DYNAMIC AND STATIC CO$_2$ MASS TRANSFER PROCESSES IN BULK HEAVY OIL AND HEAVY OIL SATURATED POROUS MEDIA

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Ali Kavousi, candidate for the degree of Doctor of Philosophy in Petroleum Systems Engineering, has presented a thesis titled, *Dynamic and Static CO₂ Mass Transfer Processes in Bulk Heavy Oil and Heavy Oil Saturated Porous Media*, in an oral examination held on April 4, 2014. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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Abstract

In the petroleum industry, the contribution of solvents to the production of oil has become more cardinal, as production from the reservoirs have advanced from primary oil production to secondary and tertiary methods. Vapour extraction (VAPEX), CO$_2$ flooding, CO$_2$ Huff-and-Puff are some of the solvent based approaches used in the industry to enhance oil recovery performance. These methods involve the injection of a vaporized solvent into the reservoir in order to reduce the viscosity of the oil and increase the oil mobility. The main mechanism that contributes in the solvent-based enhanced oil recovery method is the mass transfer from the solvent to the oil phase. Hence, it is essential to have deep knowledge about the interactions and mass transfers that occur between the solvents and oil in the solvent-EOR processes.

The primary objective of this research is to identify the main processes governing the interfacial mass transfer of CO$_2$ into heavy oil in the bulk phase under static and dynamic conditions. This study commenced with pressure decay experiments at static oil condition, where CO$_2$ was brought in contact with two different types of oil samples. It then continued by using a reactor (PARR-4560) to investigate the influence of convection in the bulk heavy oil. Experiments were directed in the reactor, where a stirrer was implemented to make a semi flowing condition in the oil phase (i.e., dynamic condition). In these experiments, pressures of 1.73–4.48 MPa and temperature of 295–305 K for the oil samples with 5 and 20 Pa.s viscosities were selected as the operational conditions. Additionally, proper mathematical model defining the experiments for each condition were developed. The model describing the static condition was solved analytically to
obtain CO$_2$ diffusion coefficient; however, numerical approach was utilized under dynamic condition. PDETWO routine, a solver for systems of partial differential equations that uses normal differential equation integration, was implemented to solve the model and obtain the diffusion coefficient.

This thesis also proposes a novel experimental design for measuring CO$_2$ diffusion coefficient in porous media. A hollow sand pack model was improvised to simulate a well-bore area, when CO$_2$ and oil are in contact. In this model, CO$_2$ is in the inner space, and the heavy oil saturated sand is placed in the outer space of the model. Six experiments in pressure range of 1.73–4.48 MPa, and at temperature of 301 K for the oil samples with 5 and 20 Pa.s viscosities were operated. Once more, pressure decay method was used to measure the solubility of CO$_2$ in the oil saturated porous model. Besides, the proper mathematical model (i.e., cylindrical diffusion equation) along with the conditions that are in agreement with the physical condition of the model were developed. PDETWO solver was then employed to determine the diffusion coefficient in oil saturated porous model. Finally, the results of CO$_2$ solubility and diffusion coefficient under different operating condition were compared and analyzed with the data gathered in the bulk studies. Moreover, by using the data obtained from these experiments and the available data in the literature, a model for CO$_2$ solubility in heavy oil is proposed.
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Nomenclatures

\( a \)  
Acceleration, \([\text{m/s}^2]\)

\( c \)  
Concentration, \([\text{g/g}]\)

\( c_0 \)  
Concentration of the solvent in the oil at final pressure, \([\text{g/g}]\)

\( dx \)  
Differential element in x direction

\( dy \)  
Differential element in y direction

\( dz \)  
Differential element in z direction

\( D_0 \)  
Diffusion coefficient \([\text{m}^2/\text{s}]\)

\( D \)  
Diffusion coefficient \([\text{m}^2/\text{s}]\)

\( \text{erf} \)  
Error function

\( E_i \)  
Error value used in least square method

\( F \)  
Formation resistivity factor

\( h \)  
Height

\( J \)  
Diffusion flux \([\text{mol./m}^2.\text{s}]\)

\( m \)  
Mass \([\text{g}]\)

\( m_{gexp} \)  
Solvent mass measured experimentally, \([\text{g}]\)

\( m_{ganal} \)  
Solvent mass calculated analytically, \([\text{g}]\)

\( M \)  
Molecular weight of solvent, \([\text{g/mol}]\)

\( n \)  
Moles of solvent, \([\text{mol}]\)

\( l \)  
Height of oil column, \([\text{m}]\)

\( P \)  
Pressure, \([\text{psi}]\)
$P_{er}$  Peclet number in $r$ direction

$P_{el}$  Peclet number in $z$ direction

$P_i$  Initial Pressure, [psi]

$P_f$  Final Pressure, [psi]

$r$  Radius [m]

$R$  Universal gas constant, [MPa.cm$^3$/mol.k]

$S$  Summation of the error

$T$  Temperature [k]

$\tau$  Time, [s] and [min]

$t_D$  Dimensionless time

$V$  Oil volume, [cc]

$v$  Convective velocity, [m/s]

$\omega$  Rotational velocity, [rpm]

$\chi$  Vertical distance of oil column, [m]

$\chi_D$  Dimensionless length

$z$  Elevation [m]

$Z$  Compressibility factor

$Z_i$  Compressibility factor at initial pressure

$Z_f$  Compressibility factor at final pressure

$\mu$  Viscosity, [Pa.s]

$\Phi$  Porosity

$\theta$  Inclination [m]
Chapter 1

Introduction

1.1 Background

Conventional crude oil has played a significant role in supplying the world’s oil demand. However, with depleted conventional oil reservoirs, heavy oil and bitumen are now being considered as possible substitutes to help meet ever increasing demands. However, there are several barriers to the rapid growth of heavy oil, extra-heavy oil, and bitumen production (e.g., environmental impact, economical issues, etc.). Enhancing the recovery of heavy oil and bitumen is very challenging and remains an issue in ongoing research (Smith 1986; Shen et al., 1999; Pooladi-Darvish et al., 1999; Maini 2001; Firoozabadi 2001; Pitts et al., 2004, Miller 2006; Torabi 2012). The effective production of heavy oil and bitumen demands specific technological solutions that are economical and environmentally benign. Among all the recovery improvement methods, solvent-based processes, either flooding or Huff-n-Puff, attracted lots of interests to researchers and pioneers to find satisfying scenarios for heavy oil recovery (Butler 1993; Lim 1996; Sarma 1998; Das et al., 1998). However, this area of study needs more attention and manoeuvres to be completed. One of the common and widely implemented practices used to improve oil production involves using light hydrocarbon or CO₂ as a solvent to inject into the reservoir. The recovery efficiency of these processes depends on the development of favourable phase behaviour or mass transfer effects when the injected gas contacts the reservoir oil. Therefore, reliable measurements of the molecular diffusion
Coefficient and solvent solubility are urgent issues for designing solvent-based recovery processes in heavy oil reservoirs. Accurate determination of these parameters and their variations with process conditions would also assist in building a more robust reservoir simulation model that is able to predict reservoir behaviour.

1.2 Comprehensive review on heavy oil

Heavy oil and natural bitumen are oils separated by their high viscosity (i.e., resistance to flow) and high density (i.e., low API gravity). These attributes manifest the presence of up to 50 weight percent asphaltenes, very high molecular weight hydrocarbon molecules incorporating many heteroatoms in their lattices. Heavy oil and tar sand can’t be defined adequately or with any degree of accuracy by a single property. Both, on the other hand, can be redefined by the recovery method. Heavy oil is usually mobile in the reservoir, whereas tar sand bitumen is immobile in the deposit. Figure 1.1 depicts the behaviour of south Alberta heavy oil viscosity versus temperature.
Figure 1.1. Response of viscosity to the change of temperature for Alberta oils (Raicar and Proctor, 1984)
Conventional light crude oil has been plentifully accessible and has easily covered the world demand of energy until recent years. Since 2007, however, worldwide demand for crude oil has increased considerably, straining the supply of conventional oil. This demand has resulted in an increased motivation to find alternatives to conventional light crude oil. Heavy crude oil and natural bitumen are perhaps the most readily available alternatives that are able to meet short and long-term needs.

Light oil, medium oil, heavy oil and natural bitumen have profound differences according to volatilities of the constituent hydrocarbon fractions: paraffinic, naphthenic, and aromatic. When the light fractions are lost through natural processes after evolution from organic source materials, the oil becomes heavy, with a high proportion of asphaltic molecules, and with a substitution in the carbon network of heteroatoms, such as nitrogen, sulfur, and oxygen. Therefore, heavy oil, regardless of source, always contains heavy fractions, asphalts that consist of resins, asphaltenes, and preasphaltenes (i.e., the carbene-carboids) (Yen, 1984). An increase or decrease in the density and viscosity of oil depends on the proportion of asphaltic molecules in the heavy oil. Removal or reduction of asphaltene or preasphaltene drastically affects the rheological properties of oil and its aromaticity (Yen, 1984).

Several processes have contributed to creating heavy oil and natural bitumen. The oil in the first suggestion may be released from its source rock as immature oil. There is general agreement that immature oils account for a small percentage of the heavy oil (Larter, 2006). Generally, most of the heavy oils and natural bitumens are expelled from the source rock as light and medium oil and subsequently migrated to a trap. If the trap is later elevated into an oxidizing zone, water washing, bacterial degradation and
evaporation can convert the oil into heavy oil. The third proposition is that biodegradation can also occur at depth in subsurface reservoirs (Head, et al., 2003; Larter and et. al; 2003; Larter et. al; 2006). This explanation permits biodegradation to occur in any reservoir that has a water leg and has not been heated to more than 176° F. The controls on the biodegradation depend on local factors rather than basin-wide factors.

1.2.1 Heavy oil recovery methods

The vast heavy oil reserves available in various parts of the world are becoming increasingly important as a secure future energy source (Safinya, 2008). In fact, cumulative recovery totals to date from the heavy oil and natural bitumen reservoirs is a low percentage of the total reserves of heavy oil worldwide.

Realizing the heavy oil resource as a promising potential relies on the technologies that can be applied and implemented to improve oil recovery for a wide range of reservoir and oil-phase conditions. Such technologies also need to be comparatively benign from an environmental point of view. Heavy oil production has been increasing in recent years and is expected to increase further in the future because of expected supply shortfalls in conventional oil and an abundance of relatively large and known heavy oil reservoirs. Up to day, heavy oil production approaches available in the industry include primary recovery, water injection, cold production and thermal and non-thermal, solvent and chemicals enhanced oil recovery methods. Figure 1.2 shows the methods that could be used to recover different types of reservoir oils.
Figure 1.2. Recovery methods based on type of the hydrocarbon reserves
1.2.1.1 Primary production

Primary recovery techniques depend entirely on natural forces within the reservoir (i.e., reservoir pore pressure), and although they are broadly suitable to recover conventional crude oil, they are less applicable to recover heavy oil. That is why the primary recovery method is not normally used to recover heavy oil. However, in high temperature reservoirs that keep the heavy oil sufficiently fluid, the primary recovery method may undoubtedly be applicable. After a period of production, natural forces in reservoirs and the primary recovery method would leave a high percentage of oil in both conventional and heavy oil reservoirs. When dealing with heavy oil reservoirs, 90 percent or more of the original oil in place can be left in the reservoir after attempts at primary or cold production (Curtis et al., 2002).

1.2.1.2 Secondary Production (Waterflooding)

After the primary production period, the first choice for improving oil recovery would be waterflooding to the reservoir (Donald, et al., 1958). Waterflooding is a form of oil recovery wherein the energy required to move the oil from the reservoir rock into a production well is supplied from the surface by means of water injection and the induced pressure from the presence of additional water. Water injection is used to prevent low pressure in the reservoir. Injected water would occupy some of the reservoir pore space, thereby keeping the reservoir pressure and production rate in a consistent condition for a period of time. Waterfloods are essentially artificial water drives and, at one time, were considered a form of enhanced recovery.
1.2.1.3 Tertiary recovery

Tertiary recovery commences when primary, waterflooding and cold production approaches are unable to recover significant amounts of oil from reservoirs, but the oil can still be extracted profitably. In this condition, an economic evaluation of the extraction cost and the current price of crude oil will be the deciding factor for continuing production. When prices are high, previously unprofitable wells are brought back into production; when they are low, production is curtailed. An extra 5 to 15 percent of the reservoir’s oil would be recovered by implementing a proper approach of tertiary recovery. In general, the tertiary production approach includes two broad categories: thermal and non-thermal methods.

The thermal recovery approach used today can be classified in two groups: processes in which a hot fluid (e.g., steam) is injected into the reservoir and processes in which heat is generated within the reservoir itself (e.g., combustion processes). The former are usually the steam-based, whereas the latter are combustion processes, such as in-situ combustion or fireflooding. Thermal recovery processes also can be classified as thermal drives or stimulation treatments. A thermal poke, on one hand, reduces the viscosity of the fluid, and on the other hand, provides a force to increase the flow rate of the production wells. In thermal drives, fluid is injected continuously into a number of injection wells to displace oil and to obtain production from other wells. The pressure force necessary to keep the fluid injection also improves the driving forces (i.e., gravity, solution gas, and natural water drive) in the reservoir, increasing the flow of crude oil. Driving forces present in the reservoir affect the improved recovery rates once the flow resistance is
reduced. Stimulation treatments also can be combined with thermal drives, in which the driving forces are both natural and imposed.

The non-thermal enhanced oil recovery method (solvents or other chemicals) are utilized to increase the oil mobility in the reservoir by reducing the viscosity or interfacial tension between the reservoir fluids. The most important solvent and chemical enhanced oil recovery methods include alkaline flooding, carbon dioxide (CO₂) flooding, cyclic CO₂ stimulation, nitrogen flooding, polymer flooding, micellar polymer flooding, and microbial enhanced oil recovery (MEOR).

Alkaline flooding (caustic flooding) is a technique to enhance the oil recovery of a reservoir in a way that an alkaline chemical, such as sodium hydroxide, sodium orthosilicate, or sodium carbonate, is injected during waterflooding or polymer flooding operations. The alkaline chemical reacts with specific types of oils and forms surfactants inside the reservoir. Eventually, the surfactants reduce the interfacial tension between the oil and water and trigger an increase in oil production. Nonetheless, alkaline flooding is not suggested for reservoirs containing calcium ions, such as carbonate reservoirs, since the mixture between the alkaline chemical and the calcium ions can produce hydroxide precipitation that may damage the formation.

Carbon dioxide (CO₂) flooding is a process whereby carbon dioxide contacts with the reservoir oil in order to increase output when extracting oil. CO₂ flooding is particularly effective in reservoirs deeper than 2,000 ft., where oil gravity is between 22º to 25º API, and CO₂ is in a supercritical state. CO₂ flooding is not affected by the lithology of the reservoir area, but simply by the reservoir characteristics. CO₂ flooding is commonly
used to recover oil from reservoirs in which the initial pressure has been depleted through primary production and possibly waterflooding (Orr et al., 1982).

Cyclic CO$_2$ stimulation, also called as the huff-n-puff method, is a single-well operation that being developing as a method of rapidly producing oil. Similar to the cyclic steam process, CO$_2$ is injected into an oil reservoir, the well is shut in for a time (providing for a soak period), and then the well is opened allowing the oil and fluids to be produced. The dissolving of the CO$_2$ in the oil reduces the oil’s viscosity and causes it to swell, allowing oil to flow more easily toward the well. The process can also be used in heavy oil reservoirs by injecting CO$_2$ at high-pressure to facilitate solubility between the oil and CO$_2$ and in cases where thermal methods are not feasible.

Nitrogen (N$_2$) flooding can be used to recover light oil that is capable of absorbing added gas under reservoir conditions. When N$_2$ is injected into a reservoir, it forms a miscible front by vaporizing lighter oil components. As the front moves away from the injection wells, its leading edge goes into solution (or becomes miscible) with the reservoir oil. Continued injection moves the bank of displaced oil toward the production wells. Water slugs are injected alternately with the (N$_2$) to increase the sweep efficiency and oil recovery. N$_2$ can be manufactured on site at a relatively low cost by extracting it from the air by cryogenic separation, which is totally inert and non-corrosive.

Polymer flooding is an enhanced oil recovery method that uses polymer solutions to increase oil recovery by increasing the viscosity of the displacing water in order to reach a favourable water/oil mobility ratio. Generally, polymer flooding is conducted in types of reservoirs that show lower efficiency than a regular waterflood. Presence of fractures
or high-permeability regions leads to channels or redirects the flow of injected water or heavy oil and subsequently decreases the oil recovery. Using a water-soluble polymer in the waterflooding technique allows the water to displace oil through more pore spaces of the reservoir rock, resulting in a higher percentage of oil recovery.

The micellar polymer flooding method uses the injection of a micellar slug into a reservoir. The micellar slug contains a mixture of surfactant, co-surfactant, alcohol, brine, and oil that moves through the oil-bearing formation, releasing much of the oil trapped in the rock. This method is one of the most efficient enhanced oil recovery methods, but it is also one of the most costly to implement.

Microbial enhanced oil recovery (MEOR) processes involve the use of reservoir microorganisms or specially selected natural bacteria to produce specific metabolic events that lead to enhanced oil recovery. The processes that facilitate oil production are complex and may involve multiple biochemical processes. Microbial biomass or biopolymers may plug high-permeability zones and lead to a redirection of the water flood, produce surfactants that lead to increased mobilization of residual oil, increase gas pressure by the production of carbon dioxide, or reduce the oil viscosity due to digestion of large molecules (Banat, 1995; Clark et al., 1981; Stosur, 1991).

1.2.1.4 Cold heavy oil production with sand (CHOPS)

In conventional heavy oil production, the idea was oil production with no sand production results in a minimized initial unit operating cost. However, this practice might prohibit several wells from arriving at their maximum oil production rate and reserve potential. Field production data indicates that heavy oil flows more efficiently when sand
is produced from unconsolidated reservoirs. In the Elk Point and Lindberg reservoirs, sand production from wells occurs regularly (Loughead, 1992; McCaffrey and Bowman, 1991). Cold heavy oil production with sand is now widely used as a production approach in unconsolidated sandstones. This practice facilitates the flow of oil foam caused by a solution gas drive in the reservoir by producing high permeable channels (wormholes) in the low cohesive-strength sands. High production rates compared to primary production and lower production costs are the main profit of the CHOPS production approach. On the other hand, sand handling problems, field development strategies, wormhole plugging for water shut-off, low ultimate recovery, and sand disposal are the main concerns involved in this process.

