
A MATHEMATICAL MODEL FOR CHEMICAL TRANSPORT CHARACTERIZING DISPERSION AND ADSORPTION WITH AND WITHOUT CHEMICAL REACTION

Jose Condor
University of Regina

Introduction

Chemical dispersion and adsorption in porous media are of increasing interest to the petroleum industry because of the increasing importance of chemical flooding operations. In a chemical flooding process, while the dispersion causes mixing of a chemical slug, adsorption can result in a real chemical loss to the reservoir. The ultimate success of the chemical recovery process is depend on the concentration of chemical additive (Polymer) and must be controlled by the nature and magnitude of the loss or adsorption.

The molecular diffusive process does not occur in straight line but through the tortuous path in the porous media. Therefore it is important to measure the dispersion coefficient for a chemical flood process.

Dispersion and adsorption both are two types. While dispersion types are traverse and longitudinal; adsorption types are:

I. Instantaneous or equilibrium adsorption

- linear isotherm
- non-linear Freundlich isotherm
- non-linear Langmuir isotherm

II. Kinetic adsorption or non-equilibrium

Objective

The objective of this course work is to find or develop a chemical transport equation characterizing dispersion, adsorption and chemical reaction of a chemical solution flowing through a porous medium. Also, solution to the developed model using appropriate boundary and initial conditions are purposed. However, due to the non-homogeneity of the equation both analytical and numerical solution to such kind of equation needs more time than expected. Also, study of the available literatures showed that, people tried to solve the equation for specific cases by the means of ignoring some parts of the equation and applying some assumptions that made the solution a little bit far from the reality. There three more papers by Langmuir, Lapidus and Barakat respectively which are more closed to this study. However, these papers are not available on the SPE website.

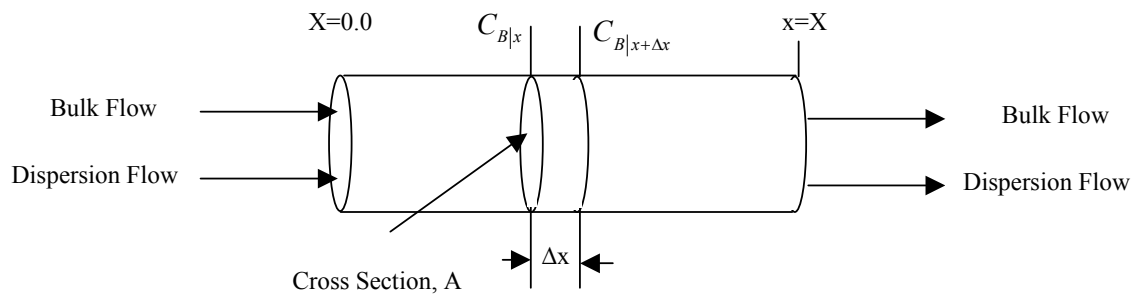
For this purpose, a system is defined (figure below) and using the mass balance equation over a small element of the core during a small time period, a second order partial differential model developed for the dispersion and adsorption at the first stage and by adding the chemical reaction term, it is extended for a system including adsorption, dispersion and chemical reaction. This model is compared with the available model for both systems in the literatures and there is an exact agreement between them. It is good to mention that all available papers used the model without proof. At the end an analytical solution for an specific case is provided according to one of the literature.1

1. No chemical reaction

Consider the following core sample and a small element along the core as a mixing zone. Also, assume that due to the adsorption process, we have an accumulation of polymer or surfactants around the rock. Before that it is good to mention that adsorption is depend on the rate of adsorption and as well as the capacity of rock to absorb the fluid.

Assumptions:

- Homogenous porous medium with constant cross section
- Fluid and rock compressibilities are negligible
- Dispersion occurs only in longitudinal direction
- Molecular diffusion is negligible
- Dispersion coefficient is independent of the chemical concentration
- No chemical reaction (First part)
- Chemical reaction (Second part)
- Adsorption process is appear
- Adsorption is a function of concentration



General Material Balance (Mass balance) Equation for the above system is based on the Component, B is:
 Input-Output=Accumulation + Disappearance due to the reaction

Entering at time $t+\Delta t$: $\left(\frac{\text{Moles of } B}{\text{Volume}}\right)(\text{Cross Sectional Area})(\Delta x)(\text{porosity})$
 $= C_B A \phi \Delta x|_t$

