CHAPTER 3

DERIVATION OF EQUATIONS USED IN THE SIMULATION

The operation of single column pressure swing adsorption systems are reported to rely on high pressure drops within the adsorption column for proper gas separation to occur. This is in contrast to traditional two column pressure swing adsorption systems where adsorbent pellets are generally large and pressure drop is generally neglected. However the use of smaller adsorbent particles in single column pressure swing adsorption systems allows consideration of the use of the equilibrium model where the adsorbed gases are considered to be in equilibrium with the gas phase.

3.1 Basic assumptions.

The basic assumption may be summarized as follows.

1. Isothermal conditions.

2. Negligible axial and radial dispersion.

3. Ideal gas behavior.

4. Instantaneous equilibrium between the gas phase and the adsorbed gas.

5. Linear adsorption isotherm.

6. Pressure, mole fraction and velocity are function of length and time

3.2 Determination of pressure drop equation.

For adsorption through porous media Darcy's law may be used to predict pressure profiles in a single column PSA [3].Using a combination of Darcy's law with the continuity equation one obtains

$$\frac{\partial p}{\partial t} = C \frac{\partial^2 p^2}{\partial z^2} \qquad (3.1)$$

(a description of the derivation of equation (3.1) is presented in appendix A)

where C is constant given by

$$C = \frac{K}{2 \varepsilon \mu} \qquad (3.2)$$

where K is the permeability and a function of particle diameter given by

$$K = \frac{\varepsilon^3 d_p^2}{150(1-\varepsilon)^2} \qquad (3.3)$$

so we can use equation (3.1) to predict the pressure profiles in the column.

3.3 Determiantion of the adsorption equation .
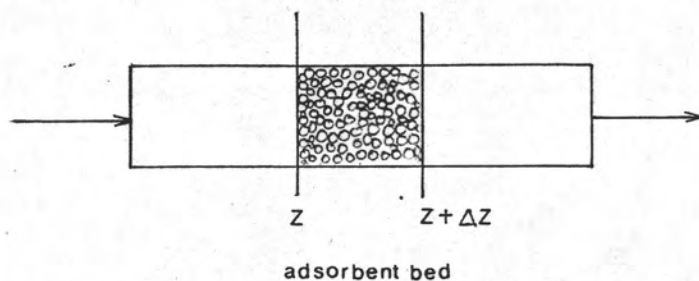
Figure 3.1 Material balance of PSA system

The system comprises of species 1,2 in the gas and both species are adsorbed in the solid instantaneously. For the above assumptions we have a mass balance for the two components as follows.

For component 1 : The material balance becomes.

$$vc_1A\Big|_z - vc_1A\Big|_{z+\Delta z} - A\,\Delta z(1-\varepsilon)\frac{\partial n_1}{\partial t} = A\,\Delta z\,\varepsilon\frac{\partial c_1}{\partial t} \qquad (3.4)$$

Then dividing by Δz and obtaining the limit as $\Delta z \longrightarrow 0$ we write

$$-\varepsilon\frac{\partial(vc_1)}{\partial z} - (1-\varepsilon)\frac{\partial n_1}{\partial t} = \varepsilon\frac{\partial c_1}{\partial t} \qquad (3.5)$$

$$\frac{\partial c_1}{\partial t} + \frac{\partial(vc_1)}{\partial z} + \frac{(1-\varepsilon)}{\varepsilon}\frac{\partial n_1}{\partial t} = 0 \qquad (3.6)$$

Similarly we can write a material balance for component 2 and obtain

$$\frac{\partial c_2}{\partial t} + \frac{\partial(v c_2)}{\partial z} + \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial n_2}{\partial t} = 0 \qquad (3.7)$$

both equation (3.6) and (3.7) are the same as those presented by Chan et al [8].

We assume an ideal gas and express c_1 and c_2 in terms of y_1 and y_2

$$c_1 = y_1 p/RT \qquad (3.8)$$

$$c_2 = y_2 p/RT \qquad (3.9)$$

where y_1 and y_2 are gas phase mole fractions of component 1 and 2 respectively.

