



## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

#### 2.1 Background

Water is a common impurity in gas streams, especially natural gas and its removal is necessary to prevent its condensation and the formation of solid ice-like crystals called hydrates. In the liquid phase, water will cause corrosion problems in pipelines and equipment, particularly when carbon dioxide and hydrogen sulfide are present in the gas (Speight, 1993). The dehydration of natural gas must begin at the source of the gas in order to protect the transmission system.

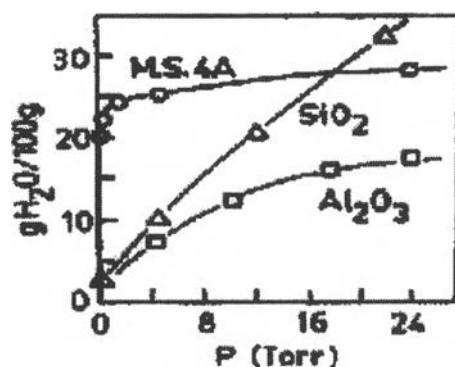
##### 2.1.1 Natural Gas Dehydration

There are basically three methods employed to reduce water content of natural gas. First one is dew point control or Joule-Thomson expansion. This technique utilizes temperature drop to remove condensed water to yield dehydrated natural gas. Next technique is liquid desiccant dehydration or Glycol absorption process. This method removes water from the gas stream by counter current contact in a tray type contactor tower with glycol solution. Through this contact, the gas gives up its water vapor to the glycol solution. The last technique for natural gas dehydration is the adsorption using solid adsorbents. Three types of mostly used adsorbents are molecular sieve, silica gel and activated alumina. Although there are several techniques for water removal from natural gas, an adsorption process using solid desiccants has been proven to be the best alternatives for water vapor removal because of their great drying ability.

##### 2.1.2 Adsorbents

In principle, all microporous materials can be used as adsorbents for gas purification and separation. The most important characteristic of an adsorbent is its high porosity. Thus, physical characterization is generally more important than chemical characterization (Yang, 1987). The search for a suitable adsorbent is generally the first step in the development of the adsorption separation process.

A high affinity and capacity for adsorption of moisture from a gas stream are simply the properties of adsorbent used as a solid desiccant. Therefore, the main requirements for an effective adsorbent are highly polar surface and high specific area. Activated alumina, silica gel, and molecular-sieve zeolites have all been used for drying natural gas (Sherman and Yon, 1991).



**Figure 2.1** Equilibrium isotherms for adsorption of water vapor at 25°C on 4A molecular sieves, activated alumina, and silica gel (Ruthven, 1984).

#### 2.1.2.1 Activated Alumina

Activated alumina is a porous high-area form of aluminum oxide, prepared either directly from bauxite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) or from the monohydrate by dehydration and recrystallization at elevated temperature. As shown in Figure 2.1, at room temperature, the affinity of activated alumina for water is comparable with that of silica gel but the capacity is lower. At elevated temperatures the capacity of activated alumina is higher than silica gel, and it was therefore commonly used as a desiccant for drying warm air or gas streams. However, for this application it has been largely replaced by molecular sieve adsorbents, which exhibit both a higher capacity and a lower equilibrium vapor pressure under most conditions of practical importance (Ruthven, 1984).

#### 2.1.2.2 Silica Gel

Silica gel is made by dehydration of high purity silica hydrogel. The final product is in high purity (99.7%  $\text{SiO}_2$ ), which contributes to its chemical inertness. The capacity of silica gel is shown in Figure 2.1, and the shape of the isotherm is similar to activated alumina. 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 (Cohen, 1991).