Leaving at time $t+\Delta t$:
 $= C_B A \phi \Delta x|_{t+\Delta t}$

Entering by bulk flow:
 $= C_B v A \phi \Delta t|_x$

Leaving by bulk flow:
 $= C_B v A \phi \Delta t|_{x+\Delta x}$

Entering by longitudinal dispersion:
 $= -K_l A \phi \Delta t \left(\frac{\partial C_B}{\partial x}\right)|_x$

Entering by longitudinal dispersion:
 $= -K_l A \phi \Delta t \left(\frac{\partial C_B}{\partial x}\right)|_{x+\Delta x}$

No chemical reaction (first part)
 Disappearance = 0.0

Now, assume that:

$\hat{C} = \frac{abC}{1+bC}$, \hat{C} is the amount of adsorbed component, a and b are constants and C is the

Therefore:

Amount of absorbed in a specific volume of rock at time t: $A(1-\phi)\Delta x\rho_{rock}\hat{C}|_t$

Amount of absorbed in a specific volume of rock at time t+ Δt : $A(1-\phi)\Delta x\rho_{rock}\hat{C}|_{t+\Delta t}$

Substituting all the equations into general Material Balance equation gives:

$$[C_B A \phi \Delta x|_{t+\Delta t} - C_B A \phi \Delta x|_t] + (A(1-\phi)\Delta x\rho_{rock}\hat{C}|_{t+\Delta t} - A(1-\phi)\Delta x\rho_{rock}\hat{C}|_t) = [C_B v A \phi \Delta t|_x - C_B v A \phi \Delta t|_{x+\Delta x}] + K_l A \phi \Delta t \left(\frac{\partial C_B}{\partial x} \right)_{x+\Delta x} - K_l A \phi \Delta t \left(\frac{\partial C_B}{\partial x} \right)_x$$

Dividing both sides by $A\phi\Delta x\Delta t$, eliminate the equal terms and using the limit approach gives:

$$A\phi\Delta x \left(\frac{C_B|_{t+\Delta t} - C_B|_t}{A\phi\Delta x\Delta t} \right) + A(1-\phi)\Delta x\rho_{rock} \left(\frac{\hat{C}|_{t+\Delta t} - \hat{C}|_t}{A\phi\Delta x\Delta t} \right) = v A \phi \Delta t \left(\frac{C_B|_x - C_B|_{x+\Delta x}}{A\phi\Delta x\Delta t} \right) + K_l A \phi \left(\frac{\frac{\partial C_B}{\partial x}|_x - \frac{\partial C_B}{\partial x}|_{x+\Delta x}}{A\phi\Delta x\Delta t} \right)$$

$$\lim_{\Delta t \rightarrow 0} \left(\frac{C_B|_{t+\Delta t} - C_B|_t}{\Delta t} \right) = \frac{\partial C_B}{\partial t} \quad \text{and} \quad \lim_{\Delta x \rightarrow 0.0} \left(\frac{\frac{\partial C_B}{\partial x}|_x - \frac{\partial C_B}{\partial x}|_{x+\Delta x}}{\Delta x} \right) = \frac{\partial^2 C_B}{\partial x^2}$$

Now, the general equation for the dispersion with chemical reaction and adsorption becomes as follow:

$$\frac{\partial C_B}{\partial t} + \left(\frac{1-\phi}{\phi} \right) \rho_{rock} \frac{\partial \hat{C}}{\partial t} = -v \frac{\partial C_B}{\partial x} + K_l \frac{\partial^2 C_B}{\partial x^2}$$

Substituting $v = \frac{q}{A\phi}$ and rearranging equation:

$$K_l \frac{\partial^2 C_B}{\partial x^2} - \frac{q}{A\phi} \frac{\partial C_B}{\partial x} = \frac{\partial C_B}{\partial t} + \frac{(1-\phi)}{\phi} \rho_{rock} \frac{\partial \hat{C}}{\partial t} \quad \text{Eq.1}$$

The last equation is exactly same as the equation, which is in the SPE paper¹.