1.3 Statement of the problem

Unlike heat conductivity or viscosity in the analogous transport phenomena, measurements of mass diffusivity of gases in bulk liquids and liquid saturated porous media are much more obscure and strenuous. In addition, no standardized procedures for such property exist. Hence, miscellaneous experimental and mathematical attempts have been exploited in recent years by the petroleum engineers to characterize this key parameter in oil media. A more complicated situation happens when solvent solubility is measured in porous media. Solvent solubility in porous media originates from a complex interplay of molecular diffusion and convective spreading (dispersion) in a different medium than bulk fluid itself. Solvent concentration differences induce the solvent into the oil phase under the diffusion process, and the oil phase spreading and mixing in the reservoir containing solvent increases the solvent solubility in the oil under the convection-dispersion process.
Solvent molecules in liquid or vapour states are in continuously random motion even if the bulk fluid velocity is zero. It results in a net movement of solute particles from regions with high solute concentrations to regions with low solute concentrations. The diffusion process is distinguished by Fick’s law (1855):

\[ j = -D_0 \frac{\partial C}{\partial x} \]  

(1.1)

Where \( D_0 \) is the diffusion coefficient, and the derivative is concentration gradient. This equation is known as Fick’s first law, and it does not describe how solute concentration changes with time and space due to diffusion. However, Fick’s second law explains how the solute concentration varies with time and space:

\[ \frac{\partial C}{\partial t} = -\frac{\partial j}{\partial x} \]  

(1.2)

\[ \frac{\partial C}{\partial t} = D_0 \frac{\partial^2 C}{\partial^2 x} \]  

(1.3)

To describe the diffusion process in porous media, two parameters should be considered. The first parameter is the cross-sectional area between the solvent and solute, and the second parameter is the path length for diffusion. The first parameter in the porous media is reduced as some space is filled with rocks, and the second parameter is increased because the complex network of interconnected pores causes solute particles to take tortuous paths. Noting that laws governing electrical conductivity and diffusion in porous media are analogous, it is shown that the diffusion coefficient in porous media is related to the formation resistivity factor by:
\( D = \frac{D_0}{F\phi} = \frac{D_0}{\tau} \) \((\text{Perkins and Johnston 1963; Lake, 1989}), (1.4)\)

Where \( F \) is the formation resistivity factor and for clean rocks a function of pore geometry only, \( \tau \) is the tortuosity of the porous medium and \( D \) is the effective diffusion coefficient. When a solute slug moves either in the bulk phase or through a porous medium, there is additional mixing due to convection. The convection-diffusion equation (CDE) is a simplified form of the general conservation equation for multiphase multi-component flow. The convection-diffusion equation describes the overall mass transport and reservoir mixing in porous media for single phase flow, equal density, equal viscosity, and without reaction term. The general mass balance equation without reaction and generation terms in a general form is given by:

\[
\frac{\partial}{\partial t} \left( \phi \sum_{j=1}^{n_p} \sum_{i=1}^{n_c} x_{ij} \rho_j S_j \right) + \nabla \cdot \left( \sum_{j=1}^{n_p} \sum_{i=1}^{n_c} x_{ij} \rho_j \vec{u}_j \right) - \nabla \cdot \left( \phi \sum_{j=1}^{n_p} \sum_{i=1}^{n_c} D_{ij} \nabla x_{ij} \right) = 0 \tag{1.5}
\]

Where \( x_{ij} \) is the mole fraction of component \( i \) in phase \( j \), and \( \rho_j \) is the mass density of phase \( j \). According to the convection-diffusion equation assumptions for a two component system:

\[
n_c = 1, n_p = 1 \text{ and } x_{ij}.\rho_j = C_{ij} = C \tag{1.6}
\]

Thus, the conservation equation is reduced to:

\[
\frac{\partial}{\partial t} (\phi C) + \nabla.C u - \nabla.\phi D(\nabla.C) = 0 \tag{1.7}
\]

For 1-D solute transport in porous media, the convection-diffusion equation is in the form of:
\[
\phi \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = \phi D \frac{\partial^2 C}{\partial^2 x}
\]  
(1.8)

Where \( C(x, t) \) is the solute concentration and \( D \) is the longitudinal diffusion coefficient.

The convection diffusion equation assumes incompressible fluid in porous media, no volume change upon mixing and spatially constant porosity.

For the bulk phase, porosity is 1, \( (\phi = 1) \) and the CDE would be:

\[
\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = D \frac{\partial^2 C}{\partial^2 x}
\]  
(1.9)

The above mathematical model is for the longitudinal system, and it is also useful for the field scale model if the diffusion dispersion process between injection and production well is assumed to be a one-dimensional process. If the geometric of the system changes from longitudinal to cylindrical, then the diffusion equation would be:

\[
\frac{\partial C(r, t)}{\partial t} = D \left( \frac{\partial^2 C(r, t)}{\partial r^2} + \frac{1}{r} \frac{\partial C(r, t)}{\partial r} \right)
\]  
(1.10)

### 1.4 Objective of this study

The inclination of this research was toward proposing a new method for measuring CO\(_2\) solubility (as the solvent) in heavy oils and determination of CO\(_2\) diffusion coefficient.

To achieve these goals, measurements were conducted in static and dynamic conditions for both bulk heavy oil and oil saturated porous media under different pressures and temperatures. The endeavour was to conduct and use more professional set-ups and apparatuses to more precisely measure CO\(_2\) solubility in heavy oil. In order to do the aforementioned tasks, this thesis has the following structure to achieve its goals:
1. To design and build a diffusion test set-up for CO$_2$/heavy oil system using diffusion cells that can handle high pressure and temperature.

2. To conduct several CO$_2$/bulk heavy oil experiments at static condition under various pressures and temperatures. These measurements were also extended by utilizing two different oil samples with different viscosities to investigate the influence of this important parameter on the solubility and diffusion coefficient of CO$_2$ in heavy oil.

3. The same experimental conditions as mentioned in 2 (i.e., two heavy oil samples under predefined pressures and temperatures) were operated at dynamic scenario. For this purpose, a reactor equipped with a mixer and controller has been exploited. These experiments are intentionally operated at the same temperatures and pressures to be compared with the results at static condition.

4. To be more realistic, a special experimental model was designed to simulate porous media and the reservoir wellbore condition. Solubility and diffusion coefficient of CO$_2$ were then determined in heavy oil saturated porous model. Similar operating conditions to the bulk oil tests were chosen to be performed in the porous model for further analysis of these properties.

5. To choose the proper mathematical model and the physical initial and boundary conditions which were assigned to the experiments. Using the data gathered from the experiments and solving the mathematical model for each specific operating condition, CO$_2$ diffusion coefficient was obtained.
6. In addition to all of the above, a data set consist of measured solubility of CO$_2$ at various conditions during this study and those obtained from previous works, was collected and a correlation was developed to be used in future research studies.

1.5 Approaches

Diffusion is the fundamental transport phenomena in mixtures and the governing mass transfer mechanism in many industrial applications. Good knowledge of this process plays an important role in the proper description of such application.

Determination of the diffusion coefficients in multicomponent mixtures has proven to be a complicated problem, especially when the compositional dependence of a diffusion coefficient in a non-ideal liquid mixture is considered. Apart from gas systems, where the kinetic theory of gases may be successfully applied (Hirschfelder et al., 1954), experimental measurements are still practically the only source of actual values of diffusion coefficients in liquids. Most of the existing methods for modeling diffusion coefficients Reid et al., (1987) and Shapiro et al. (2004) are empirical or semi-empirical and essentially focus on the correlation of the experimental results rather than the prediction of the values of the coefficients.

There are several methods and strategies for measuring the diffusion coefficient, which can be categorized into two main groups. In the first category, the composition of dissolved gas molecules would be measured along the liquid body directly. Although this method might provide the spatial gradient of concentration, it necessitates the experimental set-up to be complex and system-intrusive. Often samples are taken out to be analyzed subsequently to collect this data (Schmidt, 1989). This makes the process
quite expensive, labour-intensive and time consuming. In the other category, a parameter which varies with composition change is monitored and then related to the concentration change to help us find the diffusivity value. This parameter can be the rate of pressure decay in the diffusion cell, volume change as a result of the diffusion or the rate of gas injection, gas-liquid interface movement in cases that liquid swelling is significant, which all gets conducted in PVT cells. Imaging technology also has been applied for this measurement with NMR spectrometry or CAT scanning (Pomerantz, A., et al., 2009). Pendant drop volume analysis is also a technique that has been used to determine diffusivity (Gu Y., 2006).

Among all these methods, the pressure decay method has attracted more attention due to its simplicity and robustness. Riazi (1996) was the first to use this method. He measured the diffusivity of methane in liquid pentane by recording both the rate of pressure drop and the movement of the gas-liquid interface due to pentane swelling. In this method, solubility of the solvent is determined by relating the state functions associated with the matter, such as its temperature, pressure, volume to each other under a given set of physical conditions known as the equation of state (EOS). For a closed system, the general PVT relationship is:

\[ PV = ZnRT \]  \hspace{1cm} (1.11)

From the above equation, the amount of the gas in a gas system can be calculated:

\[ m = \frac{VM P}{RT \cdot Z} \]  \hspace{1cm} (1.12)

In a closed system, when a gas in contact with a liquid, the pressure of the gas decreases as a result of its dissolution in the bulk phase of the liquid, which is caused by differences
in the concentration of the gas in the two phases. This difference makes a mass transfer between the two phases and the mass of the gas dissolved into the liquid system can be calculated by:

\[ m = \frac{VM}{RT} \left( \frac{P_i}{Z_l} - \frac{P_f}{Z_f} \right) \]  

(1.13)

From the mass measured during the experiments, concentration profile of the gas can be measured subsequently. The experimental diffusion coefficient at microscopic and macroscopic scales is generally measured by matching the concentration profile (in our case, calculated by pressure decay method) with the solution of the diffusion equation describing the experimental model. Therefore, based on the concentration profile calculated by experiments and the proper diffusion equation defining the experimental condition, the diffusion coefficient of the solvent can be estimated. In all experiments conducted in this study, these approaches (i.e., pressure decay method for solubility measurement, and solving the appropriate diffusion model of the system for diffusion coefficient calculation) were employed to determine \( \text{CO}_2 \) solubility and diffusion coefficient in heavy oil system.

### 1.6 Organization of the dissertation

Chapter 1 of this dissertation details heavy oil and solvent recovery methods and an introduction to the research objectives and methodology. Chapter 2 demonstrates an understanding of the origin of diffusion processes in bulk fluid and saturated porous media. Moreover, a complete literature review is presented on theoretical and experimental approaches for determining \( \text{CO}_2 \) diffusion coefficients in heavy oil. In chapter 3, mathematical models that are suitable for the experimental condition will be
presented and the proper solution based on the initial and boundary conditions will be proposed. Chapter 4 describes the experimental set-ups, preparation procedure and tests that have been done in the bulk heavy oil under static condition. Besides, this chapter presents the details of calculations and methodology used to measure the diffusion coefficients of the solvent on each specific experimental condition. In chapter 5, the reactor used to make the convection diffusion process happen in the bulk oil phase is introduced. The procedure to run the experiment in dynamic condition is also explained. The proper mathematical model with the suitable experimental boundary and initial conditions along with the numerical solution are also presented to estimate the diffusion coefficient in each test. Chapter 6 belongs to porous media and the modifications that have been done to determine the solubility and diffusion coefficient of CO$_2$ in a pore space. To apply the pressure decay experiment in a diffusion cell, first the modification to the cell is described. Furthermore, the experimental procedure in which a pore space model used in the horizontal condition (governed mostly with the diffusion process) is presented. The mathematical model suitable for the radial system is implemented here and the corresponding diffusion coefficients are calculated and reported as the result of these experiments. In Chapter 7, solubility data of CO$_2$ in heavy oil system gathered from this work and from literatures are analyzed first. Then, a mathematical correlation that fits best the experimental data will be proposed. Finally, the correlation accuracy will be tested with some of the available correlations used in the research and industry. Chapter 8 summarizes the contribution, research conclusions and recommendations of this work.
Chapter 2

Literature Review

CO$_2$ injections in geological formations are performed for enhanced oil recovery (EOR), storage (confining CO$_2$ molecules in the pore network) and sequestration (the reaction of CO$_2$ molecules with mineral grains) of anthropogenic greenhouse gas emissions. The main goal of these processes is to produce more hydrocarbons from oil and gas reservoirs (Baines and Worden, 2004; Moberg, 2001; Monger et al., 1991; Holm and Josendal, 1974). Global warming concern and shortage of energy supplies have increased the interest in geological CO$_2$ storage and CO$_2$ flooding to enhance oil recovery (EOR) from hydrocarbon reservoirs. That is why, a full understanding of CO$_2$ behaviour in oil reservoir has been one of the major interests in the petroleum industry, and therefore has caused a lot of researchers and companies to take this problem seriously.

The main processes involved in any CO$_2$ injection (generally solvent injection) into geological formations are diffusion, convection-diffusion, chemical reactions, and geomechanical effects, such as porous media deformation caused by pore pressure increase (Comerlati et al. 2006) and permeability and porosity changes caused by chemical reactions with minerals (Izgec et al. 2008a, b; Sayegh et al. 1990). Only the first two processes are considered in this research study. In this chapter, methods are going to be investigated employed by various authors to arrive at concurrent values for concentrations of solvents in crude oil and the corresponding diffusion and coefficient.
2.1 Applied methods to determine the solubility and diffusion coefficient of solvents in heavy oil system

There are several methods in the literature that have been conducted to quantify the concentration of the solvents in crude oil and the related diffusion coefficient. These approaches include the direct method (compositional method), pressure decay method (and modified pressure decay), CAT scanning and low field NMR, magnetic resonance imaging (MRI), and dynamic pendant drop volume analysis (DPDVA). Recently, pore scale modeling has also been added to these methods. In this section, a detailed look at these methods is conducted with more emphasis on the pressure decay method, which is going to be used in this study.

2.1.1 Pressure decay method

Diffusion is the process by which molecules, ions, or other small particles spontaneously mix, moving from regions with relatively high concentrations into regions with lower concentrations. Quantitative measurements of the rate at which the diffusion process occurs are usually expressed in terms of a diffusion coefficient. Hence, the diffusion coefficient of CO$_2$ in heavy oil (which is one of the main solvents for heavy oil EOR methods) is the main objective of this work.

A thorough investigation of the experimental limitations and physical model assumptions for solvent mass transfer into heavy oil and bitumen has commenced quite significantly since the early pressure decay experiments and constant diffusivity models.

Riazi (1996) proposed a method for measuring the diffusion coefficient in hydro carbon liquids in high pressure and temperature conditions that is simple, but very useful and
practical. The proposed method, which is called the pressure decay method, is based on the fact that the pressure in the gas phase decays as the solvent molecules start migrating to the liquid phase in a closed diffusion cell. One of the distinct traits of this procedure is that no compositional measurements are necessary for this method. Riazi (1996) reported that the semi-analytical numerical model could accurately match experimental pressure decay results.

The experimental set-up used by Upreti and Mehrotra, (2000) included a diffusion cell of CO₂ containing CO₂ and bitumen in operating condition of 25 to 90°C and pressure of 4 MPa. The mass of carbon dioxide dissolved in the liquid phase was estimated using the pressure decay technique. The experiment was started at a given system pressure and the pressure decreased as the gas diffused into the heavy oil. Their method utilizes a comprehensive distributed parameter model of mass transfer and employs a functional optimization technique to compute the concentration dependent gas diffusivity. They assumed that the diffusivity is concentration dependent, but pressure independent at a given concentration. They presumed a quasi-equilibrium boundary condition at the interface of the solvent and heavy oil. Upreti and Mehrotra, (2000) stated that the diffusivity increased with increased temperature. This finding accords with the fact that diffusivity of a gas into a liquid is inversely related to the viscosity of the liquid phase because as the temperature of the liquid increases, the viscosity decreases.

Zhang et al., (1999) utilized the pressure decay method for measuring the diffusivity of carbon dioxide and methane in heavy oils in a high-pressure windowed cell. They assumed that the height was constant with time, or in other words, there is no swelling in
the oil phase. Their work suggested that the solubility of carbon dioxide and methane in heavy oil is a strong function of pressure and temperature.

Tharanivasan et al., (2004) measured the diffusion coefficient and solubility data for carbon dioxide-heavy oil and methane-heavy oil systems. Using a technique similar to that used by Zhang et al. (1999), the diffusion coefficient was calculated by treating the diffusion coefficient as an adjustable parameter. History matching was utilized to determine the best-fit curve between the experimental pressure data and the predicted pressure data to find the best diffusion coefficient for the experiment.

Sheikha et al. (2005) reported new graphical methods for estimating the diffusion coefficients of gases in bitumen from pressure decay measurements. In this study, the pressure data of methane, carbon dioxide, and nitrogen in Athabasca bitumen were obtained from previous studies of Upreti and Mehrotra (2000). An analytical solution was derived based on both infinite and finite condition of the experiments to determine the diffusivity. In conjunction with the calculated value of Henry's constant, the diffusion coefficients were determined by graphically estimating the intercept and slope. For each solvent and heavy oil system, the calculated value of Henry's constant was separately calculated from the volume-basis gas solubility correlations.

Creux et al. (2005) measured the diffusion coefficient of methane in heavy oil by monitoring the pressure drop in the PVT cell. They also used another technique to quantify the diffusion coefficient in which the concentration variation of marked methane molecules was used.
Jamialahmadi et al. (2006) investigated both concentration-dependent and concentration-independent diffusion coefficients of methane in dodecane and crude oil at pressures up to 40 MPa and at different temperatures. The experiments were carried out using a PVT high-pressure cell. The pressure in the system for each experimental condition was kept constant by injecting mercury into the bottom of the cell. The volume-time data of the methane diffused into the liquid phase was determined from the movement of the liquid interface and the rod position of the mercury pump. The measured volume-time data were used to calculate gas concentrations in the liquid phase and the continuity equation and a finite boundary model were employed for the gas diffusivity calculation.

Tharanivasan et al. (2006) measured the molecular diffusion coefficients of carbon dioxide, methane and propane in heavy oil under reservoir conditions using the pressure decay method. They examined three different boundary conditions of heavy oil-solvent interface using measured pressure decay results. They proposed a new theoretical strategy to determine the equilibrium pressure from solubility versus data of pressure.

El-Haj et al. (2007) conducted a series of experiments to obtain the diffusion coefficient in heavy oil. Athabasca bitumen packed with glass beads of different permeabilities was used as a porous medium in a cylindrical geometry. The experiments were carried out at room temperature using solvent butane at the dew point pressure. A detailed mathematical model was developed for butane transfer into the medium and subsequent oil production. The concentration-dependent dispersion coefficient of butane was optimally determined by matching the experimental live oil production with the model-predicted one. Results were obtained for three different permeabilities of the medium. They suggested that the dispersion coefficient is slightly higher for lower permeability or
lower size of glass beads, and explained this phenomenon is based on the interstitial area and particle shape irregularity. Moreover, they proposed that in comparison to the molecular diffusion coefficient of butane (reported in the literature), the calculated dispersion coefficient were up to three orders of magnitude higher because of underscoring of the role of convection, surface renewal and viscosity changes.

Okazawa (2009) proposed a power-law model for the dependency of the diffusion coefficient to concentration in modeling the vapour extraction (VAPEX) process using pressure decay concept.

Etminan et al. (2009) conducted experiments to measure the concentration dependent diffusivity coefficient in the solvent gas heavy oil system. They modified the pressure decay method in a way that the concentration of the solvent and the corresponding pressure at the gas liquid interface remain constant. However, pressure decay was recorded in a supply cell which was attached to the diffusion cell. A stepwise increase in pressure was used to study the concentration dependent diffusivity, and gas saturation pressure (concentration) ranging from low pressure to near gas dew point pressure was measured in five to six steps. They also considered the effect of bitumen swelling by updating the height of the oil in the cell.

2.1.2 Direct method

Islas-Juarez et al. (2004) constructed an experimental set-up to measure the effective molecular diffusion coefficient of N₂ in packed unconsolidated sands. They implemented a special set-up to take samples from different points of their sand-pack model. Analyzing the samples with a gas chromatograph, the mass of the solvent was measured
in the oil phase, and the corresponding diffusion coefficient was calculated by matching the one-dimensional mathematical model with the experimental concentration profile. This method, which undergoes to compositional or direct method, uses compositional analysis to determine the concentration of the diffusing component along the length of the crude sample with time. Before Islas-Juarez et al., (2004), researchers like Hill and Lacey (1934) and Sigmund (1976) also used this method to study the mass transfer process in porous media. The major drawback of determining the diffusion coefficients using the direct method is being time consuming, labour intensive and expensive process.

2.1.3 CAT scanning and low field NMR method

Wen et al. (2005) used the Nuclear Magnetic Resonance (NMR) method to estimate diffusion coefficients in bitumen solvent mixtures. Fick's second law was applied to mathematically model the flux and consequently measure the concentration changes and determine an apparent diffusion coefficient. The experiments were carried out at room pressure and at a temperature of 30°C. They found this method useful for determining the diffusion coefficient in porous media. The diffusion coefficient was also considered constant in their model.