For linear isotherms; [8]

$$n_1 = k_1 c_1 \qquad (3.10)$$

$$n_2 = k_2 c_2 \qquad (3.11)$$

We substitute equation (3.8) and (3.10) in equation (3.6) and equation (3.9) and (3.11) in equation (3.7), we then obtain the following,

For component 1,

$$\left[1 + \frac{(1-\varepsilon)k_1}{\varepsilon} \right] \frac{\partial(y_1 p)}{\partial t} + \frac{\partial(v y_1 p)}{\partial z} = 0 \qquad (3.12)$$

For component 2, multiply by RT and substitute y_2 with $1-y_1$ then

$$\frac{\partial p(1-y_1)}{\partial t} + \frac{\partial(vp(1-y_1))}{\partial z} + \frac{(1-\varepsilon)k_2}{\varepsilon} + \frac{\partial p(1-y_1)}{\partial t} = 0 \qquad (3.13)$$

expansion of the partial derivatives in equation (3.13) gives

$$\left[1 + \frac{(1-\varepsilon)k_2}{\varepsilon}\right]\frac{\partial p}{\partial t} - \left[1+(1-\varepsilon)k_2\right]\frac{\partial(py_1)}{\partial t} + \frac{\partial(vp)}{\partial z} - \frac{\partial(vpy_1)}{\partial z} = 0 \qquad (3.14)$$

with $\qquad K_i = \dfrac{\varepsilon +(1-\varepsilon)k_i}{\varepsilon} \qquad\qquad (3.15)$

substituting K_1, K_2 in equation (3.12) and (3.14) and obtain

$$K_1 \frac{\partial(y_1 p)}{\partial t} + \frac{\partial(vy_1 p)}{\partial z} = 0 \qquad (3.16)$$

$$K_2 \frac{\partial p}{\partial t} - K_2 \frac{\partial(py_1)}{\partial t} + \frac{\partial(vp)}{\partial z} - \frac{\partial(vpy_1)}{\partial z} = 0 \qquad (3.17)$$

Although the relationship does not include the concentration of adsorbed gas in the adsorbent, this concentration is known from the linear equilibrium relationship.

From equations (3.16) and (3.17) we omit subscript 1 from the mole fraction y and herein after y refers to the less strongly adsorbed component, which in this simulation refers to oxygen.

Adding equations (3.16) and (3.17) and expanding the derivatives we obtain

$$K_1 \frac{\partial(yp)}{\partial t} + K_2 \frac{\partial p}{\partial t} - K_2 \frac{\partial(py)}{\partial t} + \frac{\partial(vp)}{\partial z} = 0 \qquad (3.18)$$

expansion of the partial derivatives of equation (3.18) and multiplying by y gives

$$[(K_1-K_2)y^2 + K_2y] \frac{\partial p}{\partial t} + py(K_1-K_2) \frac{\partial y}{\partial t} + y \frac{\partial(vp)}{\partial z} = 0 \qquad (3.19)$$

substituting equation (3.19) in equation (3.17) and expanding the derivatives gives

$$K_1y \frac{\partial p}{\partial t} + K_1p \frac{\partial y}{\partial t} + vp \frac{\partial y}{\partial z} + y \frac{\partial(vp)}{\partial z} - [(K_1-K_2)y^2+K_2y] \frac{\partial p}{\partial t}$$

$$- py(K_1-K_2) \frac{\partial y}{\partial t} - y \frac{\partial(vp)}{\partial z} = 0 \qquad (3.20)$$

rearranging equation (3.20) gives

$$\left[\frac{y(1-y)(K_1-K_2)}{p}\right] \frac{\partial p}{\partial t} + [K_1-y(K_1-K_2)] \frac{\partial y}{\partial t} + v \frac{\partial y}{\partial z} = 0 \qquad (3.21)$$

