# MATHEMATICAL MODELING OF MASS TRANSFER RATE DURING INJECTION OF CO2 INTO WATER AND SURFACTANT SOLUTION

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## Abstract

The present study aimed at modeling rate of carbon dioxide ($CO_2$) transfer during its injection into water and surfactant solution at different operating conditions. Partial differential equation was used to describe rate of mass transfer during the process and Finite Difference Method (FDM) was used to solve the developed model subject to boundary and initial conditions. The results of the modeling show that there is a good agreement between the FDM solution and experimental result for the three liquids reported in the literature. FDM also gave better result when compared with Laplace-based solution technique that under predicted the experimental result. The model developed can be used for monitoring of $CO_2$ transfer rate into liquids and can be extended to different characteristic distance and time beyond the limit of experimental condition.

*Keywords:* Diffusion; transfer rate; pressure decline; finite difference and Carbon dioxide.

## 1. Introduction

One of the major  environmental challenges facing the whole world is Global warming and there is a broad consensus from scientific community  that global warming results primarily from increased concentrations of atmospheric greenhouse gases, especially $CO_2$ emitted largely from the burning of fossil fuels [1]. Increased anthropogenic emissions have raised the atmospheric concentration of $CO_2$ from 280 ppmv during pre-industrial times to 380 parts per million by volume (ppmv) today, and, if unabated, are projected to increase to 1100 ppmv by 2100 [2]. Research into Reduction or control of $CO_2$  in Atmosphere is ongoing and it was discovered that $CO_2$ can be stored in Oil and gas Reservoir, injection into Coal-bed Methane formation, used to Enhanced Oil production, injected into aquifer and deep sea. The major variables that affect $CO_2$ injection are diffusion rate, solubility, operating condition of pressure and temperature and composition of both phases [3].

Molecular diffusion is one of the important mechanisms that affect performance of gas-liquid binary system either as gas injection to aquifer or as solvent for oil recovery [4]. The rate of mass transfer caused by molecular diffusion is determined by diffusion coefficient of gas phase to liquid phase. Diffusion process is one of the key processes that assist the control measure to reduce $CO_2$ in the atmosphere; it also describes the behavior and estimation of the gas in liquid phase [5].

King *et al.* [6] worked on extension of different gases diffusion coefficient data in pure water to sea water system and estimated the accuracy of the model by comparing their measurement using semi-empirical relationships. For water air system these estimates agree with the corresponding measured diffusivities to 17%, with a maximum difference of 36 %. The uncertainty associated with estimating the molecular diffusion coefficient of a gas in seawater from the pure water was noticed and corrected for under variable conditions, so that the estimates made using the semi-empirical relationship can be used with reasonable confidence where measurements have not been made.

Frank *et al.* [7] developed a model for predicting diffusion coefficient and viscosity for binary system based on experimental data for carbon dioxide + water, carbon dioxide + methanol, ammonia + water, and ammonia + methanol. The results from the model developed were correlated using Arrhenius-type equations and was compared with literature data. The correlation developed have a relationship between the diffusion coefficient and the viscosity as functions of temperature and can therefore be very useful for extrapolating known diffusion coefficients to other temperatures by using liquid viscosities, which can be measured more easily. The correlation reported show typical error up to 30% for estimating diffusion coefficients in diluted systems when the result was compared with widely used published models and the error trend could be much if the model is used for extrapolation beyond values used in deve-loping the model.

Mutoru *et al.* [8] also developed an empirical model for calculating infinite dilution diffusion coefficients and composition based Fickian diffusion coefficient for carbon dioxide and water mixtures based on published data extracted from the literature. The model takes into account temperature dependence of the dipole moment of water and polarizability of $CO_2$, and fits experimental $CO_2/H_2O$ data at low and high pressures with an accuracy of 4.9% on the average. The proposed model also accurately predicts infinite dilution diffusion coefficients for other binary water mixtures where solute polarizability is close to that of $CO_2$, such as $CH_4$, $C_2H_6$, $C_3H_8$, and $H_2S$.