Afsahi (2005) utilized the NMR method to measures the diffusion coefficient of the solvent used in the VAPEX process in bitumen saturated sand. They concluded that low field NMR has a great potential to be used for in-situ monitoring the solvent mass transfer rate into heavy oil and bitumen. Moreover, they mentioned that the diffusion coefficient is strongly related to the concentration, but for a short period of time, it can be considered as a constant value.
Guerrero-Aconcha et al. (2009) used Computed Assisted Tomography (CAT) to obtain the density profiles and back calculate the concentration-dependent diffusion coefficients. A non-iterative finite volume method was used by them to obtain the diffusion coefficient dependent on the concentration. They suggested that the CAT-scan is an invaluable tool to obtain the density profiles (which can be used to calculate the concentration profile) in systems of slow diffusivity.

Wen and Kantzas (2009) tried to detect and monitor solvent interactions with heavy oil and bitumen. Two non-destructive methods, slow-field nuclear magnetic resonance (NMR), and X-ray computed-assisted tomography (CAT) were used to determine the solubility profile inside the system.

2.1.4 Magnetic resonance imaging method

Using Magnetic Resonance Imaging (MRI), useful information about the concentration gradients can be determined. Fisher et al. (2000) studied the mass transport of solvent into heavy oil during the VAPEX process using an MRI and visual glass micro-models aided by advanced image analyses. They developed a mathematical model to extract parametric information from the MRI collected data. However, they stated that a better understanding of the fundamental physics and chemistry of this process is needed to formulate the phenomena.

2.1.5 Dynamic Pendant Drop Shape Analysis (DPDSA) method

Yang and Gu (2003) developed an experimental method for measuring solvent diffusivity in heavy oil under practical reservoir conditions by applying the dynamic pendant drop shape analysis (DPDSA). The DPDSA is a special process that correlates the interfacial
tension reduction in a drop to the oil swelling effect in heavy oil as solvent diffuses into it. The DPDSA method is based on the fact that the shape of a pendant heavy oil drop keeps changing as solvent gradually dissolves into heavy oil. Solvent diffusivity in heavy oil is determined by finding the best fit of the numerically calculated drop profiles to the experimentally measured drop profiles of the dynamic pendant oil drop at different times.

This physical phenomenon was stated in a theoretical form by the Laplace equation of capillarity, and the molecular diffusion process described by the mass diffusion equation. In the experimental set-up, a windowed high pressure cell was filled with the test solvent at a desired pressure, and temperature, and then a heavy oil sample was introduced slowly through a syringe delivery system to form a pendant drop inside the pressure cell. These processes caused the shape and volume of the drop to change until equilibrium was reached. This change was captured by the means of sequential images and digitized by applying computer aided digital image processing techniques. Experimental results were compared to the numerical solution and the diffusion coefficient was determined by minimizing the associated error between experimental and numerical data. This technique is quick and allows the mass transfer coefficient to be determined at the solvent-heavy oil interface as stated by Yang and Gu (2003).

2.1.6 Pore scale networks modeling

Recently, pore-scale network modeling has attracted interests in several petroleum and other engineering applications (Oren et al., 1998 and Oren et al., 2002, Valvatne, et al., 2004, Piri, M. 2002, Blunt et al, 2002, Bryant 1992). Although this method has been implemented regularly into simple two-phase flow processes and relative permeability estimations, it is now used as a platform to explore a wide range of phenomena, including
three-phase flow, hysteresis, mass transfer between phases, and the effects of wettability. Besides that, complex geometry now can be represented by the pore scale network more precisely. In this method, the porous medium is expressed as a collection of interconnected elements (pores and throats), where each element is designated some identified geometry with effective properties that define the characteristics of real rocks. Rock and fluid properties, such as capillary pressure, permeability, diffusion-dispersion coefficient and so on can be estimated along the network by conducting the suitable rules that govern the transport and arrangement of fluids at pore-scale (Valvatne, et al., 2004, Piri, M. 2002, Blunt et al, 2002).

Garmeh et al. (2007) examined the dispersion and mixing that occurs in porous media by solving single-phase flow using pose space network modeling. They modeled the flow in a series and layered heterogeneous porous media by using many grains in different arrangements. They matched the analytical convection-diffusion solution to the concentrations from the pore-scale simulations that involves both transverse and longitudinal dispersion coefficients. In their work, they clearly describe convective spreading and mixing and explained the differences between them. They concluded that the pore-scale simulations produce similar characteristics that are observed in experimental measurements of mixing, which is the classical Perkins-Johnston relationship between longitudinal dispersion and pore Peclet number.

Jha et al. 2006 investigated the local mixing experimentally as well as computationally. They proposed using a thin electrical-conductivity probe to measure local solute concentrations to quantify local mixing. Using a homogeneous sand pack, miscible tracer displacement experiments were conducted. Solute concentrations were measured locally
at several radial and axial positions using the probe indicating non-zero local mixing. They also investigated local mixing by solving the Navier-Stokes and convection-diffusion equations in two-dimensional packing of circular disks. They suggested that computational network modeling supports the experimental results and explains the mixing mechanism inside the pore space. They also stated that mixing in pore space results from molecular diffusion and velocity variations in pore throats and bodies. Their results showed that diffusion tends to decrease local variation in solute concentrations inside the pore and the area available for diffusion process increases by an order of magnitude. In the case that the fluid velocity is not considerable, diffusion process can homogenize solute concentration inside each pore body. On the other hand, increasing the fluid velocity causes the same effect on local mixing and reduces the diffusion coefficient by the same factor.

Taheri et al. 2010 used sub-pore scale modeling approach to predict the solvent diffusion coefficient in heavy oil and bitumen. They used an image (a micro model pattern, thin section, tomographic image or microscopic picture of the rock) to characterize and build their model. After building the model, virtual porous medium properties were assigned by implementing the Navier-Stoke and continuity equations. Fick’s second law in one dimension as the governing diffusion equation was conducted to the medium to define the concentration profile of the solvent in the sub-pore scale model. Correspondingly, the effective diffusion coefficient of the system was calculated from the concentration profile. They suggested that pore scale modeling is a very robust method in predicting the effective diffusion coefficient \( D_{eff} \) of porous medium just by having an image of the medium. On the other hand, they stated that heterogeneity of the porous medium makes it
hard to generate a reliable predicting model for \( D_{\text{eff}} \) for different systems with
different properties.

### 2.1.7 Other methods and approaches

Pomeroy et al. (1933) approximated the solubility of lighter hydrocarbons in quiescent
liquids and the corresponding diffusion coefficient. They reported that up to 300 psi, the
diffusion coefficient is a weak function of pressure or concentration of the methane gas in
a solution.

Reamer et al. (1956) estimated the methane diffusion coefficient in hydrocarbon mixtures
by presuming a resistance at the interface, which was assumed to be related to the mass
transfer rate. They stated that, at lower temperatures, the diffusion coefficient is much
more sensitive to the pressure of the solvent than at higher temperatures. For instance, at
temperatures above 27°C, this dependency decreases and even the diffusion coefficient
would decrease with lifting the pressure.

Renner (1988) developed an in-situ technique for measuring the CO\(_2\) diffusion coefficient
and other solvents in porous media at high pressure. Renner reported the CO\(_2\) diffusion
coefficient in both decane and brine up to 850 psia and for ethane in decane up to 600
psia. All the tests were conducted at 100°F and both vertical and horizontal situations
were investigated. After saturating the core space and injecting the solvent into the
system, it was tried to keep the pressure of the solvent in contact with the oil or brine in a
constant value and measures the volume of the injected gas. Based on the volume of the
injected gas versus time and using Fick’s second law, they calculated the diffusion
coefficient of the solvent. Renner suggested that the CO$_2$ diffusion coefficient in hydrocarbons in vertically conducted porous media is independent of pressure.

Grogan et al., (1988) measured the CO$_2$ diffusion coefficient in the liquid phase of hydrocarbons and water at reservoir conditions. By tracking the interface displacement and matching it with the results from a numerical model, they estimated the diffusion coefficient of CO$_2$ in the oil phase.

Rasmussen and Civian (2002) developed mathematical models for predicting the diffusion of solvents in a liquid under equilibrium and non-equilibrium conditions. Their study reported that the developed analytical model can be used in determining the delay time and the diffusion coefficient of gas in oil and brine.
2.3 Summary

CO₂ solubility and the diffusion coefficient determination in heavy crude oils were investigated in recent years mostly by the indirect methods. Pressure decay, CAT scanning and low field NMR, magnetic resonance imaging are some of these methods that researchers have utilized to determine different solvents physical properties. All these measurements have their own advantages and disadvantages due to the efforts needed to set up the experiments and operate them. However, pressure decay method showed more attraction among these methods and needs less effort and is more applicable. Nevertheless, scarcity of the measurements in different heavy crude oil under different operating condition is still a need for well developing and generalizing a relation between CO₂ and heavy oil properties. Hence, a lack of these measurements in the heavy oil porous media and the bulk heavy oil is the main motivation for this work.
Chapter 3

Mathematical Formulation of the Problem

The rate at which matter is transported from a part of a system containing two or more chemicals to another part can be determined by several mechanisms. These mechanisms may include diffusion, dispersion, convection, adsorption and production, which may act simultaneously or separately. Since the mechanisms affecting the solute transport in each specific case are different, a proper mathematical model with appropriate initial and boundary conditions is solved here, not only for predicting the actual mass transport in the system, but also for analyzing the transport mechanism itself. In this chapter, the mathematical models corresponding to the experimental condition are going to be reviewed, and then the corresponding solutions for each model are offered.

3.1 Basic concept of mass transfer by diffusion

Mass transfer by diffusion is analogous to heat transfer by conduction derived by Fourier (1822). Fick (1855) some years later recognized the same behaviour in chemical contact and used this analogy to describe the diffusion processes occurring in nature. The mathematics of the diffusion process is thus based on the hypothesis that the mass transfer rate of a chemical component through the unit area of a system is proportional to the concentration gradient quantify normal to that section:

\[ j = -D_0 \frac{\partial C}{\partial x} \] (3.1)
Where \( J \) is the rate of mass transfer, \( C \) the concentration of diffusing the chemical component, \( x \) the space coordinate applied normal to the section, and \( D \) is referred to the diffusion coefficient of the diffusing substance. As it can be seen in equation 3.1, if \( J \) and \( C \) have the same unit dimension (e.g., both are gram or gram molecule), then the diffusion coefficient dimension would be \((\text{length})^2/(\text{time})\) like \( m^2/\text{day} \), which means \( D \) is not a function of concentration. However in real scenarios, concentration affects the mass diffusion process. In some matters, like dilute solutions, \( D \) can be taken as a constant, while in others, like in high polymers, it depends on the concentration. Based on equation 3.1, the general mass transfer equation can be derived for a system.

### 3.2 Mathematical formulation of diffusion in cartesian coordinate

A control volume is considered in a rectangular coordinate with parallel axis and equal length \((dx, dy, dz)\) and let \( R(x,y,z) \) be the center of this element and \( ABCD \) and \( EFGH \) are the faces perpendicular to the mass flow as shown in Figure 3.1.
Figure 3.1. Control volume of mass in a rectangular coordinate with parallel axis
The mass enters the element or volume at $x - dx$, if there is no reaction and production in the volume can be written as:

$$dydz \left( I_x - \frac{\partial J_x}{\partial x} \right)$$

(3.2)

On the other hand, the rate of loss of the substance in $R$, at $EFGH$ would be:

$$dydz \left( I_x + \frac{\partial J_x}{\partial x} dx \right)$$

(3.3)

Mass transfer occurred in this volume caused by diffusion in $x$ direction is:

$$-dx dydz \frac{\partial J_x}{\partial x}$$

(3.4)

Similarly, from the other faces it can be achieved:

$$-dx dydz \frac{\partial J_x}{\partial y} \text{ and } -dx dydz \frac{\partial J_x}{\partial z}$$

(3.5)

The rate at which the concentration is increasing is:

$$dx dydz \frac{\partial C}{\partial t}$$

(3.6)

Since the total mass balance is equal to zero or no mass was destroyed and produced, it can be written:

$$dx dydz \frac{\partial C}{\partial t} + dx dydz \frac{\partial J_x}{\partial x} + dx dydz \frac{\partial J_y}{\partial y} + dx dydz \frac{\partial J_z}{\partial z} = 0$$

(3.7)

And consequently:

$$\frac{\partial C}{\partial t} + \frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z} = 0$$

(3.8)
If we suppose that the diffusion coefficient is constant and plug in the \( J \) with equation 3.1, then:

\[
\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right)
\]  

(3.9)

Reducing simply to

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}
\]

(3.10)

Equations 3.1 and 3.10 are usually called Fick's first and second laws of diffusion, because Fick (1855) was the first person to formulate them by direct analogy with the equations of heat conduction.

### 3.3 Diffusion in a cylindrical coordinate

By considering elements of volume of different shapes or by transformation of coordinates, other forms of the above equations can be created. To transform an equation from the Cartesian system to cylindrical, two following transformation should be applied:

\[
x = r \cos \theta
\]

(3.11)

\[
y = r \sin \theta
\]

(3.12)

The general diffusion equation in cylindrical coordinate would be:

\[
\frac{\partial C}{\partial t} = \frac{D}{r} \left( \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) + \frac{1}{r} \frac{\partial^2 C}{\partial \theta^2} + \frac{\partial^2 C}{\partial z^2} \right)
\]

(3.13)

To generate the above equation, a control volume in a cylindrical shape with sides \( dr, r \, d\theta, dz \) can also be a representative to achieve the same results.
3.4 Initial and boundary conditions

In this compendium, different boundaries and initial conditions will be consider for the one-dimensional diffusion equation in a medium bounded by two parallel planes in Cartesian and cylindrical coordinates. These can be applied in practice to diffusion into a plane sheet (in EOR, the space between two wells which is subjected to solvent flooding can be considered as a plane sheet) of material or in a radial porous medium used in reactors. First, the initial and boundary condition that can happen in mass transfer processes will be defined and then the corresponding solutions will be offered.

The general initial condition for any case of chemical transfer can be written as follows:

\[ C(X, t = 0) = f(X) \]  

(3.14)

Where \( f(x) \) can be expressed in several forms, such as a steady state type condition for production, an exponentially increasing or decreasing function with \( x \), or a constant value with distance. On the other hand, at the upper boundary \( (x = 0) \), the conditions can be categorized in two classes which are referred to concentration-type boundary and flux-type boundary conditions. The concentration-type boundary condition is defined as:

\[ C(X = 0, t) = s(t) \]  

(3.15)

And the flux-type boundary condition is defined as:

\[ -D \frac{\partial C}{\partial X} + vC = vs(t) \]  

(3.16)

Where \( s(t) \) also accept several distributions, like an exponentially increasing or decreasing function with time, a constant value in time (continuous feed solution), or a pulse-type distribution.
At the lower boundary \((X = L \text{ or } X \to \infty)\), the following condition can be implemented:

\[
C(X = L, t) = 0
\]  
(3.17)

This boundary works for the early stages of a closed system where the time was not sufficient enough for the chemical to reach the outer boundary and the solvent concentration at the boundary remains zero. The second one is:

\[
\frac{\partial C}{\partial X}(x \to \infty, t) = 0
\]  
(3.18)

This boundary condition is normally called the semi-infinite boundary condition where the system is long enough which can be called infinite medium for the solvent in contact with the solute. The other practical lower boundary condition is when there is no flux at the boundary in a closed finite system which is expressed as:

\[
\frac{\partial C}{\partial X}(X = L, t) = 0
\]  
(3.19)

Where \(L\) is the column length.

### 3.5 Analytical solution for one-dimensional mass transfer process

The diffusion equation can be solved analytically provided that the diffusion equation is constant. Different initial and boundary conditions generate various solutions, which have one of two standard forms. Either the solution consists of integrals or a series of error functions, in which case it is most suitable at small times for numerical evaluations. For the early stages, however, the solution is in the form of a trigonometric function that meets the results most satisfactorily for large values of time. When diffusion occurs in a cylinder coordinate, the trigonometric function is altered to a series of Bessel functions. If
the diffusion coefficient is not constant, then the partial differential equation (PDE) both in Cartesian and cylindrical coordinate would be a non-linear PDE, which should be solved numerically.

3.5.1 Diffusion process in one dimension in finite acting domain

Figure 3.2 shows a system of two chemicals that are in contact and because of the concentration difference in the two phases, the solvent starts migrating from the solvent phase to the solute phase.

Case 1: The overall mass diffusion equation and the initial condition applicable are:

\[
\frac{\partial C}{\partial T} = D \frac{\partial^2 C}{\partial X^2} \quad (3.20)
\]

\[C(X, T = 0) = 0 \quad (3.21)\]

And the boundary conditions are:

\[\frac{\partial C(X = L, T)}{\partial t} = 0 \quad (3.22)\]

\[C(X = 0, T) = C_0 \quad (3.23)\]

To solve the diffusion equation more easily, the equation and the condition are changed based on the below dimensionless parameters:

\[x_D = X/l \quad (3.24)\]

\[t_D = \frac{D}{l^2} T \quad (3.25)\]

\[c = \frac{C}{C_{eq}} \quad (3.26)\]

Therefore, the diffusion equation would be:
\[
\frac{\partial c}{\partial t_D} = D \frac{\partial^2 c}{\partial x_D^2}
\]
Figure 3.2. Schematic of two fluids in contact in one dimension
And the conditions transferred to:

\[ c(x_D, t_D = 0) = 0 \]  \hspace{1cm} (3.28)

\[ \frac{\partial c(x_D = 1, t_D)}{\partial t} = 0 \]  \hspace{1cm} (3.29)

\[ c(x_D = 0, t_D) = 1 \]  \hspace{1cm} (3.30)

To solve this problem, the method of separation of variables is utilized. This method can be applied to linear partial differential equations, especially those with constant coefficients in the equation. If we presume \( c(x, t) \) can be expressed as a product of a function of \( x \) and a function of \( t \), then it can be written:

\[ c(x_D, t_D) = R(x_D)H(t_D) \]  \hspace{1cm} (3.31)

This is an assumption and if the solution ends up with a paradox, then the assumption was false. If there is no contradiction, then the assumption is valid. By applying the above definition to the equation:

\[ \frac{\partial^2 c}{\partial^2 x_D} = R''(x_D)H(t_D) \]  \hspace{1cm} (3.32)

\[ \frac{\partial c}{\partial t_D} = R(x_D)H(t_D) \]  \hspace{1cm} (3.33)

Therefore:

\[ R(x_D)H(t_D) = DR''(x_D)H(t_D) \]  \hspace{1cm} (3.34)

\[ \frac{H(t_D)}{H(t_D)} \frac{R''(x_D)}{R(x_D)} \]  \hspace{1cm} (3.35)

Now the left hand side of equation 3.35 involves a function of \( t \) only and its derivative and the right hand side is a function of \( x \) only. Therefore altering the value of \( t \) cannot
change the right hand side and it stays constant. Similarly, changing the x value on the
right hand side does not have any effect on the value of the right hand side. Therefore this
equality should be a constant number or:
\[
\frac{H(t_D)}{H(t_D)} = D \frac{R''(x_D)}{R(x_D)} = k
\]  
(3.36)
Where \(k\) could be positive, negative, or zero. A simple mathematical analysis helps to
determine the sign of this number can be determined. After determining the sign and
quantity of this constant, based on the initial and boundary conditions, \(H(T)\) and \(R(X)\)
are calculated:
\[
H(T) = \exp \left( -D^2 \frac{(2n + 1)^2\pi^2}{4l^2} T \right)
\]  
(3.37)
\[
R(X) = \frac{4(-1)^n}{(2n + 1)\pi} \cos \left( \frac{(2n + 1)\pi}{2l} X \right)
\]  
(3.38)
And the final solution of the diffusion equation is:
\[
\frac{C(x,t)}{C_0} = 1 + \sum_{n=0}^{\infty} \frac{4(-1)^n}{(2n + 1)\pi} \cos \left( \frac{(2n + 1)\pi}{2l} X \right) \times \exp \left( -D^2 \frac{(2n + 1)^2\pi^2}{4l^2} T \right)
\]  
(3.39)
This solution was for that specific initial and boundary conditions. There is another
boundary condition which is very common in practice and is in the early stage of the
diffusion process when the concentration profile has not reached the outer boundary and
the concentration at:
\[
C(X = 0,T) = C_0
\]  
(3.40)
\[
C(X = l,T) = 0
\]  
(3.41)
\[ C(X, T = 0) = 0 \quad (3.42) \]