For the next step we should find velocity in terms of p, y, and z. For this simulation we have 2 steps in one cycle, the first called feed gas introduction period or feed gas time and the second called reverse outward flow period or exhaust time as shown in figure 3.2.
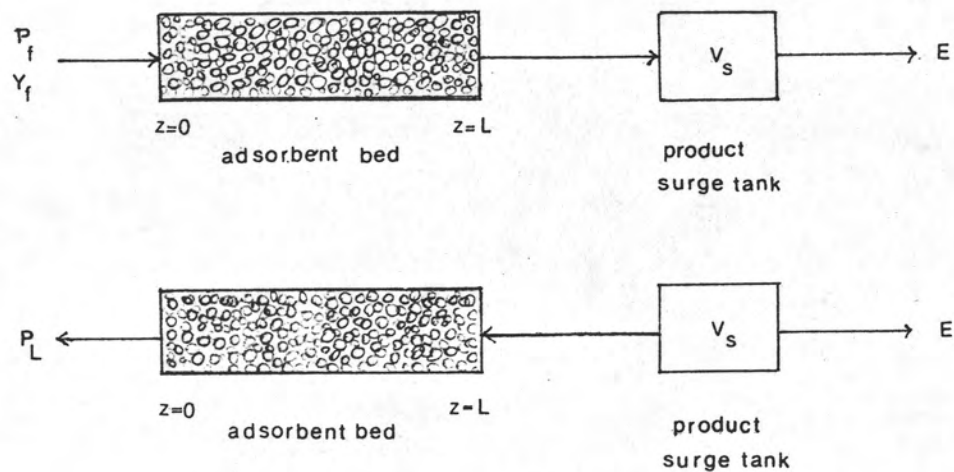
Figure 3.2 Schematic diagram for 2 step cycle of single column PSA.

We start from equation (3.17) by eliminating $\dfrac{\partial(y_1 p)}{\partial t}$ and using equation (3.16) gives

$$\frac{K_2}{\,} \frac{\partial p}{\partial t} + \frac{K_2}{K_1} \frac{\partial(vpy)}{\partial z} + \frac{\partial(vp)}{\partial z} - \frac{\partial(vpy)}{\partial z} = 0 \tag{3.22}$$

Rearranging equation (3.22)

$$\frac{\partial}{\partial z}\left[\frac{vp}{K_2} + \frac{(K_2-K_1)vpy}{K_1 K_2}\right] = -\frac{\partial p}{\partial t} \tag{3.23}$$

we place the right hand side term by equation (3.1) to give

$$\frac{\partial}{\partial z}\left[\frac{vp}{K_2} + \frac{(K_1-K_2)vpy}{K_1K_2}\right] = -C\frac{\partial^2 p^2}{\partial z^2} \qquad (3.24)$$

which equation (3.24) is the same as those presented by Sundaram and Wankat [5] with equation (3.24) Sundaram uses this equation with pressurization and blowdown steps with the column closed at one end he uses the boundary conditions with $v = 0$, $\partial p/\partial t = 0$ at $z=L$. But for this work we should have another boundary conditions. We integrate equation (3.24) to obtain

$$vp\left[\frac{1}{K_2} + \frac{(K_2-K_1)y}{K_1K_2}\right] = -C\frac{\partial p^2}{\partial z} + K' \qquad (3.25)$$

We set the boundary conditions at the closed end of the column at $z = L$ when $v = v(L,t)$, $y = y(L,t)$ and $p = p(L,t)$ we place these in equation (3.25) to obtained

$$v(L,t)p(L,t)\left[\frac{1}{K_2} + \frac{(K_2-K_1)y(L,t)}{K_1K_2}\right] + C\frac{\partial p^2}{\partial z}(L,t) = K' \qquad (3.26)$$

We obtain constant K' and substitute in equation (3.26) then we obtain the following equation from which we can find the velocity

$$vp\left[\frac{1}{K_2} + \frac{(K_2-K_1)y}{K_1K_2}\right] = -C\frac{\partial p^2}{\partial z} + C\frac{\partial p^2(L,t)}{\partial z}$$
$$+ v(L,t)p(L,t)\left[\frac{1}{K_2} + \frac{(K_2-K_1)y(L,t)}{K_1K_2}\right] \qquad (3.27)$$

Next we put the velocity term (v) from equation (3.27) in equation (3.21) then

$$K_1K_2\left[-C\frac{\partial p^2}{\partial z} + C\frac{\partial p^2(L,t)}{\partial z} + v(L,t)p(L,t)\left(\frac{1}{K_2} + \frac{(K_2-K_1)y(L,t)}{K_1K_2}\right)\right]\frac{\partial y}{\partial z}$$

$$+p[K_1-(K_1-K_2)y][y(1-y)(K_1-K_2)]\frac{\partial p}{\partial t} + p[K_1-y(K_1-K_2)]^2\frac{\partial y}{\partial t} = 0 \quad (3.28)$$

Equation(3.28) can be solved using a numerical method with the different boundary conditions for each step .

