THEORETICAL PREDICTIONS OF HEAT- AND MASS-TRANSFER COEFFICIENTS OF DYNAMIC ADSORPTION PROCESS

by

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ABSTRACT

THEORETICAL PREDICTIONS OF HEAT- AND MASS-TRANSFER COEFFICIENTS OF DYNAMIC ADSORPTION PROCESS

by Yun-Tak Lee

In this work, the approach proposed by Glueckauf is used to study the properties of the adsorption of a dilute component from a binary gas stream flowing through a bed packed with 13X zeolite. The numerical solution to the unsteady state heat- and mass-transfer equations describing the process is readily applicable to the design of a carbon dioxide removal system. The solution to these equations depends on the assumption of a nonlinear isotherm equation to relate concentration on the solid phase to concentration in gas phase, and of a linear heat removal equation to account for the accumulation rate of heat in the solid phase. These assumptions are shown to be justifiable for a dilute adsorbate with large heat of adsorption.

This approach permits the prediction of effects of adsorbate concentration, gas flow rate, and bed loading on the removal of the component. The equations involve two parameters: one characterized by the nature of the adsorbate, another by the plate-fin spacing. Values of these parameters determined for CO$_2$/13X and H$_2$O/13X adsorption systems are presented.

This work points out the mass transfer mechanism
of the adsorption process and the type of experimental data needed for a design of an adsorption process. A comparison between a model proposed by others for the same set of experimental data and the model of this work is also presented.
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1. LIST OF SYMBOLS

A Integration constant (see equation 2.3)  
A₁ e⁻Δτ/γ  
A₂ - A₁ + \( \frac{\gamma}{\Delta \tau} (A₁ - 1) \)  
A₃ 1 + \( \frac{\gamma}{\Delta \tau} (A₁ - 1) \)  
A₄ A₁/γ  
A₅ A₂/γ  
A₆ (A₃ - 1)/γ  
A₇ e⁻Δτ/β  
A₈ \( (\alpha \beta^2 / \gamma / \Delta \tau)[1 - A₇(1 + \Delta \tau / \beta)] \)  
A₉ \( (\alpha \beta^2 / \gamma / \Delta \tau)(\Delta \tau / \beta - 1 + A₇) \)  
A₁₀ -(A₈ + A₉*A₁)  
A₁₁ A₈ - A₉*A₂  
A₁₂ A₉(1 - A₃)  
A₁₃ See equation 3.41  
A₁₄ A₆(Δξ/2)  
A₁₅ See equation 3.42  
Cₐ₀ Initial adsorbate concentration in gas phase in the bed; 1b/lb N₂ or lb/cu. ft N₂  
Cₐₑ Adsorbate concentration in gas phase in exit stream; 1b/lb N₂  
Cₐₙ Adsorbate concentration in gas phase in feed stream; 1b/lb N₂ or lb/cu. ft N₂  
Cₚ₉ Heat capacity of the bed; B.T.U./lb°F  
Cₚᶠ Heat capacity of the fluid; B.T.U./lb°F
<table>
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<th>Symbol</th>
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<td>G</td>
<td>Fluid flow rate per unit bed area; lb/ft(^2)-hr or ft(^3)/ft(^2)-hr</td>
</tr>
<tr>
<td>( h_w )</td>
<td>Heat transfer coefficient; B.T.U./ft(^2)-°F-hr</td>
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<tr>
<td>I</td>
<td>Number of time segment</td>
</tr>
<tr>
<td>( K_a )</td>
<td>Mass transfer coefficient; 1/hr</td>
</tr>
<tr>
<td>( K_g )</td>
<td>Mass transfer coefficient; lb/lb-mm Hg-hr</td>
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<tr>
<td>L</td>
<td>Bed length; ft</td>
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<tr>
<td>( M_b )</td>
<td>Mass of the bed; lb</td>
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<tr>
<td>( M_V )</td>
<td>Mass flow rate of the carrier gas; lb/hr</td>
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<td>( M_w )</td>
<td>Molecular weight of the adsorbate; lb/lb mole</td>
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<tr>
<td>N</td>
<td>Number of bed segment</td>
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<tr>
<td>( N_{P_t} )</td>
<td>Prandtl number</td>
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<tr>
<td>( N_{Re} )</td>
<td>Reynold's number</td>
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<td>( P_a )</td>
<td>Adsorbate partial pressure; mm Hg</td>
</tr>
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<td>( P_{a*} )</td>
<td>Adsorbate partial pressure that would be in equilibrium with the liquid phase, ( P_{a*} ); mm Hg</td>
</tr>
<tr>
<td>( P_{ao} )</td>
<td>Initial adsorbate partial pressure in the bed; mm Hg</td>
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<td>( P_{a\infty} )</td>
<td>Ultimate adsorbate partial pressure; mm Hg</td>
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<td>( Q_a )</td>
<td>Heat of adsorption; B.T.U./lb or B.T.U./lb mole</td>
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<td>( q_w )</td>
<td>Heat flux; B.T.U./hr</td>
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<td>( r_a )</td>
<td>Transfer rate; lb/lb bed-hr</td>
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<td>T</td>
<td>Temperature; °F</td>
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<tr>
<td>( T_w )</td>
<td>Bed temperature; °F</td>
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<tr>
<td>t</td>
<td>time; hr</td>
</tr>
<tr>
<td>( t_b )</td>
<td>Breakthrough time; hr</td>
</tr>
<tr>
<td>( t_g )</td>
<td>Lag time; hr</td>
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\[ \bar{W} \quad \text{Average loading; lb/lb bed} \]

\[ W_a \quad \text{Adsorbate concentration in liquid phase; lb/lb bed} \]

\[ W_a^* \quad \text{Adsorbate concentration in liquid phase that would be in equilibrium with the gas phase; lb/lb bed} \]

\[ W_{ao} \quad \text{Initial adsorbate concentration in liquid phase in the bed; lb/lb} \]

\[ W_{aw} \quad \text{Final adsorbate concentration in liquid phase in the bed; lb/lb bed} \]

\[ z \quad \text{Axial length; ft} \]

**Greek Letters**

\[ \alpha \quad \text{Dimensionless parameter (see equation 3.16)} \]

\[ \beta \quad \text{Dimensionless heat transfer resistance (see equation 3.14)} \]

\[ \gamma \quad \text{Dimensionless mass transfer resistance (see equation 3.3)} \]

\[ \varepsilon_b \quad \text{Porosity of the bed} \]

\[ \eta \quad \text{Dimensionless constant (see equation 4.1)} \]

\[ \theta \quad \text{Dimensionless temperature} \]

\[ \mu_n \quad \text{Dimensionless parameter (see equation 3.15)} \]

\[ \xi \quad \text{Dimensionless axial length} \]

\[ \rho_b \quad \text{Density of the bed; lb/cu. ft} \]

\[ \rho_f \quad \text{Density of the fluid; lb/cu. ft} \]

\[ \tau \quad \text{Dimensionless time} \]

\[ \psi \quad \text{Dimensionless adsorbate concentration in gas phase} \]

\[ \psi_e \quad \text{Dimensionless adsorbate concentration in gas phase} \]
In exit stream

\( \psi^* \) Dimensionless adsorbate concentration in gas phase that would be in equilibrium with the liquid phase

\( \phi \) Dimensionless adsorbate concentration in liquid phase

\( \phi^* \) Dimensionless adsorbate concentration in liquid phase that would be in equilibrium with the gas phase

\( \bar{\Phi} \) Dimensionless average loading

\( w_{ao} \) Initial adsorbate concentration in gas phase per unit mass of bed; lb/lb bed

\( w_{ao} \) Adsorbate concentration in gas phase in feed stream per unit mass of bed; lb/lb bed

\( \Delta C_a \) \( C_{ao} - C_{ao} \)

\( \Delta W_a \) \( W_{ao} - W_{ao} \)

\( \Delta T_{max} \) Maximum temperature rise

**Subscripts**

i Refer to time

n Refer to position along the axial bed length
SECTION 1 INTRODUCTION

1.1 Background

In the early stages of the space program, carbon dioxide in manned spacecraft has been removed by chemical reaction with LiOH. The process is simple and was effective in early short flights. However, the chemical agent is non-regenerable. As the flight time increases, the required weight of LiOH becomes prohibitive. Recently, regenerative methods which utilized the adsorption process and principles with molecular sieve have received attention.