The same procedure from the last example should be applied to transfer the diffusion equation to the dimensionless form. However, it is not required to use the separation of variable for this case because by a simple changing of variable listed below, the diffusion equation will transfer from the partial differential form to the ordinary differential equation, which can be solved much easier:

\[ \eta = \frac{x}{2\sqrt{t}} \quad (3.43) \]

Using the above transformation, the diffusion equation will transfer to:

\[ \frac{\partial^2 c}{\partial^2 \eta} = -2\eta \frac{\partial c}{\partial \eta} \quad (3.44) \]

Implementing another changing of the variable is needed to solve this equation, which is:

\[ \frac{\partial \tilde{c}}{\partial \eta} = p \quad (3.45) \]

Therefore:

\[ \frac{\partial^2 c}{\partial^2 \eta} = \frac{dP}{d\eta} \quad (3.46) \]

Using the initial and boundary condition, the final solution for the concentration profile is achieved:

\[ \frac{C(x, t)}{C_0} = 1 - \text{erf} \left( \frac{x}{2\sqrt{D T}} \right) \quad (3.47) \]

\[ \frac{C(x, t)}{C_0} = 1 - \text{erf} \left( \frac{x}{2\sqrt{D T}} \right) \quad (3.48) \]

Where \( \text{erf} \) is called error function and is defined as:
As discussed before, the general form of the diffusion equation in the cylindrical coordinate system is:

\[
\frac{\partial C}{\partial t} = D \left( \frac{\partial}{\partial r_D} \left( r_D \frac{\partial C}{\partial r_D} \right) + \frac{1}{r_D} \frac{\partial^2 C}{\partial \theta^2} + \frac{\partial^2 C}{\partial z^2} \right)
\]

(3.50)

In this formula, \( r \) is the coordinate radius of the system. We consider that no angle dependence here because we have assumed circular symmetry. Moreover, there is no \( z \) dependence because we will be considering problems that have no extension along the \( z \)-axis (thin plates), therefore diffusion equation is reduced to:

\[
\frac{\partial U(r_D, t_D)}{\partial t} = \frac{D \left( \frac{\partial U(r_D, t_D)}{\partial r_D} + r_D \frac{\partial^2 U(r_D, t_D)}{\partial r_D^2} \right)}{r_D}
\]

(3.51)

The boundary and initial condition that are going to solve is listed as below:

\[ U(r_D = 0, t_D) = 1 \]

(3.52)

\[ \frac{\partial U(r_D = R, t_D)}{\partial r} = 0 \]

(3.53)

And

\[ U(r_D, t_D = 0) = 0 \]

(3.54)

The first variable change before we start separation of variable method to solve the problem is:
We use this definition to change the boundary condition in a way that the differential equation can be solved. Using this change of variable, the diffusion equation does not change, however the initial and boundary conditions are changed as follows:

\[ u(r_D = 0, t_D) = 0 \]  \hspace{1cm} (3.56)

\[ \frac{\partial u(r_D = R, t_D)}{\partial r_D} = 0 \]  \hspace{1cm} (3.57)

And

\[ u(r_D, t_D = 0) = -1 \]  \hspace{1cm} (3.58)

Using the separation of variable:

\[ u(r_D, t_D) = R(r_D) \cdot T(t_D) \]  \hspace{1cm} (3.59)

\[ \frac{\partial R}{\partial r_D} = R' \]  \hspace{1cm} (3.60)

\[ \frac{\partial^2 R}{\partial r_D^2} = R'' \]  \hspace{1cm} (3.61)

\[ \frac{\partial T}{\partial t_D} = T' \]  \hspace{1cm} (3.62)

Based on the above changes we have:

\[ \frac{T'}{T} = \frac{D \left( r_D \frac{R''}{R} + \frac{R'}{R} \right)}{r_D} = \beta \]  \hspace{1cm} (3.63)

The solution for this problem after applying the initial and boundary condition would be:

\[ u(r_D, t_D) = -\sum_{n=0}^{\infty} \frac{2J_1(\lambda)}{\lambda[J_0^2(\lambda) + J_1^2(\lambda)]} e^{-\lambda^2 D t_D} \times J_0(\lambda r_D) \]  \hspace{1cm} (3.64)
Where \( J_n(x) \) is the Bessel function of the first kind. These Bessel functions of the first kind \( J_n(x) \) are defined as the solutions to the Bessel differential equation:

\[
x^2 \frac{d^2 y}{dx^2} + x \frac{dy}{dx} + (x^2 - n^2) = 0
\]

These Bessel functions are sometimes called cylinder functions or cylindrical harmonics.

Using the equation 3.55 the final solution for the diffusion equation in cylindrical coordinate is:

\[
u(r_D, t_D) = U(r_D, t_D) - 1
\]

\[
U(r_D, t_D) = 1 - \frac{2}{\lambda} \sum_{n=0}^{\infty} \frac{J_1(\lambda)J_0(\lambda r)}{U_0^2(\lambda) + J_1^2(\lambda)} e^{-\lambda^2 D t} J_0(\lambda r_D)
\]

### 3.5.2.1 Analytical solution of diffusion in a hollow cylinder

The diffusion equation in cylindrical geometry without any extension in \( z \) direction and no angel dependency with a constant diffusion coefficient is:

\[
\frac{\partial C(r, t)}{\partial t} = D \frac{\partial^2 C(r, t)}{\partial r^2}
\]

Let’s suppose the diffusion process in a hollow cylinder with an inner and outer radius, \( a \), and \( R \) respectively. The concentration of the inner surface is \( C_0 \) and at the outer surface there is no flux, and initially the concentration between inner and outer surface is zero.

Therefore, the general overview of the system and the conditions are as they are depicted in Figure 3.3:
Figure 3.3. Schematic of a hollow cylinder with inner radius of $a$ and outer radius of $R$. The boundary condition is $C(r, t)_{r=a} = C_0$, and the differential equation is $\frac{\partial C(r, t)}{\partial r} = 0$ at $r=R$.
Using the cylindrical form of diffusion and the following variable changes, the diffusion equation would be:

\[ x = \frac{r}{a} - 1 \]  \hspace{1cm} (3.72)

And:

\[ c = \frac{C}{C_0} - 1 \]  \hspace{1cm} (3.73)

Therefore:

\[ c(x = 0, t) = 0 \]  \hspace{1cm} (3.74)

\[ \frac{\partial c}{\partial r} \left( x = \frac{R}{a} - 1, t \right) = 0 \]  \hspace{1cm} (3.75)

\[ c(x, t = 0) = 0 \hspace{1cm} \frac{a - 1}{a} < x < \frac{R - 1}{a} \]  \hspace{1cm} (3.76)

And:

\[ \frac{\partial c(x, t)}{\partial t} = \frac{D}{a^2 x} \left( \frac{\partial c(x, t)}{\partial x} + x \frac{\partial^2 c(x, t)}{\partial x^2} \right) \]  \hspace{1cm} (3.77)

Same as the previous problems, the separation of variables is applied to solve this problem. It is assumed that the concentration profile is comprised of two separate
functions in which each function is independent of the other. Therefore the concentration is:

\[ c(x, t) = R(x). T(t) \]  

(3.78)

Using these functions and replacing them in the equation 3.77, the answer would be:

\[ \frac{\partial(T(t))}{T(t)\partial t} = \frac{D}{a^2 R(x)x} \left( \frac{\partial(R(x))}{\partial x} + x \frac{\partial^2(R(x))}{\partial x^2} \right) \]  

(3.79)

\[ \frac{\partial(R(x))}{\partial x} = R' \]  

(3.80)

\[ \frac{\partial^2(R(x))}{\partial x^2} = R'' \]  

(3.81)

\[ \frac{\partial(T(t))}{\partial t} = T' \]  

(3.82)

\[ \frac{T'}{T} = \frac{D}{a^2 x} \left( x \frac{R''}{R} + \frac{R'}{R} \right) = \beta \]  

(3.83)

Allocating different values (e.g., positive, negative and zero value) for \( \beta \), and analyzing the answers for each case suggests that negative values would be the right value for \( \beta \), thus the \( t \) function is:

\[ T(t) = A_4 e^{-\frac{\lambda^2 D}{a^2} t} \]  

(3.84)

And the equation in \( r \) direction is:

\[ xR'' + R' + \lambda^2 xR = 0 \]  

(3.85)

Which is the first kind of Bessel partial differential equation. If the boundary conditions are applied, the final solution in \( r \) direction would be:

\[ R(x) = A_5 j_0(\lambda x) \]  

(3.86)
Since the two equations from the original function are found, the solution for the concentration would be:

\begin{equation}
\frac{\partial c}{\partial r} \left( r = \frac{R}{a} - 1, t \right) = 0
\end{equation}

\begin{equation}
\sum_{n=0}^{\infty} \frac{\partial}{\partial r} A_n e^{-\lambda^2 \frac{D}{a^2} t} x J_0(\lambda x) = 0
\end{equation}

If the other boundary of the system is recruited on the equation, the \( \lambda \) value will be determined:

\begin{equation}
J_1 \left( \frac{\lambda R}{a} - 1 \right) = 0
\end{equation}

Therefore, the roots of the above equation determine the Eigen value \( \lambda \) for the solution.

The only term that can make the above equation equal to zero is:

\begin{equation}
c(x, t = 0) = -1
\end{equation}

\begin{equation}
u(x, t = 0) = \sum_{n=0}^{\infty} A_n J_0(\lambda x) = -1
\end{equation}

If the above equation gets solved by exploiting the Bessel function properties, \( A_n \) function would be:
\[ A_n = \frac{-2J_1(\lambda)}{\lambda[j_1^2(\lambda) + j_1^2(\lambda)]} \] (3.94)

Therefore, the solution for concentration as a combination of the two separate functions is:

\[ c(x, t) = -\sum_{n=0}^{\infty} \frac{2J_1(\lambda)}{\lambda[j_0^2(\lambda) + j_1^2(\lambda)]} e^{-\lambda^2 \frac{D}{a^2} \tau} \times J_0(\lambda x) \] (3.95)

By enrolling the very first variable change for \( c(x, t) \), the answer in dimensionless form would be:

\[ \frac{C(r, t)}{C_0} = 1 - \frac{2}{\lambda} \sum_{n=0}^{\infty} \frac{J_1(\lambda)}{[j_0^2(\lambda) + j_1^2(\lambda)]} e^{-\lambda^2 \frac{D}{a^2} \tau} \] (3.96)

3.5.3 1D Convection-Diffusion process

3.5.3.1 A general overview

The Convection-Diffusion (CD) equation is implemented in a various engineering problems, including smoke plume in the atmosphere, migration of contaminants in a stream, tracer dispersion in a porous medium, dispersion of chemicals in reactors, etc. Van Genuchten 1981, Jury et al 1983, Javandel et al 1984, Leij et al., 1992, and Quezada et al., 2004 discussed their applications.

Perhaps the most commonly cited analytical solution of the CD equation is that reported by Grobner and Hofreiter and later by Ogata and Banks for a semi-infinite domain equation. In addition, an analytical solution to the one-dimensional diffusion-convection equation was presented by Mohsen and Baluch for fixed concentration boundary conditions on a finite domain. The aim of their paper was to develop an analytical
solution valid at the end points of the domain of interest. A decomposition of the original formulation of the problem, and then a separation of variables solution of the resultant equations, gave the required result. A similar goal, requiring continuity of an analytical solution at the extremities of the domain, has recently been reported for a much more complex physical situation, where a solute is transported and adsorbed in a fractured porous medium. Advective transport, molecular diffusion and mechanical dispersion of a contaminant within an array of parallel fractures, with lateral diffusive mass transport from the fractures into the porous matrix material were modeled. The formulation of the problem involved two coupled non-steady state partial differential equations; the solution developed for the porous matrix was clearly not continuous at the fracture-matrix interface, at the end point of the finite domain. Their solution for the contaminant concentration within the porous matrix was also incorrect for algebraic reasons. Davis and Johnston presented both the corrected analytical solution for the matrix, as well as an alternate solution valid at the fracture-matrix interface with enhanced convergence properties.

First, an analytical solution of the one-dimensional CD equation over the finite domain, $0 \leq x \leq L$ is presented here. The interval considered includes the two end points $x=0$ and $x=L$. It is shown that this solution is a more general form of a similar solution of the heat-conduction equation generated for the open interval $0 < x < L$, a domain that excludes the two end points. The CD equation over a semi finite domain $0 \leq x < \infty$ is then solved analytically using Laplace transform technique for two cases. Afterwards, numerical methods were used to solve the CD equation and then to compare with the exact solution.
3.5.3.2 Analytical solution of 1-D Convection-Diffusion in cylindrical domain

The Convection-Diffusion (CD) equation exhibits many of the features of petroleum reservoir simulation equations. The Convection-Diffusion equation can be written in the form of:

\[ D \frac{\partial^2 C(X,T)}{\partial^2 X} - v \frac{\partial C(X,T)}{\partial X} = \frac{\partial C(X,T)}{\partial T} \]  \hspace{1cm} (3.97)

Where \( v \) is the convective rate, \( D \) is the diffusion coefficient, \( C(x,t) \) is concentration distribution, \( x \) is location, and \( t \) is time. For the finite domain, two methods will be introduced based on the boundary conditions that we are going to consider. The first method is separation of the variable and the second would be the Laplace transform method. These two methods will result in two different solutions, but with each specific application. First, separation of the variable is brought into review. The boundary conditions for our problem are:

\[ C(X = 0,T) = C_0 \]  \hspace{1cm} (3.98)

\[ \frac{\partial C}{\partial X}(X = l,T) = 0 \]  \hspace{1cm} (3.99)

\[ C(X,T = 0) = 0 \]  \hspace{1cm} (3.100)

This means that there is no initial solvent concentration inside the system (initial condition) and at the upper boundary \( (x = 0) \), the concentration is constant, and at the lower boundary \( (x = l) \), there is no concentration flux in the system. Introducing the Peclet number:

\[ pe = \frac{vL}{D} \]  \hspace{1cm} (3.101)
Using this variable in the CD equation and converting the CD equation to a
dimensionless form, it will be modified to:

\[
\frac{\partial^2 c}{\partial x_D^2} - p e \frac{\partial c}{\partial x_D} = \frac{\partial c}{\partial t_D}
\tag{3.102}
\]

Where \(c\) is the dimensionless form of saturation \(c = \frac{C}{C_0}\), \(x\) is the dimensionless form of
distance \(x_D = \frac{X}{L}\) and \(t\) is the dimensionless value of \(t = \frac{D T}{L^2}\). The first step for
solving this equation is transferring this equation into a form that can be solved by the
available rules that can be conducted in partial differential equations. Therefore, we
defined this variable as:

\[
\psi = c \cdot \exp\left(-\frac{p e \cdot x_D}{2}\right)
\tag{3.103}
\]

Which gives:

\[
c = \psi \cdot \exp\left(\frac{p e \cdot x_D}{2}\right)
\tag{3.104}
\]

Based on this definition, we will have:

\[
c_{xx} = \left(\psi \cdot \exp\left(\frac{p e \cdot x_D}{2}\right)\right)_{xx}
\tag{3.105}
\]

\[
c_x = \left(\psi \cdot \exp\left(\frac{p e \cdot x_D}{2}\right)\right)_x
\tag{3.106}
\]

\[
c_t = \left(\psi \cdot \exp\left(\frac{p e \cdot x_D}{2}\right)\right)_t
\tag{3.107}
\]

Using the above relations in Equation 97:
Another step is needed here to convert this equation into a solvable differential equation.

Thus, following definition is introduced:

\[
\mu = \frac{pe}{2} \tag{3.109}
\]

\[
y = \frac{pe}{2}x \tag{3.110}
\]

\[
s = \frac{pe^2}{4}t \tag{3.111}
\]

Undertaking the above relations:

\[
\psi_{xx} - \frac{pe^2}{4} \psi = \psi_t \Rightarrow \psi_{yy} - \psi = \psi_s \tag{3.112}
\]

Now if the boundary condition is applied:

\[
\psi(y, s) = \frac{cosh(y - \mu)}{cosh(\mu)} + \frac{2}{\mu} \sum_{n=1}^{\infty} \frac{(2n - 1)\pi}{2\mu} \sin \left( \frac{(2n - 1)\pi}{2\mu} y \right) \cdot \exp \left( -1 \right) + \left( \frac{(2n - 1)\pi}{2\mu} \right)^2 s \tag{3.113}
\]

And replacing the values for:
Another way to solve the one-dimensional convection diffusion equation is to use Laplace transform. Cleary and Adrian (1973) used this method with the same boundary conditions that was used in the separation of variables. They reported the solution:

\[
\frac{c}{c_0} = 1 - \sum_{m=1}^{\infty} \frac{2\beta_m \sin \left( \frac{\beta_m x}{L} \right) \exp \left( \frac{v_x}{2D} - \frac{v^2 t}{4D} - \frac{\beta_m^2 D t}{L^2} \right)}{\beta_m^2 + \frac{vL}{2D} + \left( \frac{vL}{2D} \right)^2}
\]

(3.115)

Where the Eigen values \( \beta_m \) are the positive roots of:

\[
\beta_m \cot(\beta_m) + \frac{vL}{D} = 0
\]

(3.116)

The series solution converges very slowly for large values of \( \frac{vL}{D} \) and/or small values of \( \frac{vL}{L} \). For:

\[
pe = \frac{\frac{vL}{D} \cdot \frac{vL}{D}}{\frac{vL}{D}} > 5 + 40 \frac{vt}{L}
\]

(3.117)

Or:
\[
\frac{vL}{D} > 100
\] (3.118)

In these conditions, the following approximation gives very accurate answers (Van Genuchten and Alves, 1980)

\[
\frac{C}{C_0} = \frac{1}{2} \text{erfc} \left( \frac{x - vt}{2(Dt)^{\frac{1}{2}}} \right) + \frac{1}{2} \exp \left( \frac{vx}{D} \right) \text{erfc} \left( \frac{x + vt}{2(Dt)^{\frac{1}{2}}} \right)
\]

\[+ \frac{1}{2} \left[ 2 + \frac{v(2L - x)}{D} + \frac{v^2 t}{D} \right] \exp \left( \frac{vL}{D} \right) \text{erfc} \left( \frac{(2L - x) + vt}{2(Dt)^{\frac{1}{2}}} \right) \] (3.119)

\[- \sqrt{\frac{v^2 t}{\pi D}} \exp \left( \frac{vL}{D} - \frac{1}{4Dt} (2L - x + vt)^2 \right) \]

The above approximation was used by some researchers to investigate convection diffusion processes in reservoir conditions (Oguztorli et al 1984, Shrivastava 2005).
3.6 Numerical solution for PDE

The numerical solution of time dependent nonlinear partial differential equations is a complex and intricate process. In general, even slightly different partial differential equations are required the development of separate and different computer programs. In recent times, refined and reliable computer programs for solving nonlinear systems of ordinary differential equations have become available. The method of lines approach is one of these techniques and is an effort to take advantage of these developments for solving partial differential equation. In this section, the advantages and disadvantages of this methodology (e.g., the method of line) will be briefly discussed. In this section, the partial differential equations that were presented in the previous sections can be solved numerically. One of these methods is using PDETWO method. PDETWO routine has been developed in a joint effort between Boeing Computer Service Company and Kansas State University in late 1970s and early 1980s. It is a software interface to solve time-dependent coupled systems of nonlinear partial differential equations (PDEs), which are defined over a two dimensional rectangular region. The software interface employs the method of lines technique whereby centered differencing with respect to the two spatial variables results in a system of time-dependent ordinary differential equations (ODEs), which can then be solved using one of the readily available ODE integrators.