3.4 Boundary conditions

To solve equation (3.28) by a numerical method we have to set boundary conditions for the feed gas introduction period and the reverse outward flow period.

3.4.1.   Boundary conditions for feed gas introduction period.
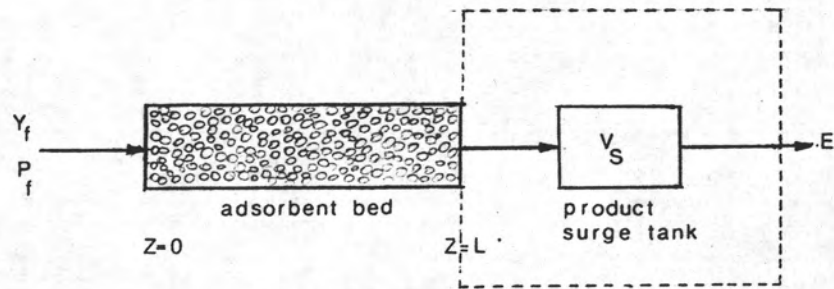
Figure 3.3   Schematic of feed gas introduction period.

If   we   feed   the   gas   at   a   constant   pressure and constant   concentration   we have the following boundary conditions at the front end of the column

$$p(0,t) = p_{feed} \tag{3.29}$$

$$y(0,t) = y_{feed} \tag{3.30}$$

and   for the back end of the column we have a material balance around the product   surge tank (V_s) which becomes

$$v(L,t)\ c(L,t)A\,\varepsilon = V_s\ \frac{\partial c(L,t)}{\partial t} + E \tag{3.31}$$

where   E   is   constant   molar flow rate (mole/s) which represents the amount   of product gas desired .Using the ideal gas law ($c = p/RT$) rewrite

$$v(L,t)\ p(L,t)\ A\,\varepsilon = V_s\ \frac{\partial p(L,t)}{\partial t} + ERT \tag{3.32}$$

and another set of boundary conditions for the back end of the column may be expressed as

$$\frac{\partial v(L,t)}{\partial z} = 0 \tag{3.33}$$

3.4.2. Boundary conditions for the reverse outward flow period.
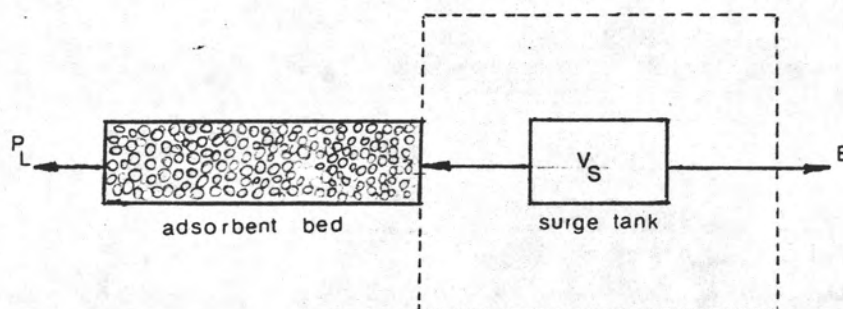
Figure 3.4 Schematic of reverse outward flow period

We exhaust the gas at atmospheric pressure so that the boundary condition at the front end of the column is given as

$$p(0,t) = p_L \tag{3.34}$$

For the back end of the column we have a material balance around the product surge tank similarly as the feed gas introduction period and obtain

$$v(L,t) \, p(L,t)A\varepsilon + ERT = - V_s \frac{\partial p(L,t)}{\partial t} \tag{3.35}$$

$$\frac{\partial v(L,t)}{\partial z} = 0 \tag{3.36}$$

and

$$y(L,t) = y_c \tag{3.37}$$

where y_c is final mole fraction in product surge tank at end of feed time.