Adsorption is the phenomenon of the operation of forces between a solid surface, or adsorbent, and the interacting molecules, or adsorbate. It can be divided into two categories: chemical adsorption and physical adsorption. Chemical adsorption, or chemisorption involves the rearrangement of the electrons of the adsorbent and adsorbate, with formation of chemical bonds. This process, in general is irreversible. In this work, chemisorption is not the determining factor and will not be discussed.

Physical adsorption, or physisorption which simulates liquefaction, is caused by the force of dipole-dipole interaction, or Van der Waals forces. In general, this process is reversible and is referred as 'adsorption'
In this work.

During the adsorption process, a certain amount of heat (heat of adsorption) is generated. The heat of adsorption raises the temperature of the bed and therefore brings nonisothermal conditions to the adsorption process.

Molecular sieves (commonly known as zeolites) which are in general crystalline, hydrated aluminosilicates, have been chosen as one agent for removal carbon dioxide because of its durable and regeneration ability. This molecular sieve has special three-dimensional voids or 'windows' of uniform size which have the ability to adsorb different molecules smaller than its voids. The type of molecular sieve studied in this work is commercially known as type 13X zeolite and has the chemical formula

$$Na_{86}(AlO_2)_{86} (SiO_2)_{106} \cdot 112O$$

and has voids of about 9 angstroms.

In adsorption tests, a carrier gas (usually $N_2$) containing the adsorbate is passed through a column packed with molecular sieve particles. The adsorbate is removed continually from the carrier fluid and accumulates upon the surface of the solid phase. Such a process proceeds until the concentration of the adsorbate on the solid reaches a value corresponding to equilibrium with the concentration in feed stream, and the outlet stream reaches the feed stream concentration. This process is generally an unsteady state process because the solid phase accumulates adsorbate continuously. This kind of process is commonly known as fixed
bed adsorption.

The efficiency of operation of a fixed bed adsorption system is influenced by the rate of adsorption and by the adsorbate capacity, or loading capacity. The loading capacity is measured in terms of amount of adsorbate adsorbed per unit mass of adsorbent, for example, pound of adsorbate per pound of adsorbent. The loading capacity is a function of feed concentration, the adsorption temperature, the fluid flow rate and the nature and the design of the adsorbent. A quantitative analysis of these variables in the design is needed to determine rate constants and to produce basic design data.

1.2 Research Objectives

The objectives of this study are twofold:

1. to determine a suitable mathematical model which might define the controlling step of the adsorption process.

2. to study the effects of bed temperature, flow rate and concentration of adsorbate (in dilute range) in feed stream, on the parameters of the model.

It is hoped that the results of this study will contribute to the basic understanding of the nonisothermal adsorption process and to a model with a minimum number of empirical functions and parameters would aid in the development of quantitative design and analysis procedure for future applications.
SECTION 2  ISOTHERMS AND DYNAMIC DATA

This section divides into two parts. The first part presents the collected data of various isotherms, or better known as loading capacity of two adsorbate, namely carbon dioxide and water on 13X zeolite. In this part, a model equation which relates the partial pressure of the adsorbate and the concentration of the adsorbed adsorbate will be discussed.

The second part which is divided into three subsections presents a qualitative description of breakthrough curves, a brief description of the dynamic adsorption experiments conducted at Airesearch Laboratories and their results (25), and an analytic technique to reduce the dynamic adsorption data into corresponding dimensionless parameters which will be used in this study. The results of these reduced data are also presented in this section.

2.1 Isotherm Data

An Isotherm gives the ultimate loading capacity of an adsorbent for an adsorbate under known conditions of temperature and adsorbate partial pressure. The Isotherm loading is usually expressed as mass of adsorbate on a unit mass of adsorbent; or as a percentage loading; i.e., mass of adsorbate per 100 mass units of adsorbent. Two different sets of Isotherms, namely CO₂ on 13X zeolite and H₂O on 13X
zeolite are of prime interest. The object of this study is to modify an equilibrium function proposed by Denbigh(11) to reduced the available data (10, 17, 25) to suit for this work. Some of the reported isotherms are plotted in Fig. 2.1 and 2.2.

To reduce the isotherm data, several known equations (Henry’s law, Langmuir equation, BET equation, etc) have been used. Although several of the equations have some degree of application in certain range of loading, no unique adsorption equation appears to exist for our system.

The Clausius-Clapeyron equation was one of the adsorption equations developed for treating this type of adsorption (11). In the Clausius-Clapeyron theory, the characteristic curve of the isotherm is given by

\[
\frac{\partial \ln P_a}{\partial T} \bigg|_{W^*} = \frac{M_W Q_a(W^*_a)}{RT^2}
\]  

(2.1)

where

- \( W^*_a \) = adsorption loading
- \( P_a \) = adsorbate partial pressure
- \( T \) = temperature
- \( M_W \) = molecular weight of the adsorbate
- \( Q_a \) = heat of adsorption per unit mass of adsorbent
- \( R \) = universal gas constant

The equation generally takes form of

\[
Q_a(W^*_a) = \ln \left( \frac{P_{a1}}{P_{a2}} \right) \left( \frac{1}{N} \right) \left( \frac{1}{T_2} - \frac{1}{T_1} \right)^{-1}
\]  

(2.2)
Fig. 2.1  Equilibrium Data of CO$_2$ on 13X Zeolite
Fig. 2.2  Equilibrium Data of H₂O on 13X Zeolite
where \( P_{a1}, P_{a2} \) = partial pressure of the adsorbate at specific loading, \( W_a^* \), at temperature \( T_1, T_2 \) respectively.

\( T_1, T_2 \) = temperature at \( P_{a1}, P_{a2} \) respectively.

It has been applied to the available equilibrium data. The heats of adsorption obtained by this procedure are plotted in Fig. 2.3 and 2.4. Heats of adsorption (3,4) which were obtained from measurements of the heat generated during adsorption in a calorimeter are included in these figures. The least squares fit curve drawn through these data is the empirical \( Q_a(W_a^*) \) function used to represent all the data. Then the isotherm equation which relates the \( Q_a(W_a^*) \) function and the adsorbate partial pressure can be taken as

\[
P_a(W_a^*) = \exp \left[ K_m + A(W_a) - \frac{Q_a(W_a^*)}{RT} \right]
\]

(2.3)

where \( A(W_a^*) \) is the integration constant of equation 2.1 and \( K_m \) is a shift constant. \( A(W_a^*) \) is calculated from

\[
A(W_a^*) = \ln[P_a(W_a^*)] + \frac{Q_a(W_a^*)}{RT}
\]

(2.4)

\( A(W_a^*) \) is assumed to be independent of the temperature and continuous. At low loadings where isotherms obey Henry's law, the function \( A(W_a^*) \) should obey the constraint

\[
\lim_{W_a^* \to 0} \left( \frac{\partial \ln A}{\partial W_a^*} \right) = 1
\]

(2.5)

The results of function \( A(W_a^*) \) calculated from
Fig. 2.3 Heat of Adsorption for CO$_2$/13X
Fig. 2.4  Heat of Adsorption for H$_2$O/13X
equation 2.4 with reported isotherms and the least square fitted \( Q_a(W_a) \) functions are plotted in Fig. 2.5 and 2.6.

The shift constant, \( K_m \), is to shift the function \( A(W_a) \) to compensate for the difference between different batches of available data which may have resulted from the experimental preparations and packing and binding of the adsorbent. The values of \( K_m \) are listed in Table 2.1 and 2.2.

To evaluate the adsorption equation for our system, the equation 2.3 has been applied to generate isotherms at different temperature of interested range. These results are plotted along with reported data in Fig. 2.1 and 2.2. A visual comparison indicated the equation is adequate.

2.2 Concept of Breakthrough Curves

Under ideal conditions, the adsorbate that enters the bed is held up and the outlet stream is free of adsorbate. When the saturation of the adsorbent is reached, then the outlet and feed streams instantaneously come to equilibrium. In a typical adsorption process, the adsorbate is held in the bed and the outlet is practically free of adsorbate until some time at which the saturation of adsorbent is approached. From then on, the outlet concentration increases rapidly toward the feed concentration.