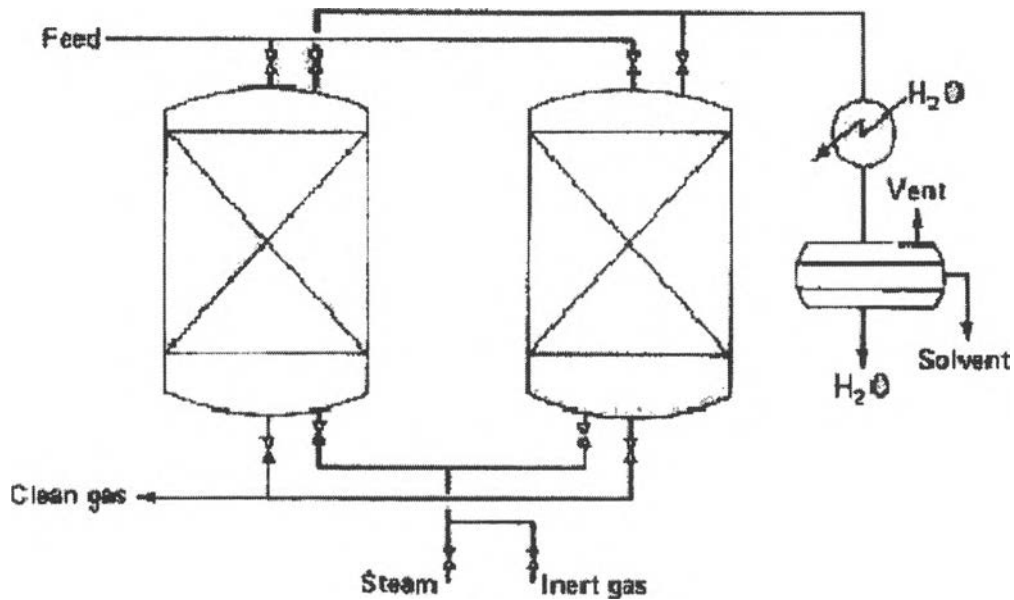
### 2.1.2.3 *Molecular-sieve Zeolites*

Molecular-sieve desiccants are members of a class of materials called zeolites. They are the crystalline framework aluminosilicates containing alkaline metal cations. The structure extends in three dimensions by a network of  $AlO_4$  and  $SiO_4$  tetrahedra linked to one another by sharing oxygen atoms. Molecular-sieves possess the high porosity which 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 of activated alumina and silica gel are not uniform in size. 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. A dew point of  $-75^\circ C$  can be obtained in a gas dried at  $90^\circ C$  with a molecular sieve that adsorbs water to the level of 1 wt%. In normal operations at ambient temperature, dew points of  $< -100^\circ C$  have been measured (Cohen, 1991).

### 2.1.3 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 desorption half-cycle to remove water from the adsorbent and to prepare it for another adsorption half-cycle. Usually, two beds are employed to allow for continuous processing. In most cases, some residual water remains on the adsorbent after half-cycle desorption because complete removal is not economically practical.

The difference between the amount of water removed during the adsorption and desorption half-cycle is termed as the differential loading, which is the working capacity available for dehydration (Cohen, 1991). A typical two-bed dehydration of natural gas, with one bed on adsorption and the other on regeneration, is shown in Figure 2.2.



**Figure 2.2** Vapor-phase adsorption system (McCabe, *et al.*, 1993).

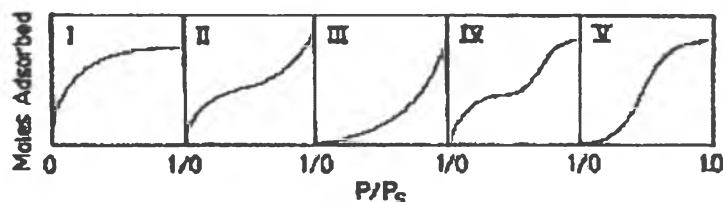
#### 2.1.4 Adsorption Isotherm

Isotherms as determined under specific conditions can yield qualitative and quantitative information about the adsorption process and also give indication of surface coverage, and thus, with certain assumptions, the surface area of the adsorbent.

Brunauer, *et al.* (1940) have divided the isotherms for physical adsorption into five classes, as illustrated in Figure 2.3. The isotherms for true microporous adsorbents, whose pore size is not very much greater than the molecular diameter of the adsorbate molecule, are normally of Type I. This is because with such adsorbents there is a definite saturation limit corresponding to complete filling of the micropores. Occasionally, if intermolecular attraction effects are large an isotherm of Type V is observed, as for example in the adsorption of phosphorous vapor on NaX. An isotherm of Type IV suggests the formation of two surface layers either on a plane surface or on the wall of a pore very much wider than the molecular diameter of the adsorbate. Isotherms of Types II and III are generally observed only in adsorbents with a wide range of pore sizes. In such systems there is a continuous progression with increasing loading from monolayer to multilayer adsorption and

then to capillary condensation. The increase in capacity at high pressures is due to capillary condensation occurring in pores of increasing diameter as the pressure is raised (Ruthven, 1984).