3.5 <u>Method of calculation.</u>

The main equations of the simulation are equation (3.1) equation (3.27) and equation (3.28) which can be solved using a finite difference method. The approximations of the partial derivatives are presented in Appendix B the simulation used a time interval $\Delta t = 0.001$ seconds and $\Delta z = 7.5$ cm which is equivalent to having 20 cells in the column.

3.5.1 Procedure used in the calculation.

The sequence of calculations proceeds as follows :

```
┌────────────────────────────────┐      ┌──────────────────────────────────────┐
│ Mathematical model parameters  │      │ set initial condition p(z,0),y(z,0),v(z,0) │
│                                │──────│        for feed gas period            │
│ Process Variables              │      └──────────────────────────────────────┘
│   feed gas period, tip         │                       │
│   exhaust gas period, tib      │      ┌──────────────────────────────────────┐
│   no of cycle, endcy           │      │ Solve equation (3.1) with boundary conditions (3.29) │
│   particle diameter, dp        │      │ and (3.32) to give  p(z,t) for feed gas period │
│                                │      └──────────────────────────────────────┘
│ Adsorption equilibrium constants│                   p(z,t)
│   k₁, k₂                        │      ┌──────────────────────────────────────┐
│                                │      │ Solve equation (3.28) with boundary conditions  (3.30) │
│ Gas properties                 │      │       to give  y(z,t) for feed gas period │
│   viscosity of air, vis        │      └──────────────────────────────────────┘
│   feed gas composition, y      │                   y(z,t)
│   density, den                 │      ┌──────────────────────────────────────┐
│                                │      │ Solve equation (3.27) with boundary conditions (3.33) │
│                                │      │       to give  v(z,t) for feed gas period │
│ System specifications          │      └──────────────────────────────────────┘
│   length of column, L          │                   v(z,t)
│   diameter, D                  │      ┌──────────────────────────────────────┐
│   volume of surge tank, Vs     │      │ Obtain p(z,t), y(z,t) and v(z,t) at feed gas period │
│   porosity, por                │      └──────────────────────────────────────┘
└────────────────────────────────┘                     │
```

Mathematical model parameters

Process Variables
  feed gas period, tip
  exhaust gas period, tib
  no of cycle, endcy
  particle diameter, dp

Adsorption equilibrium constants
  k_1, k_2

Gas properties
  viscosity of air, vis
  feed gas composition, y
  density, den

System specifications
  length of column, L
  diameter, D
  volume of surge tank, V_s
  porosity, por

set initial condition $p(z,0), y(z,0), v(z,0)$ for feed gas period

Solve equation (3.1) with boundary conditions (3.29) and (3.32) to give $p(z,t)$ for feed gas period

$p(z,t)$

Solve equation (3.28) with boundary conditions (3.30) to give $y(z,t)$ for feed gas period

$y(z,t)$

Solve equation (3.27) with boundary conditions (3.33) to give $v(z,t)$ for feed gas period

$v(z,t)$

Obtain $p(z,t)$, $y(z,t)$ and $v(z,t)$ at feed gas period

set initial condition for exhaust period $p(z,0)$, $y(z,0)$, $v(z,0)$

Solve equation (3.1) with boundary conditions (3.34) and (3.35) to give $p(z,t)$ for exhaust period

$p(z,t)$

Solve equation (3.28) with boundary conditions (3.37) to give $y(z,t)$ for exhaust period

$y(z,t)$

Solve equation (3.27) with boundary condition (3.36) to give $v(z,t)$ for exhaust period