The outlet concentration, or exit concentration, in general, expressed in term of mass of adsorbate per mass of carrier gas, may be plotted against the elapsed
Table 2.1 Values of $K_m$ for $CO_2/13X$

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<th>$K_m$</th>
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<td>Wright et al (25)</td>
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</tr>
<tr>
<td>Linde (17)</td>
<td>-0.11</td>
</tr>
<tr>
<td>Davidson (10)</td>
<td>-0.93</td>
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Table 2.2 Values of $K_m$ for $H_2O/13X$

<table>
<thead>
<tr>
<th>Source</th>
<th>$K_m$</th>
</tr>
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<tbody>
<tr>
<td>Wright et al (25)</td>
<td>0.0</td>
</tr>
<tr>
<td>Linde (17)</td>
<td>+0.39</td>
</tr>
</tbody>
</table>

Fig. 2.5 Function $A(W_0^3)$ for CO$_2$/13X
time; such a plot is termed as the breakthrough curve or concentration history for adsorption. Fig. 2.7 shows a number of possible breakthrough curves. Curve A represents the ideal case. Curve B is the typical breakthrough curve in most works and in this work. The time, $t_b$, at which adsorbate just reaches the detectable level is termed as the breakthrough time. The time, $t_g$, at which the outlet concentration reaches the arithmetic mean of initial and final outlet concentration is called the lag time. It measures the hold up capacity of the bed. The slope of the tangent at the lag time is called the index of ratio of adsorption and may be used as an indication of degree of nonlinearity in the system. An ideal adsorption system would have an infinite slope.

The breakthrough curves furnish some important parameters for the design of the bed. The most important properties are the average loading, $\bar{W}(t)$, and the outlet adsorbate concentration, $C_{ae}(t)$, in the gas phase. The average loading is the measurement of the capacity of the bed at any time during the adsorption period. The outlet concentration indicates the mass of adsorbed adsorbate on the bed at that time. These two properties are related by a mass balance equation as following:

$$\bar{W}(t) = \frac{M_v}{M_b} \int_0^t (C_{ao} - C_{ae}(t)) \, dt \quad (2.6)$$

where $C_{ao}$ = feed concentration in gas phase

$M_v$ = mass flow rate of the fluid
Fig. 2.7 Typical Breakthrough Curves
Cae(t) = outlet concentration in gas phase per unit mass of carrier gas

$\bar{W}(t) = \text{average loading}$

$M_b = \text{mass of the bed}$

t $= \text{time}$

Both properties are measurements of the loading capacity of the bed and therefore are related to the feed concentration, size of the bed and the mass transfer rate. To compare these properties, it may be useful to express the breakthrough curves in terms of dimensionless quantities. In general, the time, t, is expressed in dimensionless time, $\tau$, which is defined as following:

$$\tau = \frac{(W_a - W_o) \cdot M_h}{(C_\infty - C_o) \cdot M_v \cdot t} \quad (2.7)$$

where $C_\infty, C_o = \text{feed and initial adsorbate concentration in gas phase respectively}$

$W_a, W_o = \text{final and initial loading of the adsorbent respectively}$

$\tau = \text{dimensionless time}$

The dimensionless outlet adsorbate concentration, $\psi_e(\tau)$, is defined by:

$$\psi_e(\tau) = \frac{Cae(t) - C_o}{C_\infty - C_o} \quad (2.8)$$

The dimensionless average loading, $\bar{\phi}(\tau)$, is defined as

$$\bar{\phi}(\tau) = \int_0^\tau [1 - \psi_e(\bar{\tau})] \, d\bar{\tau}$$
where \( \xi = z/L \).

Fig. 2.8 shows a number of possible average loading curves. Curve A is the ideal case. Curve B and C are the typical curves. They closely follow the ideal curve before the breakthrough time, then they diverge and reach unity at a later time. The curvature of these curves decreases with the increasing dimensionless mass transfer resistance. Their relationship will be discussed in later section.

2.3 Dynamic Adsorption Experiment

Fig. 2.9 is a simplified schematic diagram of the adsorption system. Fig. 2.10 is a sketch drawing of the adsorption used to obtain the dynamic data in this work. Both figures are reproduced from the report by Wright and his co-workers (25). The bed was constructed with a special plate-fin arrangement to ensure an uniform temperature around the bed and to eliminate channeling around the adsorbent particles. Before the run, the adsorbent was heated to a high temperature, usually at 450-550°F and at a high vacuum around 10-20 \( \mu \)Hg, to drive out the adsorbate residues.

During the run, inert nitrogen gas was passed through the bed. When the system reached thermal equilibrium, the flow of nitrogen gas and the desire adsorbate were directed over the adsorbent bed. Throughout the adsorption period, small adjustments were made by a bypass which permitted to adjust the flow rate without disturbing the fluid in the
bed. The temperature of the adsorbent bed, the adsorbate concentration in the inlet and outlet of the bed were monitored and recorded. Their results in the reduced form are listed in Table 2.3 and 2.4.
Fig. 2.8 Typical Average Loading Curves
FIG 2.9 Schematic Diagram Of Dynamic Adsorption Process Apparatus (25)
<table>
<thead>
<tr>
<th>ID NO</th>
<th>REF (25)</th>
<th>$M_V$</th>
<th>$M_b$</th>
<th>$P_a$</th>
<th>$\Delta W_a$</th>
<th>$\Delta C_a$</th>
<th>$\tau = 1$</th>
<th>$\phi(1)$</th>
<th>$\Delta T_{max}$</th>
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<td>7.27</td>
<td>.0525</td>
<td>.308</td>
<td>.38</td>
<td>.864</td>
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</table>

Table 2.3. Reduced Experimental Results for CO$_2$/13X System
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<th>ΔCa</th>
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<th>θ_1</th>
<th>ΔT_max</th>
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<tbody>
<tr>
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<td></td>
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<td>lb</td>
<td>mm Hg</td>
<td>lb/lb</td>
<td>lb/lb</td>
<td>hr</td>
<td></td>
<td>°F</td>
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<td>.976</td>
<td>18</td>
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</tbody>
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Table 2.4. Reduced Experimental Results for H_2O/13X System
SECTION 3 MATHEMATICAL MODELLING

This section presents the theory and the mathematical formulation of the model that describes the behaviour of the adsorption bed. Mathematical modelling of adsorption process is a formulation of mathematical equations, usually differential equations, to conserve mass balance and heat balance of the process.

This section divides into three parts. The first part presents a brief description of the adsorption mechanism and a survey in the open literature. The second part presents the mathematical equations that follows Glueckauf's approach to describe the adsorption process. The last part presents a numerical technique to solve those equations.

The results of this model will be presented and discussed in the later section.

3.1. Theory

An adsorption process may be divided into the following elementary steps:

1. transport of the adsorbate from the bulk fluid phase to the surface of adsorbent particles (external mass transfer)

2. surface reaction of the adsorption process at the fluid-solid interface (surface reaction)

3. diffusion of the adsorbate in the adsorbed layer
(fluid phase internal diffusion).

4. diffusion of the adsorbate in the porous network of the particles (solid phase internal diffusion).

These are consecutive steps, if any one has a much slower rate constant than all the others, it will become rate determining. Therefore in many cases, the rate determining step is considered as the overall rate of the adsorption process.

A large number of solutions of mathematical models that describe the mechanism of the adsorption have appeared in the literature. All models can be classified on the basis of the controlling mechanism (external mass transfer, surface reaction, internal mass transfer) and on equilibrium (linear, nonlinear, reversible, irreversible). They can be further subdivided into isothermal or nonisothermal depending on the consideration of the effect of the heat of adsorption. Two separate papers by Chi and Wasan (6) and Needham et al. (19) contain an excellent review of those mathematical developments that have been used.

The approach of internal mass transfer model was originated by Glueckauf (13) and extended by Vermeulen (23). It has been applied to synthetic molecular sieve adsorbents. The early works of Glueckauf and Vermeulen were primarily to handle low concentrations of the adsorbate with general assumptions concerning constant flow rate, nonporous adsorbent, linear isotherm and isothermal conditions. The semi-
analytical solution of the resulting partial differential equations provided the generalized plots widely found in the literature.

Since then, investigators have attempted to eliminate or to replace some of these assumptions, especially the isothermal condition, by more realistic criteria. Acrivos (1) first used the external mass transfer model to treat adiabatic adsorption, but his theoretical results were not applicable to the cases where internal diffusion controls the process. Leavitt (15) used the transfer zone approach of Michaels (18) to analyze pilot data. In his paper, he indicated the temperature rise in the bed could be as much as 100 °F. Weber and Meyer (24) proposed a model for general nonisothermal problems which include both external mass transfer and intraparticle resistance. They assumed Knudsen diffusion within the particles and a Langmuir type isotherm. However, a survey of the literature found no attempt to model this problem with nonisothermal assumption.