2. With chemical reaction

Disappearance by reaction: (Negative sign)

$$-r_B = \frac{dC_B}{dt} = KC_B^n, \text{ (for first order, } n=1\text{)}$$

Change in mass of B due to the reaction:

$$= KC_B (A\phi)\Delta x\Delta t$$

Substituting this additional term into general Material Balance equation gives:

$$\frac{\partial C_B}{\partial t} + KC_B = -v \frac{\partial C_B}{\partial x} + K_l \frac{\partial^2 C_B}{\partial x^2} - \frac{(1-\phi)}{\phi} \rho_{rock} \frac{\partial \hat{C}}{\partial t}$$

Substituting $v = \frac{q}{A\phi}$ and rearranging equation:

$$K_l \frac{\partial^2 C_B}{\partial x^2} - \frac{q}{A\phi} \frac{\partial C_B}{\partial x} = \frac{\partial C_B}{\partial t} + \frac{(1-\phi)}{\phi} \rho_{rock} \frac{\partial \hat{C}}{\partial t} + KC_B$$

This equation can be rewritten in the following form:

$$K_l \frac{\partial^2 C_B}{\partial x^2} - \frac{q}{A\phi} \frac{\partial C_B}{\partial x} = \frac{\partial C_B}{\partial t} + \frac{(1-\phi)}{\phi} \rho_{rock} \frac{\partial \hat{C}}{\partial t} + KC_B \quad \text{Eq.2}$$

This is also the same as the equation, which is in the SPE paper¹ except that it is including one more term for chemical reaction. (see also reference 4)

3. Solution to the chemical flow equation in porous media with dispersion, adsorption and chemical reaction

According to the literature, the Langmuir chemical-adsorption model can be described as follows.

$$\frac{\partial \hat{C}}{\partial t} = K_1 \left(1 - \frac{\hat{C}}{\hat{C}^*} \right) C_B - K_2 \left(\frac{\hat{C}}{\hat{C}^*} \right) \quad \text{Eq.3}$$

The solution to Eq.3 for a constant C , \hat{C} at $t=0$, is given by:

$$\hat{C} = \frac{K_1 \hat{C}^*}{C_B K_1 + K_2} \left(1 - e^{-\left(\frac{(C_B K_1 + K_2)t}{\hat{C}^*} \right)} \right) C_B$$

As t tends to zero, this equation reduces to the Langmuir equilibrium adsorption isotherm:

$$\hat{C} = \frac{K_1 \hat{C}^*}{C_B K_1 + K_2} \left(1 - e^{-\left(\frac{(C_B K_1 + K_2)t}{\hat{C}^*} \right)} \right) C_B \quad \xrightarrow{t \rightarrow 0.0} \quad \hat{C} = \frac{abC_B}{1 + bC_B}$$

$t \rightarrow 0.0$

Where:

$$ab = \left(\frac{K_1}{K_2} \right) \hat{C}^*$$

$$b = \left(\frac{K_1}{K_2} \right)$$

Differentiating the above equation with respect to C and substituting the expression into the general equation must solve the general dispersion/adsorption equation to calculate the concentrations in both aqueous and solid phases. (Eq.1)

$$\frac{\partial \hat{C}}{\partial t} = \frac{\partial \hat{C}}{\partial C_B} \frac{\partial C_B}{\partial t} = \left(\frac{ab}{1 + bC_B} \right)$$

Therefore, general equation becomes:

$$K_l \frac{\partial^2 C_B}{\partial x^2} - \left(\frac{q}{A\phi} \right) \frac{\partial C_B}{\partial x} = \left(1 + \frac{(1-\phi)\rho_{rock}ab}{\phi(1+bC_B)^2} \right) \frac{\partial C_B}{\partial t}$$

To solve this equation we need initial and boundary conditions. However, before that, simplification using the dimensionless groups is an issue. To simplifying this equation we have to use the original equation, Eq=?). Defining dimensionless variables:

$$x_D = \frac{A\phi x}{V_p} = \frac{x}{L}; \quad I = \frac{qt}{V_p}; \quad C_D = \frac{C_B}{C_0}; \quad \hat{C}_D = \frac{\hat{C}}{\hat{C}^*}$$

