heat activated montmorillonite.

[b] Includes both pressure drying and dehumidification.

characteristics as well as flow rate, pressure, and temperature. Regeneration costs in thermal-swing systems include the sensible heating of the desiccant and vessel from the feed temperature to the regeneration temperature and the heat of adsorption of water on the desiccant. Some designs with two beds in regeneration (one in heating and one in cooling) allow for recovery of sensible heat.

Desiccant replacement is another operating cost, although desiccant life is usually several years in regenerable applications. Desiccant life depends on the stability of the desiccant in the given service, the frequency of regeneration, the presence of reactive contaminants, and the possibility of upsets to normal operation.

8.2. Market Data. The largest U.S. manufacturer of molecular sieves for adsorbent and desiccant use is UOP, which has a production capacity of ~30 million kg/year. W.R. Grace and Zeochem have ~5 and 9 million kg/year capacity, respectively (66). W.R. Grace is the largest producer of silica gel desiccants.

Table 5. **1997 North American Consumption of Selected Desiccants by Supplier, Million Pounds**

	Molecular sieve	Activated alumina	Silica gel	Clay[a]	Lithium chloride
UOP[b]	37	6.8			
Grace Davison[c]	12		23		
Zeochem	16				
Engelhard			3.0	4.5	
Eagle			2.4		
Atofina	2.6				
Solvay			1.0		
Alcoa		13			
Alcan		1.2			
United Desiccants (Süd Chemie)				7.0	
Cypress Foote Minerals					0.5

[a] Heat activated montmorillonite.

[b] Includes Bayer and La Roche acquisitions.

[c] Includes Crosfield.

Activated alumina for use as adsorbent and desiccant is produced by UOP (formerly LaRoche Chemicals), Aluminum Company of America, and Porocel.

The largest users of molecular sieve desiccants are the natural gas processing, insulating glass, and refrigeration industries (Table 4). Much smaller quantities of silica gel are used in these applications. Silica gel dominates the packaging industry, where the material is used to protect electronic equipment and pharmaceuticals, eg, from moisture. Silica gel is also used in dehumidification of buildings. The principal uses of activated alumina are in refrigeration, where its primary function is to adsorb organic acids rather than water, air drying, and alkylation feed stream drying in oil refineries. The data in Tables 4 and 5 are estimates of 1997 North American usage and production capacity and are considered the best available (67).

9. Emerging Applications

9.1. Energy Storage. Reactivating a desiccant stores the reactivation energy in the dehydrated desiccant. This energy-storage feature is useful if the energy source is intermittent or seasonal, such as solar energy, or interruptable. Research suggests that this energy-storage feature is especially useful if the desiccant is used to dry air for agricultural applications (68).

9.2. Desiccant Cooling. Desiccant cooling is a continuing area of research. In these systems, a desiccant is used to produce an extremely dry air stream. The dry air is then cooled in a heat exchanger and humidified with a water spray. The evaporation of the water absorbs heat from the air and produces a cold, almost saturated air stream for air conditioning. The desiccant is thermally regenerated with exhaust air, which is heated with solar energy, natural gas, or waste heat from power generation. Both liquid (69,70) and solid desiccant systems have been studied. The solid desiccant systems typically employ a wheel, which rotates a bed of desiccant particles through sectors in which drying, thermal regeneration, and cooling take place (71). These systems are extensions of existing dehumidification technology, with a strong emphasis placed on minimizing the thermal regeneration requirements. To this end, extensive basic studies have been carried out of solid desiccants and the properties of the hypothetical desiccant ideally suited to low temperature thermal regeneration. Research shows that the shape of the desiccant isotherm and the thermal properties of the desiccant, such as heat capacity, are equally important in desiccant selection (72). Organic polymers as well as inorganic materials are being considered as desiccant materials (73). An extensive body of literature on the subject is cataloged at the U.S. National Renewable Energy Laboratory web site (45).

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