The purpose of this work was to extend Gluechauf model (13) to handle the nonlinearity of the isotherm and the nonisothermal conditions which account more realistic criteria. The model which includes only mass transfer resistance in the liquid phase (fluid phase internal diffusion) was found adequate to explain the observed average loading curves.
3.2 Mathematical Model for Nonisothermal Adsorption

The model is based on the following assumptions:

1. the fluid is a binary mixture with only one adsorbate at low concentration.
2. the adsorbate concentration in the feed stream is assumed to be constant.
3. the adsorbent is a nonporous particle and is small enough that the adsorbate adsorbed uniformly on the surface of the particles and the concentration gradient of the adsorbate in the bulk fluid around the particle can be neglected.
4. the mass flow rate of the fluid is low.
5. the flow is plug flow.
6. the pressure drop across the bed is insignificant.
7. the adsorption process in the fluid-liquid interface is instantaneously.
8. the controlling step is the internal diffusion inside the adsorbed liquid layer. The driving force is linear and can be represented by

\[ r_a = K_a (W_a^* - W_a) \]  \hspace{1cm} (3.1)

where

- \( r_a \) = rate of adsorption
- \( K_a \) = mass transfer coefficient
- \( W_a^* \) = adsorbate concentration in liquid phase that would be in equilibrium with the gas phase per unit mass of the bed.
9. the bed wall temperature is isothermal.

10. the only heat generated is by the heat of adsorption of the adsorbate and is transferred to the wall by a linear rate law expressed as

\[ q_w = h_w (T - T_w) \quad (3.2) \]

where \( q_w \) = heat flux transfer to the wall
\( h_w \) = heat transfer coefficient of the adsorbent
\( T \) = instantaneous temperature of the adsorbed layer
\( T_w \) = temperature of the wall.

11. physical properties, such as viscosity of the fluid, heat capacities of the fluid and the adsorbent are assumed to be constant.

The mass balance equation can be expressed as

\[-G \frac{\partial Ca}{\partial z} = \rho_f \cdot \varepsilon_b \cdot \frac{\partial Ca}{\partial z} + \rho_b \cdot \frac{\partial q_w}{\partial t} \quad (3.3)\]

where \( G \) = volumetric flow rate of carrier gas (assumed to be \( N_2 \)) per unit area of the bed.
\( Ca \) = adsorbate concentration in the fluid phase per unit volume of the carrier gas.
\( \varepsilon_b \) = void fraction of the bed
\( \rho_b \) = density of the bed
\( \rho_f \) = density of the fluid

The term on the left side of equation 3.3 represents the flow rate per unit volume of an adsorbate entering minus the flow rate per unit bed volume of that adsorbate leaving the differential bed length. The first term on
the right side represents the accumulation rate in the gas phase with the differential bed length. This term is negligible because $\varepsilon_b$ is quite small in comparison with $p_b$ and $G$. The second term is the accumulation rate per unit bed volume on the solid phase within that bed section and is determined by the rate equation as

$$\frac{dW_a}{dt} = K_a (W_d - W_a) \quad (3.4)$$

The heat balance equation in that bed section may be expressed as

$$V_b \varepsilon_b p_f c_{pf} T + M_b c_{pb} \frac{\partial T}{\partial t} = Q_a M_b \frac{dW_a}{dt} - h_w a_w (T - T_w) \quad (3.5)$$

where

- $V_b$ = volume of the bed
- $c_{pf}$ = heat capacity of the fluid per unit mass of the fluid
- $c_{pb}$ = heat capacity of the bed per unit mass of the bed
- $M_b$ = mass of the bed
- $a_w$ = heat exchange area
- $Q_a$ = average heat of adsorption of the adsorbate (assumed to be a constant).

$p_f$ and $c_{pf}$ are assumed to be the density and heat capacity of the carrier gas, $N_2$, respectively and are assumed to be constant.

The first term on the left side of the equation 3.5 represents the heat rate per unit bed mass of a adsorbate in the differential bed length. The second term represents
the accumulation rate of heat per unit bed mass within the differential bed length. The first term on the right side of the equation represents the heat generated from the heat of adsorption by the mass of the adsorbate in that bed section. The second term represents the rate of heat transfer to the solid phase to the isothermal wall.

The initial and boundary conditions for the equations are

\[ \begin{align*}
W_a (0, z) &= W_{a0} \quad ; \quad C_a (t, 0) = C_{a0} \\
C_a (0, z) &= C_{a0} \quad ; \quad T (t, 0) = T_w \\
T (0, z) &= T_w
\end{align*} \]  

Substituting equation 3.4 into equation 3.3 and neglecting the \( \mathcal{E} \) term, gives

\[ G = \frac{\partial C_a}{\partial z} = \rho_b K_a (W_a - W_{a0}) \]  

(3.7)

Assuming

\[ C_a = \frac{P_a M_w}{RT} \]

where \( M_w \) = molecular weight of adsorbate

equation 3.7 yields

\[ \frac{G M_w}{RT} \frac{\partial P_a}{\partial z} = \rho_b K_a (W_a - W_{a0}) \]  

(3.8)

The system of partial equation 3.4, 3.5 and 3.8 can be solved with the equilibrium equation 2.3 for \( W_a^* \) and \( P_a^* \).

By defining the following dimensionless variables as;

\[ \phi = \frac{W_a - W_{a0}}{W_{a0} - W_{a0}} \]
\[
\phi^* = \frac{W_a - W_ao}{W_ao - W_ao}
\]
\[
\psi = \frac{P_a - P_ao}{P_ao - P_ao}
\]
\[
\tau = \frac{G(Cao - Cao)t}{\rho_b(W_ao - W_ao)L}
\]
\[
\theta = \frac{T - T_w}{T_w}
\]

Equations 3.4 and 3.8 and 3.5 became

\[
\frac{\partial \phi}{\partial t} = \frac{\phi^* - \phi}{\gamma}
\] (3.10)

\[
\frac{\partial \psi}{\partial \xi} = \frac{\phi - \phi^*}{\gamma}
\] (3.11)

\[
\frac{\partial \theta}{\partial t} + \nu h \frac{\partial \theta}{\partial \xi} = \alpha \frac{\partial \phi}{\partial t} - \frac{\partial \theta}{\partial \beta}
\] (3.12)

where

\[
\gamma = \frac{G(Cao - Cao)}{K_a \rho_b L (W_ao - W_ao)}
\] (3.13)

\[
\beta = \frac{C_pb G(Cao - Cao)}{h_w(W_ao - W_ao)}
\] (3.14)

\[
\nu h = \frac{C_pf(W_ao - W_ao)}{C_pb (W_ao - W_ao)}
\] (3.15)

\[
\alpha = \frac{Qa(W_ao - W_ao)}{C_pb T_w}
\] (3.16)

\( \omega_ao \) = Initial mass concentration of adsorbate in gas phase per unit mass of the bed

\( \omega_{ao} \) = mass concentration of adsorbate in gas phase per unit mass of the bed in the feed stream

The equilibrium equation 2.3 can be expressed as
\[ \psi \Delta P + \text{Pao} = \text{EXP} \left[ A (\phi^* \Delta W + \text{Wao}) + \text{km} \right. \]
\[ \left. - \frac{Qa(\phi^* \Delta W + \text{Wao})}{RT(1+\theta)} \right] \]

where \( \Delta P = \text{Pao} - \text{Pao} \) \hspace{1cm} (3.17)
\[ \Delta W = \text{Wao} - \text{Wao} \] \hspace{1cm} (3.18)

The initial and boundary conditions can now be expressed as
\[ \phi (0, \xi) = 0 ; \]
\[ \psi (0, \xi) = 0 ; \quad \psi (\tau, 0) = 1 \] \hspace{1cm} (3.19)
\[ \theta (0, \xi) = 0 ; \quad \theta (\tau, 0) = 0 \]

The system of equations can be solved numerically. The objective will be to find the relationship of the dependent variables \( \psi, \phi^*, \phi \) and \( \theta \) with the parameters \( \alpha, \beta, \) and \( \gamma \) such that the dimensionless breakthrough curve obtained from the solution simulates the experimental breakthrough curve. The criteria used to match the model breakthrough curves and the experimental data will be discussed in the later section.