3.7 PDETWO code

PDETWO (Melgaard and Sincovec 1981) is aimed to solve systems of partial differential equations defined over a region using a normal differential equation integration package. Once the domain equations are defined, PDETWO forms and calculates a discrete approximation of the partial differential equations using the method of lines. Partial
differential equations structures which are allowed by PDE TWO, covers wide range of possible PDE forms:

\[
\frac{\partial u_i}{\partial t} = f_i \left( t, x, y, u_1, \ldots, u_{NPDE}, \frac{\partial u_1}{\partial x}, \ldots, \frac{\partial u_{NPDE}}{\partial x}, \frac{\partial u_1}{\partial y}, \ldots, \frac{\partial u_{NPDE}}{\partial y}, \frac{\partial}{\partial x} \left( DH_{i,1} \frac{\partial u_1}{\partial x} \right), \ldots, \frac{\partial}{\partial x} \left( DH_{i,NPDE} \frac{\partial u_{NPDE}}{\partial x} \right), \frac{\partial}{\partial y} \left( DV_{i,1} \frac{\partial u_1}{\partial y} \right), \ldots, \frac{\partial}{\partial y} \left( DV_{i,NPDE} \frac{\partial u_{NPDE}}{\partial y} \right) \right) \]

Let us assume that NPDE denotes the number of PDEs over the region \( R \) for which a solution, \( u_i (t, x, y) = (i = 1, 2, \ldots, NPDE) \) is desired. \( R \) is defined by \( R \equiv \{(x, y)|a_1 \leq x \leq b_1, a_2 \leq y \leq b_2 \} \). The coupled system of PDEs is defined as:

\[ a_1 \leq x \leq b_1, a_2 \leq y \leq b_2, t > t_0, i = 1, 2, \ldots, NPDE \]

With horizontal boundary conditions,

\[ AH_i u_i + BH_i \frac{\partial u_i}{\partial y} = CH_i \]

at \( a_1 \leq x \leq b_1, y = a_2 \) or \( y = b_2, i = 1, 2, \ldots, NPDE, t > t_0 \)

Vertical boundary conditions,

\[ AV_i u_i + BV_i \frac{\partial u_i}{\partial y} = CV_i \]

at \( x = a_1 \) or \( x = b_1, a_2 \leq y \leq b_2, i = 1, 2, \ldots, NPDE, t > t_0 \)

And initial conditions
All functions of $f_i, DH_{ij}, DV_{ij}, AV_i, BV_i, CV_i, AH_i, BH_i, CH_i$ and $\phi_i$ are at least piecewise continuous functions of all their respective variables. The diffusion coefficient in the vertical and horizontal direction are a function of $t, x, y$ and $u$ where $u \equiv (u_1, u_2, ..., u_{NPDE})$. If $BV_i \neq 0$ (or $BH_i \neq 0$) then the boundary coefficients $AV_i, BV_i$ and $CV_i$ ($AH_i, BH_i$ and $CH_i$) may be functions of $t, x, y$ and $u$ but otherwise they may be only functions of $t, x$ and $y$. PDETWO can handle all three types of boundary conditions, Dirichlet ($BH_i$ or $BV_i = 0$), Neumann ($AH_i$ or $AV_i = 0$), or mixed ($AH_i \neq 0, BH_i \neq 0$, or $AV_i \neq 0$ or $BV_i \neq 0$) without the need to distinguish between types. Nevertheless, there are limitations over this type of definition, PDETWO is capable of handling a large variety of problems.

### 3.8 Algorithm flow of the PDETWO routine

The main routine sets all system initial variables, work arrays, assigns initial data provided from the calling program, and calls the PDETWO to accomplish equation solution. PDETWO solves the partial differential equations and calls the routines for calculating boundary conditions, diffusion parameters, and the partial differential equation function.

System characteristics and physical conditions from the calling program are allocated and the solution domain is created. PDETWO requires the user to supply the required number of solution points in all coordinate directions as well as the initial step size for the integrator. Using user complete data and solution necessities the code distributes the
domain into uniform sections and allocates memory to produce solutions at all nodal intersections as is required by PDETWO.

Input data from the program is scrutinized to determine the initial and boundary conditions, and the assumptions. After this is concluded, all data for solution is prepared and the physical properties routine is called by the main function. The main routine then checks if the system has been solved. If no solution has been attained, PDETWO is called and solution advances. PDETWO initiates solution using the boundary, diffusion, kinetic and function evaluation functions.

3.9 Performance and accuracy of PDETWO

This section examines the performance and accuracy of the PDETWO software using a known analytical solution for a partial differential equation. Before executing of the model equations, PDETWO results were first compared to known analytical results for a specified test equation. Equation (3.120) denotes diffusion equation:

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{3.120}
\]

With the following initial and boundary conditions:

\[
c(x = 0, t) = 1 \tag{3.121}
\]
\[
c(x = l, t) = 0 \tag{3.122}
\]
\[
c(x, t = 0) = 0 \tag{3.123}
\]

The solution for the Equation (3.120) is:

\[
c(x, t) = 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)
\]
Table 3.1 shows the results of the analytical and PDETW solutions for a solute column with unity length at different times and $D$ was assigned to be 0.0001. Note that PDETW was capable of matching the analytical solution to within 0.003%, evidently representing outstanding accuracy. Additional accuracy comparisons for multi-dimensional unsteady state equations can be found in published literature on PDETW (Melgaard and Sincovec 1981).
Table 3.1. Comparison between analytical and PDETWO method to solve a diffusion equation for $D = 0.001$ at different time for a unity column of solute

<table>
<thead>
<tr>
<th>t</th>
<th>Analytical</th>
<th>PDETWO</th>
<th>Relative Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>0.0253</td>
<td>0.0254</td>
<td>0.003953</td>
</tr>
<tr>
<td>1200</td>
<td>0.0412</td>
<td>0.0411</td>
<td>0.002427</td>
</tr>
<tr>
<td>1400</td>
<td>0.0587</td>
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<td>0.003407</td>
</tr>
<tr>
<td>1600</td>
<td>0.0771</td>
<td>0.0778</td>
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</tr>
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<td>0.0955</td>
<td>0.0960</td>
<td>0.005236</td>
</tr>
<tr>
<td>2000</td>
<td>0.113</td>
<td>0.115</td>
<td>0.017699</td>
</tr>
<tr>
<td>2200</td>
<td>0.131668</td>
<td>0.125</td>
<td>0.050643</td>
</tr>
<tr>
<td>2400</td>
<td>0.148915</td>
<td>0.145</td>
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</tr>
<tr>
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<td>0.007668</td>
</tr>
</tbody>
</table>
3.10 Summary

To determine a solvent diffusion coefficient in a liquid phase using indirect methods, three steps should be followed. First, solubility of the solvent should be measured using an experimental approach at a specified pressure and system temperature. Second, the mass transfer process between the two phases should be modeled using the appropriate physical condition of the system. Last, the developed model should be solved either by analytical method-if possible- or by numerical method. In this chapter, different mass transfer equations with and without convection were reviewed and partially solved analytically or numerically. Analytical methods usually are used when the mass transfer equation is not complex and usually in one or two dimension. If the model applied for an equation is complicated and there is no unique analytical approach, numerical solution can be utilized to create a solution for the mass transfer model. The numerical method proposed in this chapter was PDETWO method developed in FORTRAN environment. This approach intended to solve systems of partial differential equations defined over a region using a normal differential equation integration package. Once the domain equations are defined, PDETWO forms and calculates a discrete approximation of the partial differential equations using the method of lines. Moreover, it can handle all sorts of initial and boundary conditions that outfits the physical model. In this study, analytical method will be used for the experiments under static condition and PDETWO method will be used where convection is involved in the mass transfer process or for the study in the porous media.
Chapter 4

Solubility Measurement and Diffusion Coefficient Calculation of CO₂ in Bulk Heavy Oil under Static Condition

Solvent solubility in a liquid is an intensive property that depends on the pressure and temperature of the system, type of solvent, physical and compositional properties of the solute and the media that the solvent and the solute are in contact (bulk or porous media). The focal point of this chapter is to measure the solubility and the diffusion coefficient of CO₂ in different types of oil at different pressures and temperatures. Measuring solubility will be performed in several experiments and the diffusion coefficient will be determined using the mathematical relationship between the solubility and the diffusion process time. In this chapter, all the experiments and mathematical analysis will be covered and discussed.

4.1 Heavy oil and solvent properties

In this study, two heavy oil samples were used to perform the experimental tests, which were collected from the Plover Lake area in Saskatchewan, Canada. The compositional analysis results of these samples obtained by using simulated distillation are given in Table 4.1 and Table 4.2. These tables show that the composition of the light component under C₇ is zero, which means that there is no light oil component in either oil. Furthermore, the grouped carbon number distribution of the two heavy crude oil samples is depicted in
Figure 4.3. Moreover, the density behaviour of the two heavy oils at the experimental temperature is plotted in Figure 4.1 and Figure 4.2. As expected, these figures show that there is a linear relationship between the temperature and density of the oil samples. The attempt was to measure and report the density data for the temperature of the experimental tests. However, a very good estimation can be made by these relationships for future works. In this study, one of the oil samples has a density and viscosity of 971.75 kg/m$^3$ and 5 Pa.s at 298 K, respectively, along with molecular weight of 642.65 gr/mole. The density and viscosity of the other oil sample are 20 Pa.s and 979.74 kg/m$^3$ at 298K with 663.55 gr/mole molecular weight. Moreover, CO$_2$ with a purity of 99.99%, supplied by Praxair Inc., was used as the injected solvent.
<table>
<thead>
<tr>
<th>Carbon Number</th>
<th>Mol.%</th>
<th>Carbon Number</th>
<th>Mol.%</th>
<th>Carbon Number</th>
<th>Mol.%</th>
</tr>
</thead>
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Molecular weight: 642.65 gr/mole, Oil density: 971.75 Kg/m³

* Compositional analysis of the oil samples used in this study were carried in Saskatchewan Research Council (SRC)
Figure 4.1. Density change versus temperature of the heavy oil sample with viscosity of 5 Pa.s
**Table 4.2.** Compositional analysis results of the heavy oil sample with viscosity of 20 Pa.s

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<th>Carbon Number</th>
<th>Mol.%</th>
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</table>

Molecular weight: 663.55 gr/mole, Oil density: 979.74 Kg/m³

* Compositional analysis of the oil samples used in this study were carried in Saskatchewan Research Council (SRC)
Figure 4.2. Density change versus temperature of the heavy oil sample with viscosity of 5 Pa.s
Figure 4.3. The grouped carbon number distribution of the two heavy crude oil samples
4.2 Experimental set-up of pressure decay method (static condition)

Three 2-D cylindrical stainless steel diffusion cells with a constant volume were recruited to perform a pressure decay experiment for a CO\textsubscript{2} heavy oil system. This cylindrical cell has a 12 cm length and 6 cm diameter with a cap at each end. The top cap of the transfer diffusion cell is connected to the CO\textsubscript{2} supply cylinder through a needle valve (SS-0VS2, Swagelok, U.S.A.).

To increase the accuracy of the oil mass injected to the CO\textsubscript{2} heavy oil system, the fluid was injected manually. To measure more precisely the weight of the oil, a COLE-PARMER balance (Symmetry ED2000, Max 2000g and d= 0.1) with errors ±0.1 g errors was utilized to measure the weight of the oil, and then that oil would be introduced into the diffusion cell.

Besides this high pressure diffusion cell, there is a need for a pressure transducer to measure the inline solvent pressure versus time. Therefore, a PM digital pressure indicator from the HEISE Company with capability of two ports designed in the pressure transducer were implemented to perform the tests. This pressure transducer is used to indicate CO\textsubscript{2} pressure inside the diffusion cell with an accuracy of ±0.1 KPa. Online data gathering and pressure display are made through the HyperTerminal interface, which is available in all Windows based computers. The pressure indicator itself also has a display screen to show the pressure data. An isothermal air-bath was also designed to make a closed space through which the pressure decay tests can be conducted, and all these instruments are assembled inside the air-bath. In mean time, a temperature controller is used to adjust the heat supply from an electric heater. The temperature signal from inside the air-bath to the controller is provided by a thermocouple, which is allocated in the
middle part of the air-bath. Two fans help the heater keep a constant temperature by circulating the air inside the air-bath. Figure 4.4 shows the schematic of the air-bath with the instruments installed inside to do the pressure decay tests.

**Figure 4.4.** Schematic design for experimental measurement of CO₂ solubility and diffusion coefficient in heavy oil under static condition
4.3 Experimental procedure (pressure decay method-static condition)

In an isolated air-bath, with a heater and three fans installed, an isothermal condition was achieved for each specific test during pressure decay experiments. The system was left in the air-bath for 24 hours to ensure that the oil is at a uniform pre-set temperature. Before gas was brought into contact with the oil, the cylinder was vacuumed to remove the existing air from the empty space so that no impurities are present in the solvent phase. The cylinder was then charged with CO\textsubscript{2} with a purity of 99.99 percent supplied by Praxair at the pre-defined pressure and temperature. The pressure decay was then recorded for a period of time until no more pressure reduction was observed. At that point, the test was terminated and an additional test was set-up. The general procedure for pressure decay tests are summarized below:

1. Preparing the three stainless steel cells for the tests. Connect the connections and valves to the pressure gauge, transfer cell and vacuum pump. The whole system is connected to properly run the experiments.

2. Vacuuming the system used in the pressure decay measurements.

3. Injecting 50 gr of oil into the cylinders, setting-up the operating temperature of the system and leaving the system inside the closed air-bath for 24 hours to make sure that the oil temperature and the operating temperature are the same.

4. Injecting CO\textsubscript{2} into the cylinders at pressures of 1.73, 3.10 and 4.49 MPa at 295 K (pre-define pressures and temperatures). Reading the data until the pressure in the cells remains constant. These pressures reflect the initial operating pressure of the system.
5. Using the digital pressure gauge connected to a computer, record the pressure reduction in each cell; Continue this process until no further pressure decay occurs in the cells.

6. Stopping the experiment and cleaning the cells for the next pressure decay tests.

7. Repeating the procedure for 298, 301 and 305 K.

8. Changing the type of the oil and re-running all the tests at the defined pressures and temperatures.

4.4 Experimental results for CO$_2$ solubility under static condition

The experimental results are shown and analyzed in this section and the pressure data obtained from the experiments at the initial operating pressures under different operating temperatures are classified. In total, 24 experiments were conducted to measure the solubility of CO$_2$ in two types of heavy oil. The pressure data was used to calculate the mass of CO$_2$ dissolved in the oil phase during the experiments. Moreover, the concentrations of dissolved CO$_2$ in the oil were calculated, and then the percentage of the concentration or weight percent of the dissolved CO$_2$ were reported.

The solubility of CO$_2$ is determined by relating the state functions associated with the matter, which are temperature, pressure, and volume to each other. For a closed system, the equation for mass dissolved into the oil is:

\[
m = \frac{VM}{RT} \left( \frac{P_i}{Z_i} - \frac{P_f}{Z_f} \right)
\]  

(4.1)
Where $P_i$ and $P_f$ are the initial and final pressures of the solvent (i.e., CO$_2$), $V$ is CO$_2$ volume, $M$ is the molecular volume of CO$_2$, and $T$ is the operating temperature. In this formula, $Z_i$ and $Z_f$ are the compressibility factor of CO$_2$ at initial and final pressures that were calculated using WinProp software. Using the final and initial pressures, the dissolved mass of CO$_2$ has been calculated for 1.73 MPa and is plotted through Figures 4.4 to 4.7 for oil with 5 Pa.s viscosity at 295 K. To transform this mass value to the concentration form, the following equation has been implemented:

$$C = \frac{m_{solvent}}{m_{total}} \times 100 \frac{gr}{gr}$$ (4.2)

Figures 4.5 to 4.8 also show the corresponding weight percent concentrations of CO$_2$ for each temperature at 1.73MPa.
Figure 4.5. Pressure decay data at $P = 1.73$ MPa and the corresponding mass and concentration of CO$_2$ in oil with $\mu = 5$ Pa.s at $T = 295$ K.
Figure 4.6. Pressure decay data at $P = 1.73$ MPa and the corresponding mass and concentration of CO$_2$ in oil with $\mu = 5$ Pa.s at $T = 298$ K.
Figure 4.7. Pressure decay data at $P = 1.73$ MPa and the corresponding mass and concentration of CO$_2$ in oil with $\mu = 5$ Pa.s at $T = 301$ K.
Figure 4.8. Pressure decay data at $P = 1.73$ MPa and the corresponding mass and concentration of CO$_2$ in oil with $\mu = 5$ Pa.s at $T = 305$ K.
As it can be seen from the above figures, the solubility of CO$_2$ is decreased as the operating temperature of the system increased. Although the viscosity of the oil drops when the temperature increases, the solubility ultimately decreases. In addition, when the temperature increases, the stability of the equilibrium is more impacted. On the other hand, reaching the equilibrium condition of the experiments requires more time as the operating temperature of the system increases from room temperature to 305K. It is because by increasing the temperature, the time needed to stop the pressure decay test increased as depicted in Figures 4.5 to 4.8. The figures depict the results at one pressure and four temperatures. The rest of the pressure decay data and its solubility can be found in Appendix A. However, the final solubility values of each test are summarized in Tables 4.3 and 4.4.
Table 4.3. Solubility of CO$_2$ in heavy oil sample with $\mu = 5$ Pa.s viscosity under static condition

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<tr>
<th>$T$ (K)</th>
<th>Initial pressure (MPa)</th>
<th>Final Pressure (MPa)</th>
<th>Mass of dissolved CO$_2$ (g)</th>
<th>Solubility (wt%)</th>
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Table 4.4. Solubility of CO$_2$ in heavy oil sample with $\mu = 20$ Pa.s viscosity under static condition

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Initial pressure (MPa)</th>
<th>Final Pressure (MPa)</th>
<th>Mass of dissolved CO$_2$(g)</th>
<th>Solubility (wt%)</th>
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4.5 Effect of operating conditions on CO$_2$ solubility in heavy oil

When the temperature of the system increases, CO$_2$ solubility in both of the heavy oil samples decreases. The second law of thermodynamics can be utilized to explain the reason of this phenomenon. As the temperature of the system increases, it enables the solvent particles to move more freely between the solution and the gas phase. Thermodynamics second law foretells that these particles will change to the more disordered, more dispersed, and therefore, more probably gaseous state. On the other hand, the viscosity of the solute and solvent are affected by temperature changes. In other words, as the temperature of the solute (oil phase) increases, its viscosity decreases. The cohesive forces between the molecules in the liquid phase dominate the molecular momentum transfer between the molecules because the molecules are closely packed. When the liquid is heated, the cohesive forces between the molecules reduce, thus the forces of attraction between them reduce, which that leads to the reduction of the oil viscosity. However, a temperature increase has an adverse effect on the viscosity of fluids in gas phases. If the temperature of a system increases, the molecular momentum transfer rate increases further, which increases the viscosity of the gas.

The effect of temperature on the solubility of CO$_2$ at different initial pressures on heavy oil using pressure decay technique is shown in Figures 4.9 to 4.11. These figures are prepared using the data reported in Tables 4.3 and 4.4. As it can be seen from these figures, CO$_2$ solubility increases when CO$_2$ initial pressure increases; however, the difference between CO$_2$ solubility in two heavy oil samples decrease at higher pressures. It can be suggested that CO$_2$ solubility is more sensitive to the initial pressure of the solvent (i.e., CO$_2$) than the heavy oil viscosity. Another finding about these results is that
at higher temperature (i.e., 305 K), the difference of the solubility is higher than the results at lower temperature (i.e., 295 K) for any pressure. In other words, as the temperature of the system increases, the effect of pressure on CO$_2$ solubility decreases slightly.
Figure 4.9. Effect of temperature on CO$_2$ solubility at $P = 1.73$ MPa under static condition.
Figure 4.10. Effect of temperature on CO$_2$ solubility at $P = 3.10$ MPa under static condition.
<table>
<thead>
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**Figure 4.11.** Effect of temperature on CO₂ solubility at $P = 4.49$ MPa under static condition.
4.5.1 **Diffusion coefficient calculation at static condition**

Achieving experimental results leads us to determine the diffusion coefficient in the bulk heavy oil under different test conditions. According to the previously mentioned literatures, using the one-dimensional diffusion equation results in a relationship between the solubility of the solvent, the diffusion coefficient and the time required to obtain the desired solubility. However, it should be considered that the proper boundary and initial conditions must be assigned to the mathematical model in order to give the best solution to the problem. In this section, the whole procedure of determine the diffusion coefficient in the static condition of bulk heavy oil contacting CO$_2$ is introduced and the calculated results will be reported.