Carbon (IV) oxide usefulness in geothermal reservoir as a function of its injectivity was analyzed by Salimi *et al.* [9]. They simulated effectiveness of $CO_2$ injection in geothermal reservoir using Negative Saturation (NEGSAT) solution approach for Non-isothermal compo-sitional flow. This approach was used to study the synergy established between geothermal energy production and subsurface $CO_2$ storage. Mixed- $CO_2$ injection was simulated for geo-thermal reservoir taking into account effect of capillary Pressure and gravity. The result of their simulation show that small amount of injected $CO_2$ will reduce the maximum amount of heat extraction significantly because $CO_2$ breakthrough always occurs earlier than cold-water breakthrough. However, increasing the amount of injected $CO_2$ will not always reduce the maximum amount of heat extraction and $CO_2$ storage monotonically except in heterogeneous cases where formation of a $CO_2$-rich phase leads to a larger amount of heat extraction

Cinar *et al.* [10] investigated flow regimes of $CO_2$ injection into deep aquifer under the influence gravitational, density, viscous, and capillary effects. Quasi 2D experiments APE performed in a vertical glass bead pack in the parameter range of interest for $CO_2$ sequestration in deep aquifers and the behavior of the flow was analyzed using Bond number, Viscosity ratio and Capillary number. The work was validated with percolation theory and published models. The outcome of the investigation show that when both viscosity ratio and bond number are less than one the percolation pattern is of finite extent because of the presence of viscous forces or gravitational forces that lead to a compact macroscopic flow in its wake but this wasn't the same with other models due to absence of gravity effect. Estimate based on percolation theory regarding the flow characteristics appear to agree qualitatively well with experiments. The work suffer two main shortcomings: capillary and Bond numbers determined are slightly larger than those in practical situations and neglect of diffusion despite that consideration of (multiphase) flow dynamics.

In their work, Eke *et al.* [3], introduced surface and subsurface modeling into $CO_2$ mixing and injection into reservoir. Aspen HYSYS software was used for surface process simulation and PIPESIM was used for flow model in order to inject the $CO_2$/brine into the reservoir under different injection strategy. They recommended $CO_2$/Brine surface mixing as the best strategy because it enhanced sequestration of $CO_2$ into geological formation. They concluded that the following conditions should be closely monitored and carefully explore before solubility and diffusion of $CO_2$/Brine are adopted; the operating temperature and pressure of the vessel which have a strong link with $CO_2$/Brine solubility and also phase behavior.

In considering composition effect in modeling diffusion coefficient for $CO_2/H_2O$ mixtures, it was revealed that there was a competing effect of temperature and pressure on diffusion coefficient. Increase in temperature increases diffusion coefficient in both the $CO_2$-rich and water rich phases, increasing pressure noticeably decreases diffusion coefficient in the $CO_2$-rich phase. This large pressure effect is mutually coupled with that of increased $CO_2$ composition. Moreover, the extent of intermolecular associations (which are functions of temperature,

pressure, and composition) affect diffusion coefficient. These composition-based results imply that greatly varying rates of diffusion should be expected for specific composition, temperature, and pressure conditions of a given oil reservoir or saline aquifer.

Farajzadeh et al. [11], studied the mass transfer of $CO_2$ into water and aqueous solution of Sodium Dodeecyl Sulphate (SDS) using a PVT cell at different initial pressure and constant temperature. The experiment was described by Fick's and Henry's law; the work experimentally described the effect of pressure on diffusivity of $CO_2$ into water and SDS. It was noticed that Fick's model could not describe the rate of $CO_2$ injection into aquifer satisfactorily. The trend of predicted result was far from experimental data and consequently, the level of Fick's model was low. The reason why Laplace-based predicted result failed could be analytical solution technique used (Laplace-based technique) to solve the Fick's model. Therefore, this work is aimed at investigating the suitability and predictability of Fick's diffusion model for describing the rate of mass transfer during $CO_2$ injection process using finite-difference method (FDM) [11].

## 2. Methodology

This work involved solving Fick's law that was used for the modeling of transfer into water and surfactant solution using another solution technique called Finite Difference Method (FDM). This solution technique is needed because the earlier analytical solution technique (Laplace based technique) did not predict the experimental work of Farajzadeh et al. [11]. Mathematical model using partial differential equation was developed and the detailed derivation is shown in section below:

### 2.1 Governing Equation

Mathematical model for mass transfer rate during injection into water and surfactant solution was developed from the diffusion of the gas through liquid phase in PVT cell. Mass conservation of diffusion in slab (rectangular shape) geometry of PVT system is accomplished by identifying the simplifying assumptions, defining appropriate initial and boundary conditions. The following assumptions were made: one-dimensional mass transfer occurs; and the process is isothermal. External resistance to mass transfer in the system is neglected. The governing equation is obtained from interpretation of Figure 1 [11]:

Statement of species conservation is:

$$Time\ rate\ of\ change\ of\ mass\ in\ the\ PVT\ cell =$$
$$influx\ of\ mass\ into\ PVT\ cell - outflux\ of\ mass\ from\ PV \tag{1}$$

$$Time\ rate\ of\ change\ of\ mass\ in\ the\ PVT\ cell = \frac{\partial(c)Az}{\partial t} \tag{2}$$

$$Influx\ of\ mass\ into\ PVT\ cell = j \tag{3}$$

$$Outflux\ of\ mass\ from\ PVT\ cell = j + \frac{\partial j}{\partial z}Az \tag{4}$$

$$\frac{\partial(c)Az}{\partial t} = -\left(+\frac{\partial j}{\partial z}Az\right) \tag{5}$$

$$\frac{\partial c}{\partial t} = -\frac{\partial j}{\partial z} \tag{6}$$

Recall, first Fick's law:

$$J = -D\frac{\partial c}{\partial z} \tag{7}$$

Substitute 7 into 6 and obtain:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}D\frac{\partial c}{\partial z} \tag{8}$$

Equation 8 is partial differential equation (diffusion model) describing rate of mass transfer during injection of $CO_2$ into liquid(s) which could be applicable to oil, water or even surfactant solution. But concentration with respect to process time and space is difficult to measure; however, concentration of the gas is transformed to measurable quantity using Henry equation which now gives a new equation:

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial z} D \frac{\partial P}{\partial z} = \quad \frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial z^2} \tag{9}$$

## 2.2. Method of Solution for Diffusion Model

The model for predicting rate of mass transfer during injection of gas into water and surfactant solution in PVT cell is partial differential equation and initial-boundary value problem; which is solved by finite difference approximation. Initial and boundary conditions are:

Initial condition:

$$P(t = 0, z) = P_O \tag{10}$$

Boundary conditions are:

$$P(z = 0, t) = P_e \tag{11}$$

$$P(z = L, t) = P_e \tag{12}$$

The diffusivity values of water, surfactant and surfactant+water used for this study was extracted from the experimental work of Farajzadeh et al. [11]

## 2.3 Numerical Solution Technique (Finite Difference)

Explicit finite difference method is used in this study and equation 9 is transformed into difference equation by dividing the domain of solution to a grid of points in the form of mesh and the derivatives are expressed along each mesh point referred to as a node. Knowing the dependent variable (injection pressure) at each node initially and it is approximated for the next time step until the final step. The basis for the finite difference representation of the mesh points is written as :

$$Z_i = i\delta z \quad for \ i = 0,1,2 \dots \dots \dots m \tag{13}$$

$$T_j = j\delta t \quad for \ j = 0,1,2 \dots \dots \dots n \tag{14}$$

where $\delta z$ and $\delta t$ represent grid sizes in the x and t directions respectively and subscripts denote the location of the dependent variable under consideration. The finite difference representations of various derivatives that appear in the governing equation are derived from Taylor's series expansion:

$$P_{i,j+1} = P_{i,j} + \delta t (\frac{\partial P}{\partial t})_{i,j} \tag{15}$$

On rearrangement of Taylor's series, we have:

$$\frac{\partial P}{\partial t} = \frac{P_{i,j+1} - P_{i,j}}{\delta t} \tag{16}$$

Similarly, apply Taylor's series expansion in the z (space) direction and x direction (backward difference) keeping t constant:

$$P_{i+1,j} = P_{i,j} + \delta z (\frac{\partial P}{\partial z})_{i,j} + \frac{(\partial z)^2}{2} \frac{\partial^2 P}{\partial z^2} \tag{17a}$$

$$P_{i-1,j} = P_{i,j} - \delta x (\frac{\partial P}{\partial z})_{i,j} + \frac{(\partial z)^2}{2} (\frac{\partial^2 P}{\partial z^2}) \tag{17b}$$

Add equation 17a and 17b gives:

$$\frac{\partial^2 P}{\partial z^2} = \frac{P_{i,-1} - 2 P_{i,j} + P_{i+1,j}}{(\delta z)^2} \tag{18}$$

Equate (16) and (18) represent governing equation written as:

$$P_{i,j+1} = P_{i,j} + r[P_{i-1,j} - 2P_{ij} + P_{i+1,j}] \tag{19}$$

where $r = \frac{D_{eff} \delta t}{(\delta z)^2}$

At $z = 0, then, i = 0$, $P_{0,j+1} = P_{0,j} + r[P_{-1,j} - 2P_{0,j} + P_{+1,j}]$ (20)