3.3 Numerical Technique and Solutions

The system of equations was solved by Crank-Nicholson one-half method. The independent variables \( \xi \) and \( \tau \) are divided into discrete \( \Delta \xi \) and \( \Delta \tau \) such that
\[ \Delta \xi = (N - 1)^{-1} \]
\[ \Delta \tau = (I - 1)^{-1} \]
where \( N \) and \( I \) are arbitrary numbers of bed segment and time segment respectively.
By denoting

\[ \xi_n = N \Delta \xi \]
\[ \tau_i = \Delta \tau \]
\[ \psi_{i,n} = \psi(\tau_i, \xi_n) \]
\[ \phi^*_{i,n} = \phi^*(\tau_i, \xi_n) \]
\[ \phi_{i,n} = \phi(\tau_i, \xi_n) \]
\[ \theta_{i,n} = \theta(\tau_i, \xi_n) \]

Equation 3.10 can be rewritten as

\[ \frac{3}{\partial \tau} + \frac{\phi}{\gamma} = \frac{\phi^*}{\gamma} \]  \hspace{1cm} (3.20)

Then the exact solution of equation 3.20 at \( \xi = \xi_n \) and \( \tau = \tau_i \) can be expressed as

\[ \phi_{i,n} = \phi_{i-1,n} e^{-(\tau_{i-1} - \tau_i)/\gamma} \int_{\tau_{i-1}}^{\tau_i} \frac{\phi^* e^\tau}{\gamma} d\tau \]  \hspace{1cm} (3.21)

Assuming linearity of \( \phi^* \) with \( \tau \) for any fixed \( \xi_n \) such that

\[ \phi^*_{\tau,n} = \phi^*_{i-1,n} + \frac{\tau - \tau_i}{\tau_{i-1} - \tau_i} (\phi^*_{i-1,n} - \phi^*_{i,n}) \]  \hspace{1cm} (3.22)

then equation 3.21 can be expressed as

\[ \phi_{i,n} = A_1 \phi_{i-1,n} + A_2 \phi^*_{i-1,n} + A_3 \phi^*_{i,n} \]  \hspace{1cm} (3.23)

where

\[ A_1 = e^{-\Delta \tau/\gamma} \]
\[ A_2 = -A_1 + \frac{\gamma}{\Delta \tau} (A_1 - 1) \]  \hspace{1cm} (3.24)
\[ A_3 = 1 + \frac{\gamma}{\Delta \tau} (A_1 - 1) \]

By substituting equation 3.23 into the right side of equation 3.11, it reduces to
\[
\phi_{i,n} - \phi_{i,n}^* = A_4 \phi_{i-1,n} + A_5 \phi_{i-1,n}^* + A_6 \phi_{i,n}
\]

(3.25)

where

\[A_4 = A_1 / \gamma\]
\[A_5 = A_2 / \gamma\]
\[A_6 = (A_3 - 1) / \gamma\]

Substituting equation 3.25 into equation 3.11 gives the following:

\[
\frac{d\psi_{i,n}}{d\xi} \bigg|_{\gamma} = A_4 \phi_{i-1,n} + A_5 \phi_{i-1,n}^* + A_6 \phi_{i,n}
\]

(3.26)

Apply Crank-Nicholson one-half method to equation 3.26, \( \psi_{i,n} \) can be expressed as

\[
\psi_{i,n} = \psi_{i,n-1} + \frac{\Delta \xi}{\gamma} \left[ A_4 \phi_{i-1,n} + A_5 \phi_{i-1,n}^* + A_6 \phi_{i,n} \\
+ \frac{\phi_{i,n-1} - \phi_{i,n-1}^*}{\gamma} \right]
\]

(3.27)

Now consider

\[\theta = \theta(\tau, \xi)\]

\[
\frac{d\theta}{d\tau} = \frac{\partial \theta}{\partial \tau} + \frac{\partial \theta}{\partial \xi} \frac{d\xi}{d\tau}
\]

(3.28)
and \( \frac{d\tau}{d\zeta} = \mu_h \) (5, 8), then equation 3.28 becomes

\[
\left( \frac{d\theta}{d\tau} \right)_n = \frac{\partial \theta}{\partial \tau} + \mu_h \frac{\partial \theta}{\partial \zeta}
\]  

(3.29)

By substituting equation 3.29 into equation 3.12, one forms

\[
\frac{d\theta}{d\tau} = \alpha \frac{\partial \phi}{\partial \tau} - \frac{\theta}{\beta}
\]  

(3.30)

Combine equation 3.10 and 3.30 to form

\[
\frac{d\theta}{d\tau} + \frac{\theta}{\beta} = \alpha \left( \frac{\phi^* - \phi}{\gamma} \right)
\]  

(3.31)

Following the same approach as equation 3.21, equation 3.31 yields the exact solution as

\[
\theta_{i,n} = \theta_{i-1,n} e^{-\Delta \tau/\beta} + \frac{\alpha \beta}{\gamma} \int_{\tau_{i-1}}^{\tau_i} \frac{(\phi^* - \phi) e^{-\tau - \tau_i}/\beta}{\beta} d\tau
\]

(3.32)

Again, assume linearity for \((\phi^* - \phi)\) between \(\tau_{i-1}\) to \(\tau_i\) such that

\[
(\phi^* - \phi) = (\phi^* - \phi)_{i-1,n} + \frac{\tau - \tau_{i-1}}{\tau_i - \tau_{i-1}} (\phi^* - \phi)_{i-1,n} - (\phi^* - \phi)_{i-1,n}
\]

(3.33)
Then equation 3.32 can be expressed as

\[
\theta_{i,n} = A_7 \theta_{i-1,n} + A_8 (\phi_{i-1,n} - \phi_{i-1,n}) + A_9 (\phi_{i,n} - \phi_{i,n})
\]  

(3.34)

where

\[
A_7 = e^{-\Delta\tau/\beta}
\]

\[
A_8 = \frac{\alpha \beta}{\gamma \Delta\tau} \left[ 1 - A_7 (1 + \Delta\tau/\beta) \right]
\]

(3.35)

\[
A_9 = \frac{\alpha \beta^2}{\gamma \Delta\tau} (\Delta\tau/\beta - 1 + A_7)
\]

It can be further simplified to

\[
\theta_{i,n} = A_7 \theta_{i-1,n} + A_{10} \phi_{i-1,n} + A_{11} \phi_{i-1,n} + A_{12} \phi_{i,n}
\]  

(3.36)

where

\[
A_{10} = -(A_8 + A_9 A_7)
\]

\[
A_{11} = A_8 - A_9 A_2
\]

(3.37)

\[
A_{12} = A_9 (1 - A_3)
\]

Coefficients \( A_1 \) through \( A_{12} \) depend only on the sizes of \( \Delta\tau \) and \( \Delta\xi \) and parameters \( \alpha, \beta \) and \( \gamma \). With fixed sizes of \( \Delta\tau \) and \( \Delta\xi \) and parameters, they can be treated as constant throughout the whole numerical scheme.

The initial and boundary conditions are transformed into numerical scheme values as follows:

\[
\theta_{0,n} = 0, \quad \theta_{1,o} = 0
\]

\[
\psi_{0,n} = 0, \quad \psi_{1,o} = 1
\]

\[
\phi_{0,n} = 0, \quad \phi_{1,o} = 1
\]
\[ \phi_{0,n}^* = 0 \] (3.38)

\( \phi_{1,0}^* \) is assumed to be 1 by assumption 7.

Combining equations 3.23, 3.27, 3.36 and equilibrium equation 3.17 forms a system of simultaneous equations with four equations and four unknowns, \( \psi_{i,n}^*, \phi_i, n^* \phi_{i,n}^* \) and \( \theta_{i,n}^* \).

By expressing equation 3.27 and 3.36 as a function of \( \phi_{i,n}^* \) such that

\[ \psi_{i,n} = A_{13} + A_{14} \phi_{i,n}^* \] (3.39)
\[ \theta_{i,n} = A_{15} + A_{12} \phi_{i,n}^* \] (3.40)

where

\[ A_{13} = \psi_{i,n-1} + \frac{\Delta \xi}{2} \left[ A_{4} \phi_{i-1,n} + A_{5} \phi_{i-1,n}^* \right] + \frac{(\phi_{i,n-1} - \phi_{i,n-1}^*)}{\gamma} \] (3.41)

\[ A_{14} = \frac{\Delta \xi}{2} A_6 \]

\[ A_{15} = A_7 \theta_{i-1,n} + A_{10} \phi_{i-1,n} + A_{11} \phi_{i-1,n}^* \] (3.42)

Substituting equation 3.39 and 3.40 into equation 3.17, one forms
(A_{13} + A_{14}\phi_{i,n}^*) \cdot \Delta P + P_{ao} = \text{Exp} \left[ K_m + A(\phi_{i,n}^{\Delta W+W_{ao}}) \right. \]
\left. - \frac{Q_{ao}(\phi_{i,n}^{\Delta W+W_{ao}})}{RT_w(1 + A_{15} + A_{12}\phi_{i,n}^*)} \right]

Rearrange equation 3.43 as

\[ F(\phi_{i,n}^*) = (A_{13} + A_{14}\phi_{i,n}^*) \cdot \Delta P + P_{ao} - \]
\[ \text{Exp} \left[ K_m + A(\phi_{i,n}^{\Delta W+W_{ao}}) - \frac{Q_{ao}(\phi_{i,n}^{\Delta W+W_{ao}})}{RT_w(1+A_{15}+A_{12}\phi_{i,n}^*)} \right] = 0 \] (3.44)

and solve the root of equation 3.44, then $\phi_{i,n}^*$ can be found. By substituting it into equation 3.23, 3.39 and 3.40 $\phi_{i,n}$, $\psi_{i,n}$ and $\theta_{i,n}$ can be solved simultaneously.