Adsorption isotherms are most commonly used to select the adsorbent or even the adsorption process as a unit operation for the adsorptive separation of gases. If the adsorption isotherm shape is Type I, II, or IV, the adsorbent can be used to separate the adsorbate from the carrier gas. If it is Type III or V, adsorption will probably not be economical for the separation.

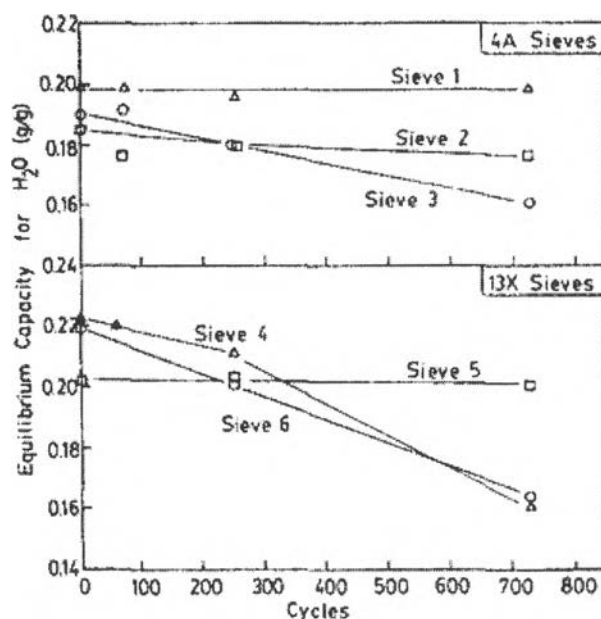


**Figure 2.3** Adsorption isotherm classification according to Brunauer, *et al.* (1940).

### 2.1.5 Deactivation

Deactivation of an adsorbent, involving either a loss of equilibrium capacity or an increase in mass transfer resistance, generally occurs during service as a result of either coke formation or loss of crystallinity. The latter is a common problem in thermal swing cycles where the sieve is used as a desiccant or even when water is present as an impurity in the feed, which is adsorbed in the first few layers of the adsorbent bed. During thermal regeneration the sieve is exposed to a combination of high temperature and high humidity, and under these conditions a slow and irreversible breakdown of the crystal structure may occur. Such effects tend to be most serious with zeolite X on account of its limited hydrothermal stability. However, with zeolite A under similar conditions, partial pore closure may occur, leading to a decrease in the intracrystalline diffusivity and an undesirable broadening of the mass transfer zone. Results from an accelerated aging study of several different commercial samples of 4A and 13X sieves are shown in Figure 2.4. The differences in initial capacity are probably due to differences in binder content. Each sample was subjected up to 725 two-hour cycles during which it was repeatedly saturated with water at room temperature and dehydrated at 260°C. It may be seen

that even under these comparatively mild conditions there was some deterioration with four of the six sieves tested. One of the 13X sieves showed essentially no deterioration over the duration of the test, however the deterioration of 13X sieves appears to be generally more severe (Ruthven, 1984).



**Figure 2.4** Results of accelerated aging tests carried out with six different commercial molecular sieve adsorbents (Ruthven, 1984).

### 2.1.6 Mathematical Model

When a fluid flows through a packed bed, there is a tendency for axial mixing to occur. Any such mixing is undesirable since it reduces the efficiency of separation. The minimization of axial dispersion is therefore a major design objective, particularly when the separation factor is small.

Flow through a packed bed may generally be adequately represented by the axial dispersed plug flow model (Ruthven, 1984):

$$-D_L \frac{\partial^2 c}{\partial z^2} + \frac{\partial}{\partial z}(vc) + \frac{\partial c}{\partial t} + \left( \frac{1-\epsilon}{\epsilon} \right) \frac{\partial \bar{q}}{\partial t} = 0 \quad (2.1)$$

where

$D_L$  = axial dispersion coefficient

$c$  = adsorbate concentration in fluid phase

$v$  = interstitial velocity of fluid

$z$  = distance measured from column inlet

$t$  = time

$\varepsilon$  = voidage of adsorbent bed; and

$\bar{q}$  = adsorbate concentration averaged over crystal and pellet

In this model, the effects of all mechanisms, which contribute to axial mixing, are lumped together into a single effective axial dispersion coefficient.