To estimate the diffusion coefficient and to obtain an analytical solution, a few simplifying assumptions were considered to solve the mass transfer equation. These assumptions were a non-reactive system, isothermal conditions, a constant diffusion coefficient, constant gas compressibility factor, non-volatile bitumen, negligible bitumen swelling, equilibrium at the gas–bitumen interface, and the applicability of Henry's law.

4.5.2 **Mathematical analysis**

In section 3.5.1, the mathematical solution for the one-dimensional diffusion equation (Fick’s second law) in a finite domain was introduced and discussed. The mathematical model for the one-dimensional diffusion equation is:

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{4.3}
\]

The model that has been used in the experiments has very good agreement with the above conditions. In this model, the initial CO$_2$ concentration in the oil phase is zero, which is
almost the case that designed in the lab. If the amount of CO$_2$ transferred from the solvent phase to the oil phase during injection time is neglected, then this assumption is applied to this problem. Since the oil used in the experiments were viscous and heavy, it can be assumed that in the short period of injection time, no mass transfer happens between the solvent phase and the oil phase. For boundary conditions used in the experiments, one of the boundaries is the interface of the oil in contact with enriched solvent. For this boundary, it is always considered that the concentration of CO$_2$ remains at its initial value, which is consistent with the conditions of our experiments. On the other hand, the oil faces a closed interface at the other end, which means that no mass flux happens as the solvent concentration reaches to this boundary. Based on these facts, the conditions for solving the diffusion equation in one-dimension are defined as:

\[
C(x, t = 0) = 0 \quad (4.4)
\]

\[
\frac{\partial C(x = l, T)}{\partial T} = 0 \quad (4.5)
\]

\[
C(X = 0, T) = 1 \quad (4.6)
\]

And the solution as mentioned in chapter 3 is:

\[
\frac{C(x, t)}{C_0} = 1 + \sum_{n=0}^{\infty} \frac{4(-1)^n}{(2n + 1)\pi} \cos\left(\frac{(2n + 1)\pi}{2l}X\right) \times \exp\left(-\frac{D^2 (2n + 1)^2 \pi^2}{4l^2} T\right) \quad (4.7)
\]

In this equation, the known values are concentration profile obtained from the pressure decay tests, the measured time values for the mass transfer process and the oil column used in the pressure decay cell. On the other hand, the diffusion coefficient is the missing parameter and is the objective of this problem. To determine CO2 diffusion coefficient, an error term, the Absolute Average Relative Error (AARE), between the measured and calculated data was defined:
\[
AARE = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{X_{\text{exp}(i)} - X_{\text{calc}(i)}}{X_{\text{exp}(i)}} \right)
\] (4.8)

Where \(X_{\text{exp}}\) is the solubility measured experimentally using the pressure decay method and \(X_{\text{calc}}\) is the solubility calculated analytically by Equation 4.2. The goal is to determine the best diffusion coefficient yielding the best scenario for analytically calculated solubility. To reach this goal, the summation of the errors (AARE) on the entire data sets should be minimized; hence, the below procedure was followed:

- Several diffusion coefficient values were selected in the range of \(1\times10^{-9}\) and \(1\times10^{-11}\) m\(^2\)/s
- Each value was incorporated into the analytical solution to generate CO\(_2\) concentration profile in the oil.
- The concentration profile resulting from each diffusion coefficient compared with the experimental CO\(_2\) concentration profile.
- Finally, the diffusion coefficient to the minimum AARE was selected as the optimum CO\(_2\) diffusion coefficient in heavy oil at each specific condition.

All the calculations using the aforementioned method have been made and the final values for the diffusion coefficients at different temperatures and pressures are tabulated in Tables 4.5 and 4.6. Moreover, the effects of temperature and pressure of the system on diffusion coefficient calculated under static condition are depicted in Figures 4.12 and 4.13. For both heavy oil samples, diffusion coefficient increases with temperature, and pressure elevation and decreases as the viscosity of oil increases. Furthermore, diffusion coefficient of CO\(_2\) showed a decrease of 4–12% when the oil viscosity changes and 18–21% when temperature of the system increases from 295–395 K. It can also be seen
that at higher temperature, the effect of pressure increase is more perceptible on CO$_2$ diffusivity.
Table 4.5. Diffusion coefficient calculated using the proper analytical method for oil with $\mu = 5$ Pa.s viscosity under static condition

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Initial pressure (MPa)</th>
<th>Final Pressure (MPa)</th>
<th>Diffusion Coefficient ($\text{m}^2/\text{s}) \times 10^{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
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<td>1.5858</td>
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</tr>
<tr>
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<td>1.7305</td>
<td>1.5961</td>
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<td>1.7278</td>
<td>1.6020</td>
<td>5.102</td>
</tr>
<tr>
<td>305</td>
<td>1.7205</td>
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<td>5.891</td>
</tr>
<tr>
<td>295</td>
<td>3.1047</td>
<td>2.9510</td>
<td>4.043</td>
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<tr>
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<td>2.9592</td>
<td>5.121</td>
</tr>
<tr>
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<td>4.460</td>
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<td>298</td>
<td>4.4888</td>
<td>4.3209</td>
<td>5.571</td>
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<tr>
<td>301</td>
<td>4.4886</td>
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<td>6.582</td>
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<td>305</td>
<td>4.4871</td>
<td>4.3375</td>
<td>7.583</td>
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</tbody>
</table>
Table 4.6. Diffusion coefficient calculated using the proper analytical method for oil with $\mu = 20$ Pa.s viscosity under static condition

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>Initial pressure (MPa)</th>
<th>Final Pressure (MPa)</th>
<th>Diffusion Coefficient ($m^2/s$) $\times 10^{10}$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1.7278</td>
<td>1.6043</td>
<td>5.029</td>
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<td>1.6094</td>
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<td>7.391</td>
</tr>
</tbody>
</table>
Figure 4.12. Effect of pressure and temperature on CO$_2$ diffusion coefficient for heavy oil sample with $\mu = 5$ Pa.s viscosity under static condition
Figure 4.13. Effect of pressure and temperature on CO₂ diffusion coefficient for heavy oil sample with $\mu = 20 \text{ Pa.s}$ viscosity under static condition
4.6 Summary

In this chapter, general procedure for measuring CO$_2$ solubility under different operating condition for two heavy oil samples was introduced. First, the experimental design for measuring the CO$_2$ solubility at pressures of $P = 1.73$, $3.10$, and $4.48$ MPa and for temperature of $T = 295$, $298$, $301$, and $305$ K for two heavy oil samples was introduced. Experimental data were then analyzed for CO$_2$-heavy oil systems to obtain the value of the diffusion coefficient at a given temperature and pressure. Using the analytical method explained earlier and implementing the proper solution based on the boundary and initial conditions of the physical model, the diffusion coefficients were calculated and presented. According to the results, the diffusion coefficient cannot be considered a constant over different concentrations. Therefore, the analyzed diffusion coefficient should be regarded as an “effective” diffusion coefficient. It was seen that the diffusion coefficient of CO$_2$ in heavy oil increased with increasing temperature at constant pressure. Furthermore, diffusion coefficient of CO$_2$ showed a decrease of 4–12% when the oil viscosity changes and 18–21% when temperature of the system increases from 295 to 395 K. It can also be seen that at higher temperature, the effect of pressure increase is more perceptible on CO$_2$ diffusivity. The solubility results at static condition also showed that at higher temperatures, the difference of the solubility is higher than the results at lower temperatures for any pressure.
Chapter 5

Measurements of Solubility and Diffusion Coefficient of CO\textsubscript{2} in Bulk Heavy Oil under Dynamic Condition

In several applications, such as evaporative or transpiration cooling, combustion, ablation, condensation, drying etc., convective mass transfer assumes important. The diffusion of a species through a fluid is more complex because of the flows that may result in the fluid due to either external forces or the diffusion mass transfer process itself. In the previous chapter, the diffusion of a species through a stationary fluid was considered. Note that the diffusion process itself will result in some bulk velocity, and therefore the fluid is not truly stationary. If there is any bulk motion of the system that species \(i\) is diffusing through (which is the usual case in a gas or liquid), then there is also a bulk mass transfer associated with the bulk velocity. In this chapter, it was tried to see the effect of oil velocity in diffusion process under different operating condition and evaluate the results from dynamic conditions with the similar ones under static condition.

5.1 Experiments

5.1.1 Materials

The two heavy oil samples under this study were collected from two heavy oil fields in Saskatchewan, Canada. In the previous chapter, the compositional analyses as well as characteristics of the crude oil samples were presented. These two samples were first cleaned, and then examined using simulated distillation technique by gas
chromatography. The first oil sample has a density and viscosity of 971.75 kg/m$^3$ and 5 Pa.s at 298 K, respectively, along with molecular weight of 642.65 gr/mole. The density and viscosity of the other oil sample are 20 Pa.s and 979.74 kg/m$^3$ at 298K with 663.55 gr/mole molecular weight. $M_{oil} = 642.64$ These analyses show that the composition of the light components, lighter than C$_7$, is zero, confirming no light oil components exist in the oil samples as was explained in the last chapter. Moreover, CO$_2$ with a purity of 99.99%, supplied by Praxair Inc., was used as the injected solvent.

5.1.2 Experimental set-up for pressure decay tests under dynamic condition

A mini bench-top reactor (PARR-4560) from Parr Instrument Company was exploited to make a semi-flowing environment with constant velocity in the system. The experiments were carried out in the reactor equipped with controllers for temperature and agitation speed, using two four-blade impellers. These reactors are equipped with different types of vessels that allow experiments to be conducted up to a maximum working pressure of 20.6 MPa (207 bar) and a maximum temperature of 623 K. The schematic of the reactor’s vessel is shown in Figure 5.1.
**Figure 5.1.** Schematic of the reactor vessel used to conduct the pressure decay experiments for CO$_2$ solubility calculation in heavy oil system
The pressure decay experimental setup utilized in this study mainly consists of high pressure stainless steel cylinders (i.e., diffusion cells), TELEDYNE syringe pump (ISCO 500D series), high accuracy digital pressure gauges equipped with dual display LCD digital indicator from HEISE Co., and data acquisition system. The entire setup was placed in an air-bath in order to maintain the temperature of the system constant using heater and digital temperature controller (Love Controls Co.). Figure 5.2 shows the schematic diagram of the experimental setup used to determine the CO$_2$ solubility under static condition. Under this condition, it was assumed that there is no convection inside the oil phase. However, for dynamic condition, convective flow inside the oil phase was applied. In this condition, the diffusion cell was replaced by a mini bench-top reactor (PARR-4560 from Parr Instrument Company).
Figure 5.2. Schematic experimental design of CO₂ solubility measurement under dynamic condition
5.2 Experimental procedure

Same as the previous pressure decay tests, an isothermal condition was achieved in an isolated air-bath. The reactor used in this study was not equipped with a heating system. However, the inside temperature was monitored by the thermocouple installed inside the vessel, and the oil inside the vessel was controlled by the air-bath temperature. After injecting the oil, all the connections and the empty space of the vessel were vacuumed to remove the air. The system was then left inside the air-bath for a period of time to stabilize the temperature inside the air-bath and inside the reactor’s vessel. The vessel was then charged with CO\textsubscript{2} with the purity of 99.99 percent supplied by Praxair at the pre-defined pressure and temperature.

Pressure decay was then recorded for a period of time until no more pressure reduction was observed. At that point, the test was terminated and an additional test was set-up. The general procedure for pressure decay tests are summarized below:

1. Preparing the reactor for the tests, Connecting the connections and valves to the pressure gauge, transfer cell and vacuum pump. The whole system should be connected in a way that the experiments can be run properly.

2. Injecting 50 gr of the oil sample into the vessel, setting the operating temperature of the system and leaving the system inside the closed air-bath for enough period of time to make sure that the oil temperature and the operating temperature are the same.

3. Vacuuming the system involved in the pressure decay measurements.
4. Injecting CO\textsubscript{2} into vessel at pressures of 1.73 K at 295 K (pre-define pressures and temperatures) and read the data until the pressure in the vessel stay constant at the operating condition.

5. Using the digital pressure gauge connected to a computer, record the pressure reduction inside the vessel; Continue this process until no further pressure decay occurs in the cell. After four to five hours, system pressure would not change further; however, the tests usually kept running for at least a day.

6. Stopping the experiment and cleaning the vessel for the next pressure decay tests.

7. Repeating the procedure at 3.10 and 4.49 MPa for pressure and at 298, 301 and 305 K for temperature.

8. Changing the type of oil and re-run all the tests at the defined pressures and temperatures.

5.3 Experimental results

5.3.1 Solubility measurement

Figures 5.3 to 5.6 show the pressure decay data and the corresponding mass and weight percent of CO\textsubscript{2} dissolved in the oil phase for each temperature at the pressure of 1.73 MPa. Throughout this study, the solubility was defined as the ratio of the total mass of dissolved CO\textsubscript{2} in original crude oil sample and was calculated by using the mass balance and gas equations for the dissolution process. Detailed derivations of CO\textsubscript{2} solubility ($x_{CO2}$) are as follows:
\[ m_{\text{CO}_2, \text{dissolved}} = m_{\text{CO}_2, \text{f}} - m_{\text{CO}_2, \text{i}} \]
\[ = \left( \frac{P_{\text{VM}}}{Z RT} \right)_{\text{CO}_2} - \left( \frac{P_{\text{VM}}}{Z RT} \right)_{\text{fCO}_2} \]
\[ = \frac{(MV)_{\text{CO}_2}}{RT} \left[ \frac{P}{Z} - \frac{P}{Z} \right] \]  
\[ (5.1) \]

\[ x_{\text{CO}_2} = \frac{m_{\text{CO}_2, \text{dissolved}}}{m_{\text{oil}}} \times 100 \]
\[ = \frac{(MV)_{\text{CO}_2}}{\rho RT V_{\text{oil}}} \left[ \frac{P}{Z} - \frac{P}{Z} \right] \times 100 \]  
\[ (5.2) \]
Figure 5.3. Pressure decay data at $P = 1.73$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5$ Pa.s viscosity at $T = 295$ K.
Figure 5.4. Pressure decay data at $P = 1.73\text{ MPa}$ and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5\text{ Pa.s}$ viscosity at $T = 298\text{ K}$. 
Figure 5.5. Pressure decay data at $P = 1.73$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5$ Pa.s viscosity at $T = 301$ K.
Figure 5.6. Pressure decay data at $P = 1.73$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5$ Pa.s viscosity at $T = 305$ K.
5.3.2 \textit{CO}_2 \textit{concentration inside the liquid}

Overall, trends of the concentration profiles for all experiments is analogous, and consequently only the progress of \textit{CO}_2 profile inside the oil with initial pressure of 1.73 MPa and temperature of 298 K is presented here. Nevertheless, the description stands for all experiments. Figure 5.7 displays the advancement of \textit{CO}_2 concentration inside the heavy oil sample (i.e., \( \mu_0 = 5 \text{ Pa.s} \)) with time. The concentration variation is given in the legend bar right beside the figures. By examining this profile, it can be perceived that the dissolution process is started right after \textit{CO}_2 is brought in contact with oil sample. The \textit{CO}_2 concentration is higher near the center of the vessel and decreases in magnitude as it approaches the vessel wall. Once the concentration profile starts moving in the \( z \)-direction as a result of \textit{CO}_2 concentration difference between two phases, the convection effect generated by the stirrer advances the dissolution process. By assuming that the concentration of \textit{CO}_2 remains constant at the interface, the \textit{CO}_2 profile reaches the lower boundary after almost 2 hours for this oil sample and operating condition. After reaching the lower boundary, the dissolution time increased substantially until there was no change in the concentration profile inside the oil phase. This behavior can be assigned to the reason that near the boundaries the driving force slightly vanishes. Since, at the boundaries, the convection velocity is zero, and the only driving force in dissolving \textit{CO}_2 is molecular diffusion, dissolution time increased significantly.
Figure 5.7. Evolution of CO$_2$ concentration profiles inside the heavy oil as a function of time at an initial pressure of $P = 1.73$ MPa and temperature of $T = 298$ K generated by PDETwo software.
Tables 5.1 and 5.2 present the results of CO$_2$ solubility ($x_{CO2}$) in both of heavy oil samples at various operating conditions (i.e., $P = 1.73$–$4.48$ MPa; $T = 295$–$305$ K; $\mu_{oil} = 5$ and 20 Pa.s). As it can be seen from the above figures and the results reported in Table 5.1 and Table 5.2, similar findings compared to the static condition were achieved. This means that temperature has an adverse effect on the solubility of CO$_2$ in heavy oil no matter how the operating pressure changes. Viscosity reduction caused by increasing temperature has a minor effect. However, the ultimate result by increasing temperature is a reduction of solubility. In addition, when the temperature increases, the stability of the equilibrium is more affected. On the other hand, reaching the equilibrium condition of the experiments requires more time as the operating temperature of the system increases from room temperature to 305 K. That is why, by increasing the temperature, the time needed to stop the pressure decay test increased as it is depicted on the Figures 5.3 to 5.6. The above figures are just the results at four different temperatures, but at a constant pressure. The rest of the pressure decay data and its solubility can be found in Appendix B. One of the other major parameters that shall be acknowledged is the time needed for the dissolution of CO$_2$ in heavy oil. Time is considerably decreased at a constant mixing velocity (in this work 30 rpm was chosen, which is equivalent to 0.094 m/s) because of the convection that occurred in the oil bulk phase. At a constant mixing velocity, temperature and pressure have the same impact on the solubility as in the static condition. In this case, however, increasing the temperature does not have that much effect on the stability of the pressure because the solvent mixing occurred in the bulk phase using the stirrer.
Table 5.1. Solubility of CO$_2$ in heavy oil sample with $\mu = 5$ Pa.s viscosity under dynamic condition.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Initial pressure (MPa)</th>
<th>Final Pressure (MPa)</th>
<th>Mass of dissolved CO$_2$(g)</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>1.728</td>
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Table 5.2. Solubility of CO$_2$ in heavy oil sample with $\mu = 20$ Pa.s viscosity under dynamic condition

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Initial pressure (MPa)</th>
<th>Final Pressure (MPa)</th>
<th>Mass of dissolved CO$_2$(g)</th>
<th>Solubility</th>
</tr>
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</table>
5.3.3 **Diffusion coefficient calculation under dynamic condition**

Achieving experimental results leads us to determine the diffusion coefficient in the bulk heavy oil under different test conditions. In the literature mentioned in the chapter 3, two general methods (i.e., analytical and numerical methods) were introduced to solve the convection diffusion equation. Between these two methods, numerical calculation was chosen due to the complexity over analytical solution of the mathematical model for convection diffusion equation. Moreover, the proper boundary and initial conditions defining the experiments must be assigned to the mathematical model to give the best solution of the problem. In this section, the whole procedure to determine the diffusion coefficient in the dynamic condition of bulk heavy oil contacting CO₂ in the reactor’s vessel is introduced and the calculated results will be reported.

The same assumptions that were used to calculate the diffusion coefficient in the static condition were also considered in the dynamic condition. These assumptions were a non-reactive system, isothermal conditions, a constant diffusion coefficient, constant gas compressibility factor, non-volatile bitumen, negligible bitumen swelling, equilibrium at the gas–bitumen interface, and the applicability of Henry's law.