There are many numerical techniques for finding the root of equation 3.44. The most used methods are Newton's method; secant method and modified falsi method (also known as false position method).

Modified falsi method is preferred in this work because of two reasons;

1. other more sophisticated methods, for example Newton-Raphson, required the knowledge of second or third
derivatives of the function. This requires considerable amount of computation. To use Newton-Raphson method for equation 3.44, each step of iteration will then has to evaluate one additional derivative, \( \frac{\partial F}{\partial \phi} \), which again computed from two additional functions, \( \frac{\partial A(W^*)}{\partial \phi} \) and \( \frac{\partial Qa(W^*)}{\partial \phi} \).

In this work, considerable amount of trials is frequently necessary, the computation cost for one additional derivative and two functions might increase as much as 50% computer time.

2. With the knowledge that \( \phi_{i,n}^* \) lies in the range of \( 0 \leq \phi^* \leq 1 \), the solution of equation 3.44 is bounded. In this case, the modified falsi method converges towards the root almost quadratically. Moreover, if Newton-Raphson method is used, it might yield a small but negative root when \( \phi_{i,n}^* \) approaches zero. This invalidates assumption 7 and should be avoided.

A detailed description of the modified falsi method as well as others can be found in Conte and Boor's text (7).

A complete numerical solution to the system of equations is obtained with the computations done by two different digital computers. The reduced results will be presented in the following section.
SECTION 4 THEORETICAL PREDICTION OF MODEL PARAMETERS

Fourteen representative experimental runs (134401-8; 131801-5 and 131808) by Wright et al. (25) have been simulated on a Rice IBM 370/155 digital computer and a NASA UNIVAC 1108 EXEC II digital computer. The results indicated the model described previously is adequate to predict the isothermal and nonisothermal dynamic behaviour of the adsorption process.

In this section, the model results will be presented and their relationship with the experimental parameters will be discussed. Theoretical prediction of model parameters are also presented.

This section divides into four parts. The first part presents a criteria to determine the model parameters and the lists of the results. The second part presents a theoretical predication for the heat transfer coefficient \( h_w \) from the heat transfer resistance \( \beta \) and the experimental data. Correlation equations for heat transfer coefficients are listed in this subsection. The third part presents the theoretical predicted values of mass transfer coefficients \( K_a \). The relationship between \( K_a \) and the experimental data are discussed. The last part presents comparison results computed from the predicted parameters and the experimental parameters in the form of plots and figures.
4.1 Criteria to Determine the Model Parameters

There are four parameters in the model, namely, $\alpha$, $\beta$, $\gamma$, and the isotherm data. Among them, $\alpha$ and the isotherm data are determined by the nature of the adsorbent. $\beta$ and $\gamma$ are free parameters and are determined by the dynamic behaviour of the adsorption process.

The isotherm data were evaluated from the heat of adsorption and the loading capacity of the adsorbent. Their relation has been discussed in section 2.

Correlations reported by Phillip et al. (20) were applied to evaluate the coefficient of heat capacity of the solid phase, $C_{pb}$, of the adsorbent, which in turn determine the value of $\alpha$. The correlation equation can be expressed as

$$C_{pb} = 0.176 + 2.48 \times 10^{-4} T - 1.88 \times 10^{-7} T^2$$

where $T$ is expressed in degree Fahrenheit.

It was found that the value of $C_{pb}$ is in the range of 0.23-0.235 for this study. This range was further confirmed by the value reported in Davidson literature (10).

The remaining two parameters, $\beta$ and $\gamma$, are determined by matching the model solution $\Phi(1)$ and the maximum temperature rise $\Delta T_{\text{max}}$ with the experimental $\Phi(1)$ and the maximum temperature rise $\Delta T_{\text{max}}$ respectively. This approach was proposed by Davis (9) and has been effectively used by Sampat (21) and Bernard (5).

To find the value of $\gamma$, it was first assumed $\alpha$ and $\beta$
were zero, i.e. the system was assumed at isothermal conditions. The value of $\gamma$ was determined at which the model $\Phi(1)$ matched the experimental $\Phi(1)$. Then the value of $\gamma$ was held invariably and the value of $\beta$ was changed until the model $\Delta T_{\text{max}}$ matched the corresponding experimental data. This method is termed as discrete method in this work. Table 4.1 and 4.2 list the pairs of $\beta$ and $\gamma$ that matched the model solutions with the experimental behaviour.

Another method to determine the pair of $\beta$ and $\gamma$ is to vary the values of $\beta$ and $\gamma$ simultaneously $(5,6)$, until the experimental behaviour matched. Table 4.3 shows some of the results obtained by this simultaneous method. The results indicated that the variation of $\gamma$ is insignificant in comparison with the experimental error in $\Phi(1)$. Hence the discrete method was used to save computer time.

To use Davis' approach (9), it is necessary to have functions $\Phi(1)$ and $\Delta T_{\text{max}}$ of $\gamma$ and $\beta$ respectively. The function $\Phi(1)$ has been studied thoroughly by a computer study. It was found that function $\Phi(1)$ is inversely proportional to parameter $\gamma$. Some of these functions are plotted in Fig. 4.1 and 4.2.

For the function $\Delta T_{\text{max}}$, it was found that the values of $\Delta T_{\text{max}}$ when in the neighbourhood of experimental $\Delta T_{\text{max}}$ are directly proportional to the parameter $\beta$. Some of these functions are plotted in Fig. 4.3 and 4.4.
<table>
<thead>
<tr>
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<th>MODEL PARAMETERS</th>
<th>MODEL SOLUTIONS</th>
</tr>
</thead>
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<tr>
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<td>( \tilde{\Phi}(1) )</td>
<td>( \alpha )</td>
</tr>
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<tr>
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Table 4.1 Model Solutions for CO\(_2\)/13X
<table>
<thead>
<tr>
<th>EXPERIMENTAL PARAMETERS</th>
<th>MODEL PARAMETERS</th>
<th>MODEL SOLUTIONS</th>
</tr>
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<td>Φ(1)</td>
<td>ΔT_{max} (°F)</td>
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<tr>
<td>LB/LB</td>
<td></td>
<td></td>
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<tr>
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Table 4.2  Model Solutions for H$_2$O/13X
Table 4.3  Comparison of Obtained by Different Iteration Methods

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<th>DISCRETE METHOD</th>
<th>DIFF %</th>
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Fig. 4.1 Function $\Phi(1)$ for CO$_2$/13X
Fig. 4.2  Function $\Phi(1)$ for $H_2O/13X$
Fig. 4.3. Function $\Delta T_{\text{max}}$ for CO$_2$/13X
Fig. 4.4 Function $\Delta T_{\text{max}}$ for H$_2$O/13X
4.2 Theoretical Prediction of $h_w$

Heat transfer coefficient in the bed can be correlated by an equation developed by Gamson et al. (12,22)

$$\frac{h_w}{C_{pbG}} = \eta N_{Re}^{-.51} N_{Pr}^{-2/3}$$  \hspace{1cm} (4.1)

where $N_{Re}$ is the Reynolds number and $N_{Pr}$ is the Prandtl number for gas. Using this relationship for $h_w$ with $\eta$ evaluated from the following equation;

$$\eta = \frac{(C_{ao} - C_{ao}) N_{Re}^{.51} N_{Pr}^{2/3}}{(W_{ao} - W_{ao})\beta}$$  \hspace{1cm} (4.2)

By neglecting the small variation in the Prandtl number due to the small change of viscosity of the gas, the results indicate that the size of the plate-fin of the bed has a strong effect in the adsorption system. The evaluated $h_w$ can be divided into two groups according to the size of the plate-fin design; one for 1" spacing; another for 1/2" spacing. Computed values of $h_w$ are listed in Table 4.4.