Then, calculate $P_{-1,j}$ (pseudo pressure at external mesh point) which can be removed by representing finite difference in term of central difference approximation which turn the final equation to:

$$P_{0,j+1} = P_{0,j} + 2r\left[P_{1,j} - P_{0\,j}(1 + \delta z)\right] \qquad (21)$$

The resulting equations from the numerical analysis was implemented in MATLAB by developing codes in it so as to obtain different pressure values at different process periods of time and characteristic space in PVT cell during enhanced oil recovery process in reservoir subject to ($\frac{D_{eff)}\,\delta t}{\delta z} \leq \frac{1}{2}$) for stability and convergence of the solution. Then, statistical interpretation of the finite-difference, Laplace approach and experimental data was carried out in standard program in excel Microsoft spreadsheet. The agreement between predicted and experimental results was further evaluated using Average Percentage Error (APE) and Average Absolute Percentage Error (AAPE) gotten from the work of Hammatti and Kharrat [12].

## 3. Results and Discussion

### 3.1 Prediction of $CO_2$ Gas Transfer Rate in Water, SDS+NaCl and SDS

The quantification of the mass transfer rate was based on the measurement of gas pressure from pressure-time graphs as indicated in the Figure 1. The predicted results in Figure 1, using initial pressure of 11.85 psi, for carbon dioxide transfer in water, revealed that about 3.5 psi pressure was declined during the process. The predicted result in the same Figure shows that the rate of pressure declination was rapid at the beginning of the process and consequently rate of mass transfer during the process was rapid. The behavior of predicted data is similar to previous work [11]. It was also noticed from the figure that rate of pressure depletion was slow after 20hrs.
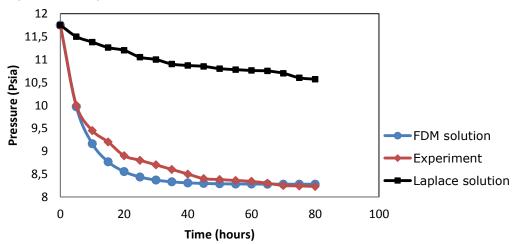


Figure 1 Comprison of new solution technique with Laplace solution

From the analysis of result of the model using FDM, Laplace method of solution may not be suitable for solution of diffusion equation. It was noticed that total declination of pressure using Laplace approach was small compared to FMD and experimental approach. Again, equilibrium pressure depletion point for Laplace approach was 10.5psi. However, FMD solution approached equilibrium point at 8.3psia. The equilibrium point for FMD is closer to experimental equilibrium point.

With normalized pressure profile, the predicted transfer rate into pure water, as indicated in figure 2(i), for initial stage of the process was significant in 10hrs. It was observed that 50 % of transfer was made between 1-10hrs. The latter stage showed that the predicted pressure decline rate in Figure 2(i) was slow with less than 15% pressure declination between 35-45hrs. The same predicted pressure declination profile was observed in Farajzadeh et al. [11].
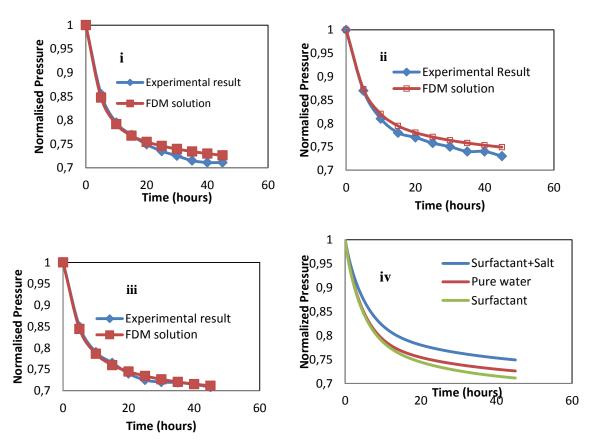
Figure 2 Comparison of experimental result and FDM model for pure water, SDS + NaCl solution and SDS solution

Diffusion model (partial differential equation) was equally used to predict rate of normalized pressure depletion at different period of process time when carbon dioxide is injected into Surfactant + Salt (SDS+NaCl) solution as indicated in Figure 2(ii). It was observed that the total normalized pressure declined was 0.28. The predicted curve in Figure 2(ii) revealed that as the process time progresses the rate of pressure is declining. It was observed that predicted data attained equilibrium point at 45 hrs and it was equally noticed that experimental normalized pressure depletion rate was attained equilibrium point (pressure declination rate is constant) at the same period of predicted data. The same trend was noticed in the case of prediction of rate for carbon dioxide transfer into Surfactant solution (SDS) which is represented in Figure 2(iii).