**5.3.3.1 Mathematical analysis**

In this section, the mathematical model and solution for the one-dimensional convection-diffusion equation in a finite domain is introduced. A soluble solvent can be transferred into a solute system by molecular diffusion and/or convection processes as a result of fluid motion. Considering no chemical reactions inside the system between solvent and the solute, the general mass conservation law is given as follows:
\[ R_d \frac{\partial c}{\partial t} + v \nabla c = \nabla \cdot D \nabla c - k_d c \]  

(5.3)

Where \( c \) is the concentration of the solvent in the liquid phase, \( v \) is the liquid phase velocity, \( k_d \) is the coefficient of decay, which is assumed to be zero, \( R_d \) is the retardation factor related to the partitioning coefficient by the relation \( R_d = 1 + k_d \) \( R_d = 1 + k_d \), and \( D \) is the diffusion coefficient. By assuming that the concentration profile in angular direction is uniform, the mass transfer equation (i.e., Eq. 5.3) for the case of convection condition can be re-written in cylindrical coordinate as given:

\[
\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial z} + v \frac{\partial c}{\partial r} = D \left( \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2} \right) 
\]  

(5.4)

Where \( z \) and \( r \) are the longitudinal coordinate, parallel to the column axes, and the radial coordinate, respectively. The velocities in \( z \) and \( r \) direction considered constant and equal due to the type of stirrer used in the reactor vessel. Eq.5.4 can be rearranged into a dimensionless form by employing the following dimensionless parameters:

\[
c^* = \frac{c}{c_0}; t^* = \frac{u_d t}{L}; z^* = \frac{z}{L}; r^* = \frac{r}{R}
\]

Where \( R \) and \( L \) are, respectively, the radius and the length of the column, and \( c_0 \) is the scale of concentration. Substituting the defined parameters, Eq.5.4 can be expressed as:

\[
\frac{\partial c^*}{\partial t^*} + u \frac{\partial c^*}{\partial z^*} + v \frac{\partial c^*}{\partial r^*} = \frac{\eta}{D} \left( \frac{\partial^2 c^*}{\partial r^*^2} + \frac{1}{r^*} \frac{\partial c^*}{\partial r^*} + \frac{\partial^2 c^*}{\partial z^*^2} \right) + \frac{1}{D} \frac{\partial^2 c^*}{\partial z^*^2}
\]

(5.5)

Where \( Pe_r \) and \( Pe_l \) are Peclet numbers defined in \( r \) and \( z \) directions respectively, and \( \eta \) is a conversion factor, which are presented as following:

\[
P_{er} = \frac{u_R}{D}; P_{el} = \frac{u_L}{D}; \eta = \frac{L}{R}
\]
The diffusion coefficient can be determined by solving Eq. 5.5 under predefined initial and boundary conditions, utilizing obtained experimental concentration profile.

The initial concentration of \( \text{CO}_2 \) in the oil phase is negligible; thereby, at \( t = 0 \), the concentration in the oil column was zero. For the boundaries, in the \( r \) direction, it was assumed that \( \text{CO}_2 \) concentration was zero in the wall of the reactor and in the center the concentration rate change was zero. And for the \( z \) direction it was assumed at the surface of the oil and gas the concentration is constant and the bottom of the cell the \( \text{CO}_2 \) change is zero. These initial and boundary conditions are taken into account in order to solve \( \text{CO}_2 \) mass transfer process represented by:

\[
c^*(r^*,z^*,t^* = 0) = 0
\]  
(5.6)

\[
c^*(r^* = 1, z^*, t^*) = 0; \frac{\partial c^*}{\partial r^*}(r^* = 0, z^*, t^*) = 0
\]  
(5.7)

\[
c^*(r^*, z^* = 0, t^*) = 1; \frac{\partial c^*}{\partial z^*}(r^*, z^* = 1, t^*) = 0
\]  
(5.8)

In this study the mixing velocity of the stirrer was used to estimate the fluid flow inside the system. Based on this condition, models proposed in the literatures suitable for laminar flow was used in this study to determine the convection velocity term. Schwartzberg and Treybal (1968) determined the fluid motion in tanks with turbine stirrers by visualizing the rotation using streak photography. They found that outside the stirrer discharge zone, the velocities \( (u) \) can be defined using the following equation:

\[
u \propto \frac{nd^2}{V^\frac{7}{2}} = \frac{nd^2}{(D^2H)^\frac{7}{2}}
\]  
(5.9)

Where \( n \) is the mixer velocity (rad/sec), \( d \) is the mixer diameter (m), \( V \) is the volume of the liquid inside the tank \( (m^3) \), \( D \) is the tank diameter (m) and \( H \) is the height of the liquid.
inside the tank (m). After detailed evaluation of the tests results, Eq.4.15 can be quantitatively expressed as follows:

\[ u = 3.5 \times 10^{-2} \frac{nd^2}{(D^2H)^{1/3}} \]  

(5.10)

In this work, Eq. 5.10 was used to calculate the flowing velocity and consequently numerically determined CO\textsubscript{2} concentration profile under dynamic condition. In this study the angular velocity of the reactor was 30 revolutions per 60 second leading to 0.094 m/s linear velocity. Using Eq. 5.10 the average velocity of the oil inside the reactor can be estimated. Since the height of the oil inside the reactor is relatively short this value was considered the average velocity of the oil column. All the calculations using the aforementioned method have been made and the final value for the diffusion coefficients at different temperatures and pressures are tabulated in Table 5.3 and Table 5.4.
**Table 5.3.** Diffusion coefficient calculated using the PDETWO method for the oil with $\mu = 5$ Pa·s viscosity under dynamic condition.

<table>
<thead>
<tr>
<th>$T$(K)</th>
<th>Initial pressure (MPa)</th>
<th>Final Pressure (MPa)</th>
<th>Diffusion Coefficient of CO$_2$($m^2/s$) $\times 10^{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>1.726</td>
<td>1.574</td>
<td>4.450</td>
</tr>
<tr>
<td>298</td>
<td>1.731</td>
<td>1.590</td>
<td>4.856</td>
</tr>
<tr>
<td>301</td>
<td>1.729</td>
<td>1.593</td>
<td>5.502</td>
</tr>
<tr>
<td>305</td>
<td>1.722</td>
<td>1.600</td>
<td>6.858</td>
</tr>
<tr>
<td>295</td>
<td>3.107</td>
<td>2.942</td>
<td>4.801</td>
</tr>
<tr>
<td>298</td>
<td>3.108</td>
<td>2.950</td>
<td>5.455</td>
</tr>
<tr>
<td>301</td>
<td>3.106</td>
<td>2.957</td>
<td>6.268</td>
</tr>
<tr>
<td>305</td>
<td>3.107</td>
<td>2.964</td>
<td>7.852</td>
</tr>
<tr>
<td>295</td>
<td>4.487</td>
<td>4.302</td>
<td>5.091</td>
</tr>
<tr>
<td>298</td>
<td>4.485</td>
<td>4.316</td>
<td>5.956</td>
</tr>
<tr>
<td>301</td>
<td>4.489</td>
<td>4.320</td>
<td>6.922</td>
</tr>
<tr>
<td>305</td>
<td>4.486</td>
<td>4.303</td>
<td>8.970</td>
</tr>
</tbody>
</table>
Table 5.4. Diffusion coefficient calculated using the PDETWO method for the oil with $\mu = 20$ Pa.s viscosity under dynamic condition

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Initial pressure (MPa)</th>
<th>Final Pressure (MPa)</th>
<th>Diffusion Coefficient of CO$_2$ (m$^2$/s) $\times 10^{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>1.728</td>
<td>1.578</td>
<td>4.410</td>
</tr>
<tr>
<td>298</td>
<td>1.732</td>
<td>1.591</td>
<td>4.575</td>
</tr>
<tr>
<td>301</td>
<td>1.724</td>
<td>1.596</td>
<td>5.094</td>
</tr>
<tr>
<td>305</td>
<td>1.725</td>
<td>1.601</td>
<td>6.585</td>
</tr>
<tr>
<td>295</td>
<td>3.107</td>
<td>2.944</td>
<td>4.851</td>
</tr>
<tr>
<td>298</td>
<td>3.108</td>
<td>2.950</td>
<td>5.221</td>
</tr>
<tr>
<td>301</td>
<td>3.106</td>
<td>2.957</td>
<td>6.061</td>
</tr>
<tr>
<td>305</td>
<td>3.107</td>
<td>2.964</td>
<td>7.742</td>
</tr>
<tr>
<td>295</td>
<td>4.484</td>
<td>4.302</td>
<td>5.291</td>
</tr>
<tr>
<td>298</td>
<td>4.489</td>
<td>4.316</td>
<td>5.723</td>
</tr>
<tr>
<td>301</td>
<td>4.487</td>
<td>4.320</td>
<td>6.758</td>
</tr>
<tr>
<td>305</td>
<td>4.483</td>
<td>4.303</td>
<td>8.828</td>
</tr>
</tbody>
</table>
Figure 5.8 shows the numerical and experimental progress of CO\(_2\) dissolution in the heavy oil sample with 5 Pa.s at 1.73 MPa and 298 K under dynamic condition. The results of the other conditions (i.e., different pressures and temperatures) followed the same progress with only a difference in the dissolution time. It was tried to depict numerical results with different diffusion coefficient values along with the experimental result. Moreover, the effect of operational conditions on CO\(_2\) diffusion coefficient in two heavy oil samples (i.e., pressure, temperature and oil viscosity) is illustrated in Figures 5.9 and 5.10. Similar to the static condition, it can be seen that the diffusion coefficient increases with higher temperature and pressure. However, the effect of temperature is more pronounced in dynamic condition than pressure. Furthermore, the analysis of these results clearly shows that at higher temperature, the effect of pressure is more perceptible than at lower temperatures. This behavior can be seen in both static and dynamic conditions and can be explained by the effect of temperature on the surface tension of the oil molecules. As the temperature of the system increases, the surface tension between the heavy oil molecules and the oil viscosity decreases. Therefore, if the initial pressure of the system increases at higher temperature, the rate of transfer of CO\(_2\) molecules to the heavy oil phase increases consequently. This effect yields to higher increase in diffusion coefficients at higher temperature under both static and dynamic conditions. It was also found that the diffusion coefficient is more dependent on operational parameters under static conditions. Diffusion coefficient changes at higher temperature were relatively higher under dynamic condition compared to those under static condition. This behavior is attributed to the fact that under dynamic condition the effect of higher temperature can be seen both on molecular diffusion and convection effect inside the oil phase. Therefore,
change in the diffusion coefficient at higher temperature is more noticeable under
dynamic condition.
Figure 5.8. Experimental data versus numerical results for different diffusion coefficients under dynamic condition at $P = 1.73$ MPa and $T = 298$ K for oil with $\mu = 5$ Pa.s viscosity
Figure 5.9. Effect of pressure and temperature on CO₂ diffusion coefficient for heavy oil sample with $\mu = 5$ Pa.s viscosity under dynamic condition
Figure 5.10. Effect of pressure and temperature on CO$_2$ diffusion coefficient for heavy oil sample with $\mu = 20$ Pa.s viscosity under dynamic condition
5.4 Comparison of the results of the solubility under static and dynamic conditions

CO\textsubscript{2} solubility was measured under static and dynamic conditions at different pressures and temperatures. As it was seen from the results, temperature elevation reduces the CO\textsubscript{2} solubility in oil samples and pressure promotion increases the CO\textsubscript{2} solubility in oil crudes. In this section, the results of the CO\textsubscript{2} solubility under different pressure and temperature are analyzed when the operating condition changes from static to dynamic condition. Figures 5.11–5.13 show the results of CO\textsubscript{2} solubility for the oil with 5 Pa.s and 20 Pa.s viscosities, respectively. These figures demonstrate CO\textsubscript{2} solubility versus equilibrium pressure under different operating conditions. Maximum changes in CO\textsubscript{2} solubility were seen under pressure of 4.48 MPa and the least changes were observed under 1.73 MPa. These changes show that at higher pressure, the effect of convective term is more pronounced than the similar one at lower pressures. Changes of 2\% in CO\textsubscript{2} solubility were seen at pressure of 1.73 MPa and approximately 20\% of change at 4.48 MPa. Although there was an almost straight relationship between CO\textsubscript{2} solubility under different pressures, the effect of temperatures was somehow irregular. If lower pressures data were excluded from the results, it was seen that at higher temperature (i.e., 305 K) minimum change in CO\textsubscript{2} solubility was seen (i.e., 4\%) and as the temperature decreases, this differences become more sensible.
Figure 5.11. Comparison of the CO$_2$ solubility results under static and dynamic conditions for the pressure of $P = 1.73$ MPa
Figure 5.12. Comparison of the CO₂ solubility results under static and dynamic conditions for the pressure of $P = 3.10$ MPa
Figure 5.13. Comparison of the CO₂ solubility results under static and dynamic conditions for the pressure of $P = 4.48$ MPa
5.5 Summary

In this chapter, a novel experimental setup for measuring CO₂ solubility in heavy oil system was proposed. It was tried to establish a uniform velocity inside the oil system to improve the solubility time under dynamic condition through the pressure decay approach. In the pressure decay method, especially for heavy oil system, the experimental time is likely huge and several days are needed to reach an established pressure decline in the solvent pressure. However, using a Mini bench-top reactor, it was very much easier, and the pressure of the solvent usually was established after a day or so. The results of the CO₂ solubility under different operating condition demonstrate that the $x_{\text{CO}_2}$ increases with operating pressure under dynamic conditions for both of the oil samples. This behaviour is mainly attributed to the reason that the concentration of dissolved CO₂ is proportional to the partial pressure of the CO₂. In addition, it was observed that the CO₂ solubility in heavy crude oil samples benefits from lower operating temperature (e.g., for oil sample A, $x_{\text{CO}_2}$ approximately decreases 30% when temperature increased by 10 K). Furthermore, comparing of the effect of temperature on CO₂ solubility with the effect of viscosity, demonstrates that the temperature is the dominant factor on CO₂ solubility in heavy oil system. In other words, increasing the temperature reduces the viscosity of the oil sample, which can be helpful for increasing the solubility of CO₂ in the oil phase. However, conversely, the temperature increase also amplifies the energy of the CO₂ molecules and their preference to stay at gas rather than liquid phase (i.e., lower solubility at higher temperature). Altogether, results showed that the solubility of CO₂ in heavy oil is principally affected by temperature change rather than viscosity change and ultimately decreases by increasing the temperature of the system. Eventually, using a
numerical method, the diffusion coefficient of CO$_2$ was determined using PDETWO approach and the effect of operating condition on CO$_2$ diffusion coefficient and solubility under static and dynamic conditions were discussed.
Chapter 6

Experimental Measurement of Solubility and the Diffusion Coefficient of CO₂ in Oil Saturated Porous Media

The solubility measurement and diffusion coefficient calculation of CO₂ in bulk heavy oil system has been studied in previous chapters. In this chapter, the same procedure as the bulk oil is going to follow except a porous media saturated with two heavy crude oil samples is going to be used. In this regard, a special pore design has been planned to study the mass transfer process in porous media and to determine CO₂ solubility and diffusion coefficient in the presence of pores and throats at different operating conditions. To conduct this study, like the bulk heavy oil samples, the swelling factor of the heavy crude oil in presence of CO₂ inside the porous media was neglected. Experimental and mathematical models used will be introduced and presented. The numerical method used to determine the diffusion coefficient is the same as the previous chapters (i.e., PDETWO). Furthermore, the determined solubility and diffusion coefficient in the porous media will be compared with corresponding results at bulk liquid. Totally six experiments in porous media were studied and the results were compared with the results at the bulk conditions. These measurements carried out at $P = 1.73, 3.10, 4.48 \text{ MPa}$ at $301K$ for both of the heavy oil samples with 5 and 20 Pa.s viscosities.
6.1 Experimental setup

To measure CO\textsubscript{2} solubility in the porous media, two main careful thought should be considered in the developed model. First, there should be enough volume of CO\textsubscript{2} in presence of the porous media to be able to saturate the oil inside the porous media at each specific operating condition. Second, the physical model should be developed in a way that the mathematical assumptions for the measurements are minimized. To perform these two main tasks, the same size of cylinder full of CO\textsubscript{2} was used to be connected to the porous media for solubility measurement. Also, to better present the physical model for diffusion coefficient calculation, a hollow cylinder designed inside the porous media was planned. Figure 6.1 depicts the schematic of the physical model used in this study to measure the CO\textsubscript{2} solubility.
Figure 6.1. Schematic of the cylinder designed for CO$_2$ solubility measurement in presence of porous media
To develop this experimental model, the following preparation was followed:

1. The same cylinder used for solubility measurement of CO$_2$ in bulk heavy oil (i.e., stainless steel cylinder with 12 cm length and 6 cm diameter) is used for assembling the porous media model.
2. A metal screen with the same length of the cylinder (i.e., 12 cm), and 1cm diameter was cut to be installed inside the model.
3. A fine stainless steel type 316 woven wire mesh with 150×150×0.0026" dimension from Ferrier Wire Goods Company was used to cover the outer face and the upper faces of the screen. This cover was used to prevent the sands movement from the porous space to the inside of the screen. To hold the mesh on the face of the screen, metal string was used in all the length of the screen.
4. Afterwards, this screen with the mesh cover was placed in the center of the cylinder and stuck to one face with glue. Then the cap with the screen was left for an hour to make sure that the two faces are fixed together.
5. Thereafter, an Ottawa sand #530 (Bell and Mackenzie Co. ltd., Canada) was used to pack the hollow physical model. This is white sand and with a rounded grain shape and 99.88% Silicon Dioxide (SiO2). The specific gravity of the sand used was 2.65 ($\gamma_{H2O}=1.0$).
6. Figure 6.2 shows the Particle Size Distribution (PSD).
7. A wet packing process was conducted to fully pack the model inside the cylinder. First, the model was partially filled with the aforementioned sand, and then water was gradually added to the sand. Subsequently, the sand was added to the model until filled. Next, ABU38 pneumatic ball vibrator from Deca Vibrator Industries
Inc. was used to shake the cylinder and the sand to compact the system. Five hours of shaking was operated to fully pack the model and whether any additional sand is needed. After packing, the cylinder was closed, and the air was injected to the porous media for 24 hours to push water out of the model. Thereafter, the porous media was vacuumed for another 24 hours to remove any impurities inside the pore space.

After all this preparation, the model is ready for oil injection and CO₂ solubility measurement. For all tests, this procedure was followed to prepare the model for oil injection.
Figure 6.2. Particle size distribution of the Ottawa sand
Other than the porous model, there are components in the experimental setup used for solubility measurement which will be introduced here. This experimental setup mainly consists of two diffusion cells, one transfer cell, a TELEDYNE syringe pump (ISCO 500D series), high accuracy digital pressure gauges equipped with dual display LCD digital indicator from HEISE Co., and data acquisition system. The experimental setup includes two high pressure cylinder or diffusion cell. One of these cells is the porous model, and the other one is the supply cell. Since the volume of the hollow space inside the porous model is not big enough (18.85 cm$^3$) for holding sufficient CO$_2$ through the whole time of the experiments, the supply cell is used to provide high volume of CO$_2$ at each specific operation condition. The total bulk volume of the hollow space was measured by subtracting the total volume of the cylinder from the screen volume, which is 94.28 cm$^3$. The entire setup was placed in an air-bath in order to maintain the temperature of the system constant using heater, digital temperature controller (Love Controls Co.), and the fan. Figure 6.3 shows the schematic diagram of the experimental setup used to determine the CO$_2$ solubility in the porous space employed for this study.
Figure 6.3. Schematic of the experimental design used to measure CO\textsubscript{2} solubility in oil saturated porous model
6.2 Experimental procedure

Before the solubility measurement, the system was tested for leakage using nitrogen at around 5 MPa. The volume of the oil to be injected to the porous model was measured using the injected water volume recorded by the pump. This measurement was carried out by injecting the water to the beneath of the transfer cell until the oil inside the transfer cell takes pressure. The inside pressure of the transfer cell was controlled by the pressure gauge installed on the top of the transfer cell. At this point, the water injection from the pump was stopped. From now on, it was assumed that the injected water volume to the transfer cell is the same as the volume of the oil injected from the transfer cell to the porous model. This volume was used to calculate the porosity of the porous model. To measure the solubility of CO$_2$ in the oil saturated porous media, the following procedure was followed:

1. After the preparation of the instruments, the air-bath temperature was set to high temperature of 45°C. This high temperature was chosen to reduce the viscosity of the heavy oil samples for better saturation of the porous model. The system was then left for 5 hours to make sure that all the system was at the uniform temperature condition.