Using the definition of the above dimensionless groups:

$$\frac{C_0 A \phi}{L V_p} \frac{\partial^2 C_D}{\partial x_D^2} = \frac{\partial^2 C_B}{\partial x^2}$$

$$\frac{C_0 A \phi}{V_p} \frac{\partial C_D}{\partial x_D} = \frac{\partial C_B}{\partial x}$$

$$\frac{C_0 q}{V_p} \frac{\partial C_D}{\partial I} = \frac{\partial C_B}{\partial t}$$

$$\hat{C}_D = \frac{\hat{C}}{\hat{C}^*} \Rightarrow \partial \hat{C}_D = \frac{1}{\hat{C}^*} \partial \hat{C}$$

$$\Rightarrow \frac{\partial \hat{C}_D}{\partial I} = \frac{V_p}{q \hat{C}^*} \frac{\partial \hat{C}}{\partial t}$$

$$I = \frac{qt}{V_p} \Rightarrow \partial I = \frac{q}{V_p} \partial t$$

Also,

$$\left. \begin{aligned}
& \left\{ \begin{aligned}
\hat{C}_D = \frac{\hat{C}}{\hat{C}^*} \Rightarrow \partial \hat{C}_D = \frac{1}{\hat{C}^*} \partial \hat{C} \\
I = \frac{qt}{V_P} \Rightarrow \partial I = \frac{q}{V_P} \partial t
\end{aligned} \right\} \Rightarrow \frac{\partial \hat{C}_D}{\partial I} = \frac{V_P}{q \hat{C}^*} \frac{\partial \hat{C}}{\partial t} \\
& \left\{ \begin{aligned}
\hat{C} = \frac{abC_B}{1+bC_B} \\
C_D = \frac{C_B}{C_0}
\end{aligned} \right\} \Rightarrow \frac{\partial \hat{C}}{\partial t} = \frac{\partial \hat{C}}{\partial C_B} \frac{\partial C_B}{\partial t} = \frac{ab}{(1+bC_B)^2} \frac{\partial C_B}{\partial t} \\
& \left\{ \begin{aligned}
I = \frac{qt}{V_P} \\
C_D = \frac{C_B}{C_0}
\end{aligned} \right\} \Rightarrow \frac{\partial C_B}{\partial t} = \frac{qC_0}{V_P} \frac{\partial C_D}{\partial I} \\
& \left. \begin{aligned}
& \Rightarrow \frac{\partial \hat{C}}{\partial t} = \frac{ab}{(1+bC_B)^2} \frac{qC_0}{V_P} \frac{\partial C_D}{\partial I} \\
& \frac{\partial \hat{C}_D}{\partial I} = \frac{V_P}{q \hat{C}^*} \frac{ab}{(1+bC_B)^2} \frac{qC_0}{V_P} \frac{\partial C_D}{\partial I}
\end{aligned} \right\}
\end{aligned}$$

Substituting this one in the equation (?) gives:

$$K_l \frac{C_0 A \phi}{LV_P} \frac{\partial^2 C_D}{\partial x_D^2} - \left(\frac{q}{A \phi} \right) \frac{C_0 A \phi}{V_P} \frac{\partial C_D}{\partial x_D} = \frac{C_0 q}{V_P} \frac{\partial C_D}{\partial I} + \frac{(1-\phi)}{\phi} \frac{q \hat{C}^*}{V_P} \rho_{rock} \frac{V_P}{q \hat{C}^*} \frac{ab}{(1+bC_B)^2} \frac{qC_0}{V_P} \frac{\partial C_D}{\partial I}$$

According to the literature, longitudinal dispersion can be rewritten in to the following form:

$$K_l = \lambda \frac{q}{A \phi} = \lambda u$$

$$C_B = C_0 C_D$$

Substituting this term in the above equation and simplifying that gives:

$$\lambda \frac{q}{A \phi} \frac{C_0 A \phi}{LV_P} \frac{\partial^2 C_D}{\partial x_D^2} - \left(\frac{q}{A \phi} \right) \frac{C_0 A \phi}{V_P} \frac{\partial C_D}{\partial x_D} = \frac{C_0 q}{V_P} \frac{\partial C_D}{\partial I} + \frac{(1-\phi)}{\phi} \rho_{rock} \frac{q \hat{C}^*}{V_P} \frac{V_P}{q \hat{C}^*} \frac{ab}{(1+bC_B)^2} \frac{qC_0}{V_P} \frac{\partial C_D}{\partial I}$$