The mass balance for an adsorbent particle yields the adsorption rate expression, which may be written as:

$$\frac{\partial \bar{q}}{\partial t} = f(q, c) \quad (2.2)$$

Mass transfer between fluid and solid phase can be described with the linear driving force model as:

$$\frac{\partial \bar{q}}{\partial t} = k(q^* - \bar{q}) \quad (2.3)$$

where  $k$  is the overall mass transfer coefficient and  $q^*$  represents the equilibrium adsorbed phase concentration. The term  $\partial \bar{q} / \partial t$  represents the overall rate of mass transfer for adsorbed component average over a particle. A general equilibrium relation can be expressed as:

$$q^* = f(c) \quad (2.4)$$

The dynamic response of the column is given by the solution  $[c(z, t), \bar{q}(z, t)]$  to Equations (2.1) and (2.2) subject to the initial and boundary conditions imposed on the column. The response to a perturbation in the feed composition involves a mass transfer zone or concentration front which propagates through the

column with a characteristic velocity determined by the equilibrium isotherm. The location of the front at any time may be found simply from an overall mass balance, but in order to determine the form of the concentration front Equations (2.1) and (2.2) must be solved simultaneously (Ruthven, 1984).

## 2.2 Literature Survey

The previous works related to experimental and mathematical modeling for constructing a breakthrough curve, gas adsorption, and adsorption isotherm are summarized in this section.

The adsorption of  $\text{NH}_3$  on silica gel was studied at 298, 313, 333 K by using a packed bed method (Kuo *et al.*, 1985). Equilibrium isotherms were calculated from the adsorption data, and were modeled by the Langmuir and modified Polanyi potential equations. Experimental breakthrough curves were obtained for six concentrations of 997, 1984, 3037, 5016, 7050, and 10000 ppm  $\text{NH}_3$  in dry helium gas at each temperature. It was found that although the experimental adsorption data could be fit relatively well with the Langmuir equation except for the higher concentrations, a better fit was obtained with the modified Polanyi potential equation.

Sánchez *et al.* (1996) have studied temperature programmed desorption (TPD) curves of water from zeolite Linde 4A using the Monte Carlo method taking into account the effect of readsorption and repulsive lateral interactions. TPD technique was used to allow identification of different bonding sites and evaluation of kinetic parameters associated with those sites. It was found that Monte Carlo results reproduced quite well the experimental curves for the set of parameters determined by TPD. The shift in the peak temperature to higher values as the coverage decreases was due to a larger number of sites available for readsorption. This was reflected in the simulations as an increasing coverage desorption probability.

The adsorption of trichloroethylene (TCE) vapor was investigated in a laboratory-scale packed-bed adsorber by using granular activated carbon (GAC) at constant pressure (101.3 kPa). The effects of TCE inlet concentration, operating



temperature, and mass of adsorbent on the TCE breakthrough curves were investigated, respectively. The deactivation model was tested for these curves by using the analogy between the adsorption of TCE and the deactivation of catalyst particles. It was found that the deactivation model described the experimental breakthrough curves more accurately compared to Harkins–Jura, Brunauer–Emmett–Teller, Freundlich, Langmuir, and Dubinin–Radushkevich–Kagener isotherms (Suyadal *et al.*, 2000).

Lertviriyakijskul (2000) studied the competitive adsorption between the hydrocarbon and water on activated alumina prepared by sol-gel technique including the effects of calcination temperature on the water adsorption capacity of alumina. It was found that the hydrocarbons were adsorbed first, and then they were replaced by the adsorption of water because sol-gel alumina has higher affinity of water than hydrocarbons. In addition, these sol-gel aluminas provided a high water adsorption capacity and low desorption temperature of 100°C. Bamrunget (2001) followed the works that have been done by Lertviriyakijskul by changing the adsorbent from activated alumina to modified clinoptilolite. The results showed the same trend of competitive adsorption between water and hydrocarbons.