In all the three cases considered for carbon dioxide diffusion into water, surfactant and surfactant+ salt solution, the predicted curves followed an exponential trend in all the Figures 2(i-iii) for rate of normalized pressure decline which is combined and represented in Figure 2(iv).

### 3.2. Prediction of $CO_2$ Gas Transfer Rate in Water Phase at Different Lengths (Space)

The sudden change in pressure profile in Figure 3 revealed the behavior of the process at the initial stage of the diffusion process. It was noticed from the predicted curves that the dynamics of the pressure injected could be predicted using finite-difference technique. Consequently, start-up and shut-down dynamics of the process could be predicted using figure 3. Experimental work could only describe rate of pressure declination with time but it could not predict rate of pressure declination at different space (characteristic distance).

The same figure predicted the time the process will take to attain stability. It was visible from the figure that the process was unstable at initial stage of process. The initial pressure was 11.85psi but it was observed that the pressure dropped to10.2psi before it becomes

normal according to predicted curve in Figure 3. However, the process becomes stabilized at the first 30 minutes as it was demonstrated in the Figure. The same phenomenon was reported in in Farajzadeh *et al.* [13]. The phenomenon observed in the figure predicted the fluctuation in pressure injection at the beginning of the process. However, experimental results could not describe these imbalances. It was further observed that rate of pressure depletion at space 2 was the best and consequently rate of mass transfer during the injection at the characteristic length is satisfactory.
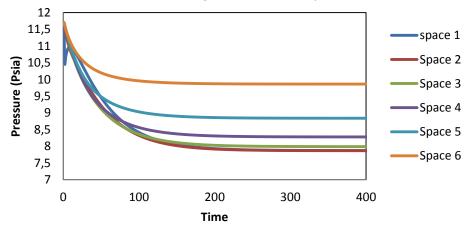


Figure 3 Description of Mass transfer of Carbon Dioxide
at different distance in water

## 3.3. Comparative Study on Predicted and Experimental Results for Pressure Decline Rate

The comparative analysis between experimental and predicted normalized pressure decline rate during carbon dioxide injection into water, surfactant and surfactant + salt solution at different periods of process time was analyzed with the use of correlation coefficient ($R^2$ value), Average Percentage Error (APE) and Absolute Average Percentage Error (AAPE) tabulated in Table 1. The APE for water, surfactant, surfactant + salt, FDM solution and Laplace based solution are 0.102, 0.173, 1.526, 0.165 and -24.858 respectively. The trend when consider AAPE is similar to that of APE for the predicted model with the exception of Laplace based prediction that underpredicted the experimental result by 24.858 percent. According to Azoubel and Murr [14], value of AAPE and APE less than or equal to 10% indicates good prediction of experimental data and the lower the percentage the better the model for predictive purpose. This indicates that the model, with the aid of FDM, for carbodioxide transfer rate during the process predicts satisfactory. The correlation coefficient of the predicted results for carbon dioxide diffusion into water, surfactant, surfactant + salt, FDM solution and laplace based solution gave a value of 0.9927, 0.9974, 0.9999, 0.9683 and 0.8505 respectively. The closer the value to 1 the better the prediction and it was noticed that all the prediction produced in this work APE very close to 1.

Table 1 Statistical Interpretation of Model

|  | APE | AAAPE | $R^2$ Value |
|---|---|---|---|
| Surfactant + NaCl | 1.5256 | 1.5256 | 0.999 |
| Water | 0.102 | 0.102 | 0.9927 |
| Surfactant | 0.173 | 0.173 | 0.9974 |
| New Solution | 0.1656 | 0.1821 | 0.9683 |
| Previous approach | -24.858 | 24.858 | 0.8505 |

## 4. Conclusion

At the end of this modeling work the following deductions were made:

- It was established that Fick's law is a good model that can be used for the prediction of diffusion of gas into liquid irrespective of the fluid type.
- FDM solution technique is a better tool for solving partial differential equation related to diffusion especially when the result from FDM was compared with result from Laplace based method.
- There is a close agreement between the experimental and predicted result for all the experimental result reported in the literature used for this study. The correlation coefficient of the predicted results for carbon dioxide diffusion into water, surfactant, surfactant+salt, FDM solution and Laplace based solution gave a value of 0.9927, 0.9974, 0.9999, 0.9683 and 0.8505 respectively while APE and AAPE value is less than 10%.
- The model developed can be used to monitor diffusion of $CO_2$ into liquid at given condition and can be extrapolated to space and time not specified by the experimental result.

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