There is considerable variation in the values of $\eta$ in both groups. It may be caused by the difference in locating $\Delta T_{max}$ which in term determines $\beta$. In the model, $\Delta T_{max}$ was found by searching for the maximum value of $\Delta T_{max}$. It was found that the maximum temperature rise occurred at the adsorption front at each time step. The temperature rise became stable after $\tau$ greater than .3 and began to decrease when the front reached the exit of
<table>
<thead>
<tr>
<th>ID NO</th>
<th>D (in)</th>
<th>G (lb/ft²-hr)</th>
<th>N_Re</th>
<th>N_Pt</th>
<th>β</th>
<th>η</th>
<th>h_w (BTU/ft²-hr-F)</th>
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Table 4.4 Theoretical Predicted Values of Heat Transfer Coefficients
the bed. Then it eventually reached the feed conditions when the bed became saturated. This finding is confirmed by others (19).

In the experiment, thermocouples might be evenly placed in the bed and the temperature rises were monitored periodically. Hence it might only record the local maximum temperature rises where the termocouples were. They might not be the actual maximum temperature rise. This uncertainty introduces a high percentage of error in matching $\Delta T_{\text{max}}$.

Without further refined data, the heat transfer coefficient $h_w$ may be correlated as

$$\frac{h_w}{C_p b G} = \begin{cases} 110 \ N_{\text{Re}}^{-0.51} \ N_{\text{pt}}^{-2/3} & \text{for } \frac{1}{2} \text{" spacing} \quad (4.3a) \\ 30 \ N_{\text{Re}}^{-0.51} \ N_{\text{pt}}^{-2/3} & \text{for } 1\text{" spacing} \quad (4.3b) \end{cases}$$

4.3 Theoretical Prediction of $\gamma$

The goal of this study was to find a simple value of $\gamma$ that can be used to produce acceptable predictions for the dynamic behaviour of the adsorption process. An attempt was made to evaluate mass transfer parameter from the CO$_2$/13X and H$_2$O/13X breakthrough curves. In order to do this, the value of the mass transfer coefficient $K_a$ had to be obtained. Experimental data was not available, therefore $K_a$ was derived from the model solutions. This was done as follows;
From the definition of $\gamma$, $K_a$ can be expressed as

$$K_a = \frac{M_v (C_{ao} - C_{ao})}{M_b (W_{ao} - W_{ao})\gamma} \quad (4.4)$$

The computed values of $K_a$ are listed in Table 4.1 and 4.2.

The evaluation yielded one value of $K_a$ (after discarding 134406 and 131808) for each adsorbate which gives a good fit for the experimental breakthrough curves. The values are

$$K_a = \begin{cases} 
11.62 \text{ Hr}^{-1} \text{ for } CO_2/13X & (4.5a) \\
.86 \text{ Hr}^{-1} \text{ for } H_2O/13X & (4.5b)
\end{cases}$$

In evaluating $K_a$, 134406 was not used because the original data was missing in Wright's report and 131808 was discarded because the value of average loading $\bar{\Phi}(1)$, was inconsistent with 131802 which had similar operating conditions but lower $\bar{\Phi}(1)$.

4.4 Simulations of the Breakthrough Curves

The computed values of $K_a$ and the correlation equations 4.3a and 4.3b were used to predict the model parameters. The results of the predicted values are listed in Table 4.5 and 4.6.

The predicted values of $\beta$ and $\gamma$ were then used to simulate two experimental runs. Run 134403 was chosen because it has largest deviation of $\gamma$ in $CO_2/13X$ group. Run 131805 was chosen because it has smallest deviation
<table>
<thead>
<tr>
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<th>% ERROR BETWEEN PREDICTED &amp; SIMULATED PARAMETERS</th>
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<td>( \beta )</td>
<td>( \gamma )</td>
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Table 4.5 Theoretically Predicted Model Parameters for CO\(_2\)/13X
<table>
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<th>PREDICTED PARAMETERS</th>
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Table 4.6 Theoretically Predicted Model Parameters for \( H_2O/13X \)
of $\gamma$ in H$_2$O/13X group. Fig. 4.5 and 4.6 show the predicted curves, together with the curves computed with $\beta$ and $\gamma$ from Table 4.1 and 4.2 (best fitted curves). Table 4.7 lists the comparison of the model solutions and the experimental data.

A visual comparison of the plots indicated both simulations gave a fair account of the dynamic behaviour of the adsorption process. As predicted, in run 134403, $\Phi(1)$ is higher than the experimental data. However, the difference is negligible. Also, the results indicated that a large deviation of $\beta$ does not affect the value of $\Phi(1)$ but changes the value of $\Delta T_{\text{max}}$ by a corresponding percentage. This finding confirms the validity of function $\Delta T_{\text{max}}$ shown in Fig. 4.3.

Run 131805 almost matched the experimental data except $\Psi_e$. Since the value of $\Phi(1)$ is computed from the shape of the breakthrough curve, a change in the shape of the curve would change the value of $\Phi(1)$. In Fig. 4.5, the difference of $\Psi_e$ may be as high as 33%, but the difference of $\Phi(1)$ is insignificant. The reason why the change of the shape of the breakthrough curve has no strong effect on the value of $\Phi(1)$ is not clear. It may be caused by the method of computing $\Psi_e$, in which $C_{\text{aq}}$ was assumed to be constant but was found to be varied as much as 18%. However, one may note that the shape of the breakthrough curves (simulated and experimental) are similar. The fact that the
Fig. 4.5 Simulated Breakthrough Curves for Run 134403
Fig. 4.6  Simulated Breakthrough Curves for Run 131805
Table 4.7. Comparison Between Predicted Solutions and Experimental Data

<table>
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<tr>
<th>EXPERIMENTAL DATA</th>
<th>PREDICTED SOLUTIONS</th>
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</thead>
<tbody>
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<td>$\bar{\Phi}(1)$</td>
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</table>
Simulated curves matched the upper portion of the experimental curves indicates that the major resistance of the mass transfer of the adsorption is inside the adsorbed layer. Hence one may conclude that the fluid phase internal diffusion model is adequate for this type of adsorption.
As mentioned in section 3.1, the possible controlling steps were external mass transfer, surface reactions, fluid phase internal diffusion, and solid phase internal diffusion. Surface reaction was not considered because in general, the reaction rate of molecular sieve adsorption varies with particle sizes. Solid phase internal diffusion was ruled out because the driving force is nonlinear (2, 19, 25).

Investigations with external mass transfer as the controlling step have been carried out. Bernard (5), using an external mass transfer model and similar assumptions studied the same dynamic adsorption process. He attributed the controlling mechanism to the gas-to-particle resistance for mass transfer. In this section, his model will be briefly presented here together with a short comparison with the fluid phase internal diffusion model. Hereinafter, reasons for preferring the internal diffusion model will be pointed out and conclusions will be drawn.

This section divides into four parts. The first part presents a brief description of the external mass transfer model. The second part presents the solutions of the model (5) and a brief discussion of the results. The third part presents the predicted breakthrough curves by the
external mass transfer model and by this work. Reasons for preferring the fluid phase internal diffusion model are given here. The last part presents the conclusions drawn from this study.

5.1 Description of The External Mass Transfer Model

Assumptions made in the external mass transfer model are similar to the assumptions stated in section 3.3, except assumption 8 in which the driving force equation was replaced by

\[ r_a = \frac{\partial W_a}{\partial t} = K_g (P_a - P^{*}_a) \]  \quad (5.1)

where \( K_g \) = mass transfer coefficient which is a function of gas flow rate, pressure and temperature

\( P^{*}_a \) = adsorbate concentration in gas phase which would be in equilibrium with the adsorbate on the solid phase, \( W_a \).

Under these assumptions, the mass transfer equation 5.1 together with the mass balance equation 3.3 and heat balance equation 3.5 can be used to describe the dynamic behaviour of the adsorption process. By the same approach described in section 3, equations 3.3, 3.5 and 5.1 can be reduced into a system of dimensionless equations with a set of dimensionless variables and parameters analogous to equations 3.9, 3.14, 3.15 and 3.16. The final form of the reduced equations are
\[ \frac{\partial \psi}{\partial \xi} = \frac{\psi^* - \psi}{\gamma} \]  
(5.2)

\[ \frac{\partial \phi}{\partial \tau} = \frac{\psi - \psi^*}{\gamma} \]  
(5.3)

\[ \frac{\partial \theta}{\partial \tau} + \nu \frac{\partial \theta}{\partial \xi} = \frac{\alpha \frac{\partial \phi}{\partial \tau} - \theta}{\beta} \]  
(5.4)

where

\[ \gamma = \frac{M_v M_w}{\rho g R T w M_b K_g} \]

\[ \psi^* = \frac{P_a^* - P_{a_0}}{P_{a_0} - P_{a_0}} \]

Using similar numerical techniques, solutions which are similar to those obtained by this work are reported (5).