$$\frac{\lambda}{L} \frac{\partial^2 C_D}{\partial x_D^2} - \frac{\partial C_D}{\partial x_D} = \frac{\partial C_D}{\partial I} + \frac{(1-\phi)}{\phi} \rho_{rock} \frac{ab}{(1+bC_0 C_D)^2} \frac{\partial C_D}{\partial I}$$

or

$$\frac{\lambda}{L} \frac{\partial^2 C_D}{\partial x_D^2} - \frac{\partial C_D}{\partial x_D} = \left[1 + \left(\frac{(1-\phi)}{\phi} \rho_{rock} \frac{ab}{(1+bC_0 C_D)^2} \right) \right] \frac{\partial C_D}{\partial I}$$

Eq.4

Now, equation-4 is the simple form of chemical flow in the porous media including both adsorption and dispersion. However, chemical reaction is not included for this stage.

If adsorption is negligible, equation reduced to the well-known dispersion equation. A series of initial and boundary conditions could apply to solve the simple form of the dispersion equation. Due to this fact that the solution for such kind of non-homogenous partial differential equation is time consuming, I will refer to some numerical and analytical solutions that are prepared for specific cases.

It is good to mention that, the dispersion and Langmuir rate-controlled adsorption behavior of chemical in porous media is controlled by a set of four dimensionless groups:

$$\text{Dispersion group, } N_D = \frac{\lambda}{L}$$

$$\text{Adsorptive capacity group, } N_A = \frac{\rho_{rock}(1-\phi)\hat{C}}{\phi C_0}$$

$$\text{Flow rate group, } N_q = \frac{C_0 K_1 V_P}{q \hat{C}^*}$$

$$\text{Kinetic rate group, } N_K = \frac{K_2}{K_1 C_0}$$

Or

$$\text{Adsorptive capacity group } N_{Ae} = \left[1 + \left(\frac{(1-\phi)}{\phi} \rho_{rock} \frac{ab}{(1+bC_0C_D)^2} \right) \right]$$

It should be noted that N_{Ae} is zero in the absence of adsorption since $a=0$ and $C^*=0$.

Analytical solution

For a finite system, the initial and boundary conditions to solve the transport equations are:

$$C(x, 0) = 0 \quad 0 \leq x \leq L$$

$$\hat{C}(x, 0) = 0 \quad 0 \leq x \leq L$$

$$\left(C - \lambda \frac{\partial C}{\partial x} \right)_{x=0} = C_0 \quad 0 < t$$

$$\left(\frac{\partial C}{\partial x} \right)_{x=L} = 0 \quad t > 0$$

Note: In our case, $C=C_B$ and we need to transfer these conditions to the dimensionless groups. Lapidus and Amundson considered flow through a semi-infinite medium and linear equilibrium adsorption such that:

$$\hat{C} = aC$$

This is the special case of Langmuir equation where $b=0$. Solution for effluent concentration is given by:

$$\frac{C}{C_0} = 0.5 \operatorname{erf} \left(\frac{1 - I/\theta}{2\sqrt{I\lambda/\theta L}} \right) - \left[\frac{\sqrt{I\lambda}}{\pi L \theta} \frac{\exp \left[-\frac{\theta L}{4I\lambda} \left(1 - \frac{I}{\theta} \right)^2 \right]}{1 + \frac{I}{\theta}} \right] \left[1 - 6 \frac{\frac{I}{\theta}}{1 + \frac{I}{\theta}} - \frac{2 \left(\frac{I}{\theta} \right)^2}{\left(1 + \frac{I}{\theta} \right)^2} \right]$$

Where:

$$\theta = 1 + \frac{\rho_{rock}(1 - \phi)a}{\phi}$$

References:

A.Satter, Y.M.Shum, W.T. Adams and L.A.Davis: "Chemical transport in porous media with dispersion and rate-controlled adsorption" Society of Petroleum Engineers (1980).

W.Fred Ramirez, Patrick J.Shuler, Francous Friedman: "Convection, Dispersion, and adsorption of surfactants in porous media" Society of Petroleum Engineers (1980).

Octave Levenspiel: "Chemical reaction engineering" Johnwiley&sons, Newyork, 1999
http://www.water.hut.fi/wr/kurssit/yhd-12.126/oppimateriaali/ads_1_e.htm