The effect of pressure drop on the dynamic behavior of a fixed-bed adsorber was studied by Chahbani and Tondeur (2001). Concerning saturation with a constant volume flow rate, neglecting pressure drop gave rise to a late breakthrough time compared to the case with pressure drop.

The mathematical model was developed by Thipkhunthod *et al.* (2001) to predict the water and hydrocarbon adsorption from the competitive adsorption of natural gas and water on activated alumina prepared by the sol-gel technique. The model was established based on the unsteady state mass transfer and Langmuir-Freundlich equilibrium adsorption equation. The adjustable parameters in the equilibrium adsorption model were determined from equilibrium adsorption data of single component using FORTRAN programming language. With the pre-determined parameters, the equilibrium adsorption model can be used to well predict the water and hydrocarbon adsorption.

Brosillon *et al.* (2001) studied mass transfer in volatile organic compound (VOC) adsorption on zeolite. Simulations of the breakthrough curves of industrial

solvents; n-heptane, n-octane, acetone, and methyl ethyl ketone (MEK), based on the Linear Driving Force (LDF) model, were proposed. Experiments were run on fixed beds of hydrophobic commercial zeolites. To improve the model and to study the parametrical effects on the breakthrough curves, a parameter sensitivity analysis was performed. The sensitivity of the two mass-transfer coefficients,  $k_f$  (interphase mass-transfer coefficient) and  $k_p$  (intrapellet mass-transfer coefficient), were investigated. It was found that the sensitivity of the external mass transfer ( $k_f$ ) was low, but the sensitivity of the  $k_p$  parameter was high. Therefore, it can be deduced that the overall mass transfer is controlled by internal mass transfer. A good agreement between experimental and numerical results was found when an adjustable value of the internal mass-transfer coefficient is used. A constant value of effective diffusivity was found independent of the nature and the amount of VOCs adsorbed. A relation linking intrapellet mass-transfer coefficient, equilibrium constant and average effective diffusivity was proposed to predict breakthrough curves of any kind of volatile organic pollutant in gaseous effluents.

Chua *et al.* (2002) showed that adsorption characteristics of pure water vapor onto two different types of silica gel at temperatures from 298 to 338 K and at different equilibrium pressures between 500 and 7000 Pa by a volumetric technique. The thermophysical properties such as the skeletal density, BET surface area, pore size, pore volume, and total porosity of silica gel were determined. Tóth's equation was found to be able to sufficiently describe the performance of Type A and RD silica gels with water vapor.

Chaikasetpaiboon *et al.* (2002) studied the experimental and mathematical modeling of water vapor adsorption onto a multi-layer adsorber. The commercial adsorbents, silica gel and 4A-zeolite, were packed in layers in a fixed bed. Simulations of the breakthrough curves of water vapor, based on an axial dispersion plug flow and Linear Driving Force (LDF) model, was obtained by solving the set of mathematical equations. The method of lines (MOL) combined with the finite difference and computer programming were utilized to obtain the theoretical breakthrough curve. The mathematical models suggested that the overall mass transfer coefficient ( $k_e$ ) of approximate  $1.0 \times 10^{-4}$  was practically acceptable for all experimental case scenarios. Although the mathematical models were also able to

predict the adsorption capacity at satisfactorily high degree of accuracy, their estimation of the breakthrough time was shorter than that from the experiments by about 27% in average. The mathematical model suggested by Chaikasetpaiboon *et al.* (2002) can be written as Equation (2.5):

$$-D_{L,\text{eff}} \frac{\partial^2 c}{\partial z^2} + v \frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} + \left( \frac{1 - \epsilon_{\text{eff}}}{\epsilon_{\text{eff}}} \right) \frac{\partial \bar{q}_{\text{eff}}}{\partial t} = 0 \quad (2.5)$$

The parameters used in the model were treated as the effective values of the parameters for the properties of materials in the whole bed. Moreover, the equilibrium adsorption isotherm of the multi-layer adsorber (three commercial adsorbents packed in layers in the adsorber) was determined and used in the dynamic adsorption model in order to construct the theoretical breakthrough curve. In contrast, for this work, for improving the previous model (Chaikasetpaiboon *et al.*, 2002), the parameters and the equilibrium adsorption isotherm determined and constructed for each adsorbent were utilized in the dynamic adsorption model in order to obtain the theoretical breakthrough curves.