$v(z,t)$

Obtain $p(z,t)$, $y(z,t)$ and $v(z,t)$ at exhaust period

3.5.2   Flow diagram of simulation program in the C language

```
┌─────────────────────────┐
│   PARAMETER INPUT       │
│   tip , tib , endcy     │
└─────────────────────────┘
            │
            ▼
┌──────────────────────────────────────────────────┐
│ Calculate cycle of feed gas period\exhaust period │
│                                                    │
│ cyp = tip/Δt , cyb = tib/Δt , max = l/Δz          │
└──────────────────────────────────────────────────┘
            │
            ▼
┌─────────────────────────┐
│  INITIALIZATION :       │
│                         │
│  for m =1 to max        │
│    p[m,0] = p_L         │
│    y[m,0] = y_f         │
└─────────────────────────┘
            │
            │         K = 1
            ▼
      ┌──────────────┐
      │ Main program │
      └──────────────┘
            │
            ▼
┌──────────────────────────┐
│ CALL FUNCTION  prez(  ) :│
└──────────────────────────┘
            │
            ▼
┌──────────────────────────┐
│ for m =1 to max          │
│    v[m,0] = 0            │
└──────────────────────────┘
            │
            │         J = 1
            ▼
┌──────────────────────────────────────────┐
│ for m = 1 to max calculate p[m,n+1]       │
└──────────────────────────────────────────┘
            │
            ▼
┌──────────────────────────────────────────┐
│ for m = 1 to max calculate y[m,n+1]       │
└──────────────────────────────────────────┘
            │   J = J+1
            ▼
┌──────────────────────────────────────────┐
│ for m = 1 to max calculate v[m,n+1]       │
└──────────────────────────────────────────┘
            │
            ▼
```

```
                                              │
                                              ▼
                    NO                   ┌──────────┐
              ┌─────────────────────────│ J = cyp  │
              │                          └──────────┘
              │                               │
              │                              YES
              │                               │
              │                               ▼
              │                        ┌───────────────┐
K = K+1       │                        │ Main program  │
              │                        └───────────────┘
              │                               │
              │                               ▼
              │                  ┌──────────────────────────┐
              │                  │ CALL FUNCTION  BLOW( ) :  │
              │                  └──────────────────────────┘
              │                               │
              │                               ▼
              │                     ┌────────────────────┐
              │                     │ for m =1 to max     │
              │                     │     v[m,0] = 0      │
              │                     └────────────────────┘
              │                               │
              │                               ▼
              │          ┌────────────────────── J = 1
              │          │                        │
              │          │                        ▼
              │          │     ┌────────────────────────────────────────┐
              │          │     │ for m = 1 to max calculate p[m,n+1]     │
              │          │     └────────────────────────────────────────┘
              │          │                        │
              │          │                        ▼
              │          │     ┌────────────────────────────────────────┐
J = J+1       │          │     │ for m = 1 to max calculate y[m,n+1]     │
              │          │     └────────────────────────────────────────┘
              │          │                        │
              │          │                        ▼
              │          │     ┌────────────────────────────────────────┐
              │          │     │ for m = 1 to max calculate v[m,n+1]     │
              │          │     └────────────────────────────────────────┘
              │          │                        │
              │          │       NO          ┌──────────┐
              │          └───────────────────│ J = cyb  │
              │                               └──────────┘
              │                                    │
              │                                   YES
              │                                    │
              │                                    ▼
              │                             ┌───────────────┐
              │                             │ Main program  │
              │                             └───────────────┘
              │                                    │
              │                NO                  ▼
              └────────────────────────────┌──────────────┐
                                           │  K = endcy   │
                                           └──────────────┘
                                                   │
                                                  YES
                                                   │
                                                   ▼
                              ┌─────────────────────────────────────────┐
                              │ Solution of p(z,t), y(z,t), v(z,t)      │
                              └─────────────────────────────────────────┘
```

3.5.3 Parameter used in the simulation.

TABLE 3.1 Physical parameter used in the simualtion.

Adsorbent bed			
L	(cm)	150	
D	(cm)	7.62	
V_s	(cm^3)	2250	
		0.43	
d_p	(cm)	0.013 - 0.018	
A	(cm^2)	45.62	
Feed gas			
μ	(N.s/m^2)	1.85 e -5	[10]
ρ	(gm/cm^3)at T=300 K	1.1769 e-3	[12]
MW	(air)	29	[12]
P_L	(atm)	1	
P_{feed}	(atm)	4.4	
y_{feed}		0.21	
t_{feed}	(second)	0.5 - 1.5	
t_{exh}	(second)	5 - 10	
E	(mole/s)	0.02-0.03	
k_1		5.4	[11]
k_2		9.94	[11]