5.2 Theoretical Predictions of \( K_g \) and \( h_w \)

Table 5.1 and 5.2 list the unique pairs of \( \beta \) and \( \gamma \) that determined by \( \Delta T_{\text{max}} \) and \( \Phi(1) \). One should note the values of \( \beta \) was determined by matching the experimental temperature rise with the model temperature rise at \( \tau = 0.6 \) in Bernard's work. Hence no comparison of the values of \( h_w \) predicted by this work and by Bernard's results.

Two correlation equations were reported to predict the value of mass transfer resistance, \( \gamma \). They are as follows;

\[ \gamma = \begin{cases} 
0.0103 \ N_{Re}^{0.525} \ & \text{for CO}_2/13X \\
0.0163 \ N_{Re}^{0.525} \ & \text{for H}_2O/13X 
\end{cases} \]

The results of Bernard's proved two interesting findings of this work. First, from Table 5.1 and 5.2,
### Table 5.1 Unique $\beta$, $\gamma$ pair for $\text{CO}_2/13X$

<table>
<thead>
<tr>
<th>ID NO</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\gamma_1$</th>
<th>Deviation of $\gamma$ (%)</th>
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</thead>
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<tr>
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<td>-</td>
<td>.2332</td>
<td>-</td>
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<td>134402</td>
<td>.02742</td>
<td>.0697</td>
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<td>-</td>
<td>.0576</td>
<td>-</td>
</tr>
<tr>
<td>134406</td>
<td>-</td>
<td>-</td>
<td>.0794</td>
<td>-</td>
</tr>
<tr>
<td>134407</td>
<td>-</td>
<td>-</td>
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<td>-</td>
</tr>
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<td>134408</td>
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<td>.0718</td>
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<td>12.3</td>
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</tbody>
</table>

### Table 5.2 Unique $\beta$, $\gamma$ pair for $\text{H}_2\text{O}/13X$

<table>
<thead>
<tr>
<th>ID NO</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\gamma_1$</th>
<th>Deviation of $\gamma$ (%)</th>
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</thead>
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<td>.1173</td>
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<tr>
<td>131804</td>
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<tr>
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<td>.00111</td>
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<td>.0672</td>
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</table>

$\gamma_1$ refers to isothermal conditions
the deviation of $\gamma$ is insignificant. Hence, it confirmed that the value of $\gamma$ is independent of $\beta$. Therefore, the discrete method described in section 4.2 is more efficient than the simultaneous method.

Table 5.3 and 5.4 present the values of $K_g$ computed from equation 5.5. As will be shown, these values further proved that the controlling step is inside the adsorbed layer.

If the controlling step was the gas-to-particle resistance, the value of $K_g$ would be a function of fluid flow rate, temperature and pressure. The results did not show a clear relationship of $K_g$ upon the flow rate. Noting the values of $K_g$ of runs 134404 and 134408, the flow rate dependence is uncertain. Furthermore, it appears that the values of $K_g$ stayed relatively constant, which suggest that the major part of the mass transfer resistance is inside the adsorbed layer (2, 6).

Moreover, using a published correlation equation by Lee and Cumming (16), the predicted values of $K_g$ for CO$_2$/13X adsorption should be in the range of $0.004 - 0.0068$ lb/lb-mm Hg-hr. These values are somewhat lower than that values computed from Bernard's work.

In summary, with the argument that $K_g$ differs from the published correlations by a factor of 10 and the values of $K_g$ stayed relatively constant, one might conclude that the gas-to-particle resistance might not be the controlling mechanism. Therefore, using the same argument, the
Table 5.3  Theoretically Predicted $K_g$ for CO$_2$/13X

<table>
<thead>
<tr>
<th>ID NO</th>
<th>$\gamma$</th>
<th>$K_g$ 1b/1b-mm Hg-hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>134401</td>
<td>.2332</td>
<td>$3.55 \times 10^{-2}$</td>
</tr>
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<tr>
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<td>.0734</td>
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</tr>
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<td>.0794</td>
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</table>

Table 5.4  Theoretically Predicted $K_g$ for H$_2$O/13X

<table>
<thead>
<tr>
<th>ID NO</th>
<th>$\gamma$</th>
<th>$K_g$ 1b/1n-mm Hg-hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>131801</td>
<td>.1255</td>
<td>$1.39 \times 10^{-2}$</td>
</tr>
<tr>
<td>131802</td>
<td>.1352</td>
<td>$6.96 \times 10^{-3}$</td>
</tr>
<tr>
<td>131803</td>
<td>.1085</td>
<td>$7.66 \times 10^{-3}$</td>
</tr>
<tr>
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<td>.0979</td>
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<td>$9.30 \times 10^{-3}$</td>
</tr>
<tr>
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<td>$2.43 \times 10^{-2}$</td>
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</table>
resistance to the mass transfer is inside the adsorbed layer. However, these arguments did not rule out the possibility of a series of mechanism in which external mass transfer played a role.

5.3 Breakthrough Curves

Three computer runs were made to determine the characteristics of the breakthrough curves obtained from the external mass transfer model. Fig. 5.1, 5.2 and 5.3 show various model simulated curves plotted against the experimental data for runs 134402, 134407 and 131805 respectively.

It is noted that in CO₂/13X case, both models appear to fit the data in both shape and breakthrough time. Although the breakthrough time predicted by this work occurred at a later time, this was caused by the size of the time step and the allowable tolerance in iterating the transcendental equation 3.44. This can be improved by a smaller time step and lower allowable tolerance but at the expense of more computer time.

One might observe that the upper portion of the curves were matched almost exactly by the internal diffusion model while those predicted by the external mass transfer model deviated. This phenomenon became more evident in the H₂O/13X system. In run 131805, the deviation in τ is as much as .2 (equivalent to 1.4 hr in
Fig. 5.1 Comparison of Breakthrough Curves for 134402
Fig. 5.2 Comparison of Breakthrough Curves for 134407
Run 131805

Fig. 5.3 Comparison of Breakthrough Curves for 131805
real time. From this point, one might conclude that the fluid phase internal diffusion model is more preferable in predicting the breakthrough curves for CO$_2$/13X and H$_2$O/13X adsorption systems.

5.4 Summary and Conclusions

This work has outlined a system of equations which describes the heat and mass transfer characteristics of the fixed-bed adsorption process. This system of equations can be used for predicting the breakthrough curves, with the aid of properly defined dimensionless equations and parameters. A discussion of the mathematical treatment of these equations as well as their solutions prepared by digital computer programs were presented along with comparison of the predicted and experimental data.

A comparison between the external mass transfer model and this work was also discussed. Hence, the following conclusions are drawn from this research;

1. Equilibrium isotherm data may be obtained using Clausius-Clapeyron Theory.

2. The resulting breakthrough curves for nonisothermal and isothermal adsorption may be predicted by appropriate mathematical models.

3. For CO$_2$/13X and H$_2$O/13X adsorption systems, the modified Glueckauf model fits the data. For the assumptions basic to this model, the rate controlling
step appears to be the fluid phase internal diffusion.

4. The values for the mass transfer coefficients of CO₂/13X and H₂O/13X are constants and were found to be

$$K_a = \begin{cases} 11.62 \text{ Hr}^{-1} \text{ for CO}_2/13X \\ 0.86 \text{ Hr}^{-1} \text{ for H}_2O/13X \end{cases}$$

5. The values of heat transfer coefficients are functions of flow rate and the sizes of the plate-fin design and were found to be

$$\frac{h_w}{C_{p,b}G} = \begin{cases} 110 \text{ N}_{Re}^{-0.51} \text{ N}_{Pt}^{-2/3} \text{ for } \frac{1}{2} \text{ spacing} \\ 30 \text{ N}_{Re}^{-0.51} \text{ N}_{Pt}^{-2/3} \text{ for } 1 \text{"} \text{ spacing} \end{cases}$$
REFERENCES


10. Davidson Literature, PC/ADS-104-172.


17. Linde Literature, No-F-3035-5.