2. Then the porous model was vacuumed for 24 hours to remove all the impurities. All the connections and the diffusion supply cell for CO$_2$ were also vacuumed afterwards. The CO$_2$ was then introduced to the diffusion supply cell at the desired pressure. All the system again was left for another two to three hours to make sure that the temperature was uniform in all components.
3. Afterwards, the oil injection with a very low constant flow rate (i.e., 0.05 cm$^3$/sec) was started to the porous model. The injection process was from the top of the model to the empty space, and then pressurizing this oil at the center column for pushing the oil from the center to the pore space of the model.

4. This pressurization of the oil column was operated in three steps at a constant pressure of the pump. Pressure of 3.447 MPa (500 Psi), 5.171 MPa (750 Psi), and 6.894 MPa (1000 Psi) was selected to inject the oil to the porous model. Three days gap were between each re-pressurization of the model until the flow rate became zero at that pressure. And after the 10 days it was assumed that the model was fully saturated since at the constant pump pressure there was no flow rate recorded.

5. After the saturation process, the system temperature was set at the experiment condition (i.e., 301 K) and left 24 hours for uniform temperature distribution.

6. At this point, the porous model was connected to the CO$_2$ cylinder from the top of the model. Then, CO$_2$ was injected to the center line of the model to push the oil from the bottom of the model. The CO$_2$ injection was stopped when 18.85 cm$^3$ of the oil (the same volume of the center space) was collected. Then, the supply cell immediately was connected to the center line of the porous model.

7. From this point, the pressure decay was recorded until there is no pressure reduction in the supply diffusion cell was observed.

8. At the end of each test, the pressure of the porous model was released carefully and the system was detached and cleaned for the next measurement.
6.3 Operational conditions and theoretical developments

To perform the solubility measurement in the porous model, three operating pressures of 1.73, 3.10, and 4.48 MPa at 301 K (28°C) was selected. These conditions were employed on the two heavy crude oil samples used in the bulk study. These operational conditions were chosen due to the similarity of these conditions with the bulk heavy oil samples. After CO$_2$ solubility measurements in porous media, the diffusion coefficient were determined to further analysis of the pore space effect on this parameter as well. Overall, six tests, each operated in almost a month, were carried out in this study. To conduct these measurements and calculations, some assumptions were also considered for this study as listed below:

1. It was assumed that the CO$_2$ diffusion coefficient in oil saturated porous media is constant in each pressure decay test.
2. The porous column is homogenously distributed.
3. Natural convection is neglected in the porous column.
4. The oil swelling effect is negligible through each experiment.
5. The oil evaporation to the CO$_2$ gas phase is insignificant.

6.4 Mathematical model simulating the CO$_2$ diffusion process in porous model

Assuming that diffusion process occurs just from the center space containing CO$_2$ into the saturated porous media with a constant mass transfer coefficient, the diffusion equation can be present as:
\[ \frac{\partial c}{\partial t} = D_{\text{eff}} \left( \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right) \]  

(6.1)

Where \( c \) is the gas concentration in the oil phase, \( t \) is the time, \( r \) is the radial distance from the center of the model, and \( D_{\text{eff}} \) is the effective diffusion coefficient of CO\(_2\) into the oil phase. The boundary and initial conditions are needed to solve this partial differential equation. These conditions are defined based on the physical model developed for saturated porous mode as follows:

\[ c(r,t = 0) = 0 \]  

(6.2)

\[ c(r = 0,t) = 1 \]  

(6.3)

\[ \frac{\partial c}{\partial r} \bigg|_{r = R,t} = 0 \]  

(6.4)

To solve the mass transfer equation applied for this case, the PDETWO solver was used similar to the previous chapters. PDETWO is a software interface to solve time-dependent coupled systems of nonlinear partial differential equations (PDEs), which are defined over a two dimensional region. The general procedure to apply PDETWO solver on a typical PDE was already summarized in Chapter 3.
6.5 Results and discussion

6.5.1 Solubility measurement

The same procedure elaborated in the previous chapters was employed to calculate the solubility inside the bulk oil is followed to determine CO\textsubscript{2} solubility in the porous model. Using the pressure data obtained by the experiments, the mass and solubility of CO\textsubscript{2} inside the oil at 1.73, 3.10, 4.48 MPa and 301 K for both heavy oil samples with 5 and 20 Pa.s is calculated first by the following PVT analysis:

\[
m_{\text{CO}_2,\text{dissolved}} = m_{\text{CO}_2,\text{i}} - m_{\text{CO}_2,\text{f}}
\]

\[
= \left( \frac{PVM}{ZRT} \right)_{\text{CO}_2,\text{i}} - \left( \frac{PVM}{ZRT} \right)_{\text{CO}_2,\text{f}}
\]

\[
= \left( \frac{MV}{RT} \right)_{\text{CO}_2} \left[ \left( \frac{P}{Z} \right)_{\text{i}} - \left( \frac{P}{Z} \right)_{\text{f}} \right]
\]

\[
x_{\text{CO}_2} = \frac{m_{\text{CO}_2,\text{dissolved}}}{m_{\text{oil}}} \times 100
\]

\[
= \frac{(MV)_{\text{CO}_2}}{\rho RT V_{\text{oil}}} \left[ \left( \frac{P}{Z} \right)_{\text{i}} - \left( \frac{P}{Z} \right)_{\text{f}} \right] \times 100
\]

Figure 6.4 and Figure 6.5 show the experimental pressure decay results and the dissolved mass of CO\textsubscript{2} in the heavy oil samples at 1.73–4.48 MPa and 301 K in porous model. The results of the CO\textsubscript{2} solubility under different operating condition demonstrate that the \(x_{\text{CO}_2}\) increases with operating pressure for both oil samples, similar to the bulk oil condition. The effect of porous media on the solubility can be observed through the dissolution time. In the early times the dissolution happens faster, and as the dissolution continues, the pressure drop rate decreased after five or six days more significantly and after that the dissolution becomes very slow. This effect can be explained that during the first days the concentration difference near the inner wall makes the dissolution easier. However, as the
near area becomes more saturated with CO₂, the resistance becomes higher between the two phases. Not only the resistance between the two phases becomes higher, but also the transfer rate between different layers of the oil is tougher when the oil is in the porous media. The overall CO₂ dissolution in the oil saturated porous model for pressure 3.10 MPa is shown in Figure 6.6. The dissolution profile for the other conditions is omitted here due to similar behavior. However, the explanation stands for all of them.
Figure 6.4. Pressure decay results of the all tests conducted in the porous media at temperature of $T = 301$ K
Figure 6.5. Mass dissolved in the oil saturated porous media measured using pressure decay approach at temperature of $T = 301$ K
Figure 6.6. CO₂ dissolution in the oil saturated porous media at different experimental time for the oil with \( \mu = 5 \) pa.s and initial CO₂ pressure of \( P = 3.10 \) MPa.
6.5.2 Diffusion coefficient calculation

The same procedure as the bulk oil procedure will be utilized to determine the diffusion coefficient of CO$_2$ in oil saturated porous media. Solubility data were used to compute the CO$_2$ diffusion coefficient under experimental conditions. In order to determine the optimum diffusion coefficient of CO$_2$ in heavy oil saturated porous model at each specific operating condition, the following procedure was followed:

- Several diffusion coefficient values were selected in the range of $1 \times 10^{-8}$ and $1 \times 10^{-11}$ m$^2$/s
- Each value was incorporated into the numerical model to generate CO$_2$ concentration profile in the oil (using PDEtwo software).
- The concentration profile resulting from each diffusion coefficient compared with the experimental CO$_2$ concentration profile.
- Finally, the diffusion coefficient to the minimum AARE was selected as the optimum CO$_2$ diffusion coefficient in heavy oil at each specific condition.

The Absolute Average Relative Error (AARE) is defined by:

$$AARE = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{|X_{\text{exp}(i)} - X_{\text{cal}(i)}|}{X_{\text{exp}(i)}} \right)$$  \hspace{1cm} \text{(6.7)}$$

CO$_2$ concentration profiles resulted from numerical simulation for different diffusion coefficient along with the experimental data at 3.10 MPa and 301 K is illustrated in Figure 6.7. The results of the remaining calculations are omitted here due to the similar behavior. Finally, diffusion coefficients for each specific operating condition were determined, and the results are reported in Table 6.1.
Figure 6.7. Numerical analysis of the CO₂ mass dissolved in heavy oil at pressure of $P = 3.10$ MPa and $T = 301$ K versus experimental data
Table 6.1. Experimental data for calculating diffusion coefficient of CO$_2$ in the oil saturated porous media

<table>
<thead>
<tr>
<th>$P_i$ (MPa)</th>
<th>$P_f$ (MPa)</th>
<th>$\mu_o$ (Pa.s)</th>
<th>$x_{CO2}$ (wt%)</th>
<th>$D$ (m$^2$/s) × 10$^{10}$</th>
</tr>
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<tbody>
<tr>
<td>1.728</td>
<td>1.503</td>
<td>5</td>
<td>3.810</td>
<td>1.453</td>
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<td>1.870</td>
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<tr>
<td>4.485</td>
<td>4.312</td>
<td>5</td>
<td>10.422</td>
<td>2.641</td>
</tr>
<tr>
<td>1.730</td>
<td>1.511</td>
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<td>1.132</td>
</tr>
<tr>
<td>3.103</td>
<td>2.885</td>
<td>20</td>
<td>6.840</td>
<td>1.343</td>
</tr>
<tr>
<td>4.487</td>
<td>4.341</td>
<td>20</td>
<td>9.521</td>
<td>1.764</td>
</tr>
</tbody>
</table>
6.6 Comparisons of the results obtained in bulk heavy oil and oil saturated porous model

CO₂ solubility and diffusion coefficient in bulk heavy oil and in porous model were determined at static and dynamic conditions and showed different behaviours in all conditions. Since, these properties were measured at 301 K in the porous model, this comparison was conducted for this temperature and pressures of 1.73, 3.10 and 4.48 MPa. For both oil samples with 5 Pa.s and 20 Pa.s viscosity, solubility of CO₂ were decreased when the condition is changed from bulk to the porous media. This reduction is due to the reduction in the contact area between the CO₂ and oil phase. For this study, a reduction of 5% in solubility at pressure of 1.73 MPa for the oil with 5 Pa.s viscosity and 12% for the oil with the 20 Pa.s viscosity were noticed. It implies that as the oil become more viscous, CO₂ solubility is more affected by the oil physical condition. Similar behaviours were seen for the other two pressures. Moreover, this reduction can be assigned to the asphaltene deposition that can happen inside the system. Although for the oil at bulk conditions viscosity has less effect in comparison to pressure and temperature, in porous media viscosity showed a bigger contribution. When the data in the porous model were compared with the results at bulk conditions, it can also be concluded that there were no convection inside the porous model. Since the solubility data calculated in porous model showed less error in respect to static condition than dynamic condition (i.e., 5% to 15%), it may be concluded that the convection term is negligible in the porous model. Furthermore, at lower pressure (i.e., 1.73), CO₂ solubility is more affected when the oil condition changed from bulk to porous model than the condition of higher pressure. This can be attributed to the fact that at higher pressure, the driving force for
CO₂ to move the dead end area is higher than the similar one at lower pressures. This behaviour can be seen in the dissolution of CO₂ when numerically solve the diffusion process at different pressures. For the operating conditions studied for the porous model, CO₂ diffusion coefficient reduced substantially when the oil condition changed from bulk to porous media. Diffusion coefficient calculated numerically for almost all the pressures in the porous model were half of the same values in the bulk at dynamic and 40% less than the same values at static conditions. This behaviour again can be contributed to the less contacted area between CO₂ and the oil phase and the asphaltene deposition that may happens inside the system. Even though, Tortuosity helps in the diffusion process inside the porous media, the overall diffusion coefficient decreased substantially.
6.7 Summary

A new design for calculating CO$_2$ solubility in oil saturated porous media was presented in this chapter. CO$_2$ solubility was measured at 301 K and 1.73–4.48 MPa for two heavy crude oil samples. To measure the solubility in porous media, pressure decay technique was applied in a hollow space porous model saturated with the oil. The CO$_2$ was placed inside the inner space of the model, which is connected to an auxiliary cylinder filled with CO$_2$. Pressure reduction in the auxiliary cell was then used to calculate the amount of CO$_2$ mass dissolved in the oil. The mathematical model representing the porous model was also presented and solved numerically to calculate the diffusion coefficient inside the porous model. After all the experimental and numerical calculation, the result of CO$_2$ solubility and diffusivity in the porous model was compared to the results of the bulk heavy oil system. When the experimental condition changes from bulk to porous media, a reduction of 5% in solubility of CO$_2$ solubility at pressure of 1.73 MPa for the oil with 5 Pa.s viscosity 12% for CO$_2$ solubility in oil with the 20 Pa.s viscosity were noticed. It was also seen that at porous model, CO$_2$ solubility is more affected by viscosity change in comparison to the bulk heavy oil condition.
Chapter 7

Developing a Generalized Correlation for Co₂ Solubility in Heavy Oil System

Thus far to this chapter, the experimental setup and procedure for measuring the CO₂ solubility in heavy oil system described and analyzed. Different pressures and temperatures of the CO₂ along with two heavy oil samples were tested, and CO₂ solubility was measured in each specific operating condition. These experiments showed the effect of temperature, pressure, and viscosity on CO₂ solubility in heavy oil system. As it was explained earlier, viscosity of the oil can contribute on the CO₂ solubility less than the other two parameters. In the literature, for correlating the CO₂ solubility in heavy oil system, heavy oil viscosity effect was neglected by amplifying the effect of temperature of the system. However, besides pressure and temperature, there are other parameters that should be considered to properly generate a correlation for CO₂ solubility in heavy oil system. For example, molecular weight and density can highly contribute on the solubility of gases in liquid phase. In addition to these two parameters, mole fraction distribution can also be involved in the correlation. However, because of the scarcity of the data regarding the mole fraction distribution, it was very hard to involve these data in the correlation. In this chapter, first the available methods and correlations in previous studies are attempted to be presented. All the available data gathered from the literature and this study will then be presented, and the correlation will be proposed subsequently.
At the end the available error based on this study and the other correlations will be compared and analyzed.

7.1 Previously developed correlations for CO₂ solubility in heavy oil

Simon and Graue (1964) presented correlations for predicting solubility, swelling, and viscosity behavior of CO₂/crude-oil systems. Correlations developed from their experimental data have been widely used in reservoir engineering. The limitation of the Simon-Graue correlations is that there is no mathematical form of the correlation; therefore, they are not readily implemented in a computer simulator. Simon and Graue correlations uses mole fraction instead of volume fraction for composition units. Thus, the molecular weight of heavy crude has to be determined experimentally.

Mehrotra and Svrcek (1982) proposed an empirical correlation for CO₂ solubility in the Marguerite Lake and Athabasca heavy oil and bitumen. In their model, CO₂ pressure and temperature were the governing parameters affecting the solubility of CO₂ in the oil. They claimed that their correlation has Absolute Average Deviation of almost 12% for Marguerite Lake heavy oil and 6.3% for the Athabasca bitumen.

\[
\nu = c_1 + c_2 P + c_3 \frac{P}{T} + c_4 \left(\frac{P}{T}\right)^2
\]

Where, \(\nu\) is the volumetric solubility (cm³/cm³) at 273.16K and 101.325 kPa. In this correlation, pressure unit is MPa and temperature unit is K and \(c_1\) to \(c_4\) are the correlation constants. They generated three sets of coefficients for Athabasca and Marguerite Lake heavy oils based on the pressures limitation. Moreover, to convert the data obtain from
this equation to mole fraction the following transformation equation presented by Lasater (1985) was used:

\[
Sol(\text{mol fraction}) = \left( \frac{0.0148 \text{Sol} \left( \frac{m^3}{m^3} \right)}{0.0148 \text{Sol} \left( \frac{m^3}{m^3} \right) + 350 \frac{\gamma}{MW}} \right)_{stdc}
\]

Chung et al., (1988) also provided a correlation for the solubility, swelling factor, and viscosity of CO\(_2\) in the heavy oil. Their experiments were based on the method that Miller and Jones (1984) proposed previously. Their correlations require the values for temperature, pressure, and the oil specific gravity for CO\(_2\) solubility prediction.

\[
R_s = \left[ \frac{1}{a_1 \gamma a_2 T a_7 + a_3 T a_4 \exp \left( -a_5 P + \frac{a_6}{P} \right)} \right]
\]

Where \(\gamma\) is the specific gravity of the heavy oil, P and T are in psia and °F and the \(a_1-a_7\) are empirical constant.

Sayegh et al., (1990) measured the solubility and physical properties of the CO\(_2\)-heavy oil mixture at two different temperatures and various pressures. They mentioned that the densities of the saturated mixtures didn’t change significantly by increasing the saturated pressure.

Emera and Sarma (2006) suggested the correlations to predict CO\(_2\) solubility, oil swelling factor, and CO\(_2\) oil viscosity for both light or heavy oils using a genetic algorithm (GA) based technique. Their correlation uses pressure temperature, specific gravity, and molecular weight of the oil to predict CO\(_2\) solubility in heavy and light oil systems. They
proposed their correlation based on the temperature of the operating system. For temperatures greater than $T_c$, $\text{CO}_2$ (for all pressures) and temperatures less than $T_c$, $\text{CO}_2$ (for pressures less than $\text{CO}_2$ liquefaction pressure):

$$\text{Sol(mol fraction)} = 2.238 - 0.33y + 3.235y^{0.6474} - 4.8y^{0.25656}$$

Where

$$y = \gamma \left[ 0.006897 \left( \frac{1.8T + 32}{P_s} \right)^{0.81} \exp \left( \frac{1}{MW} \right) \right]$$

For this correlation, the $\text{CO}_2$ solubility at 1 atm ($P_h$) is taken to be equal to zero. For temperatures less than $T_c$, $\text{CO}_2$ and pressures greater than the $\text{CO}_2$ liquefaction pressure (the solubility depends on the same previous parameters plus $\text{CO}_2$ liquefaction pressure):

$$\text{Sol(mol fraction)} = 0.033 + 1.14y - 0.7716y^2 + 0.2176y^3 + 0.02183y^4$$

Where

$$y = n \left[ \frac{P_s}{P_{liq}} \right]^{\exp \left( \frac{1.8T + 32}{MW} \right)}$$

Badamchi-Zadeh et al., (2009) also obtained a correlation for $\text{CO}_2$ solubility in crude oil based on the simplified Henry’ law. Their model claimed to fit well with the experimental data obtained by Simon and Graue (1964) study.

$$\text{Sol(mol\%)} = \frac{p}{H_{\text{CO}_2}} = \frac{p}{ln\frac{d_1}{T} + \frac{d_2}{T} + \frac{d_3p}{RT}}$$
Where \( H_{CO2} \) Henry’s constant at \( T, R \) is universal gas constant, and \( d_1 - d_3 \) are empirical constants. Before using the data in the literature, it should be mention that some of the correlations and data were reported by \( cm^3/cm^3 \) or \( wt\% \) in the literature. To convert the data obtain from this equation to mole fraction or to convert the data, the Lasater (1958) expressions were used:

\[
Sol(\text{mol fraction}) = \left( \frac{0.0148 \text{Sol (m}^3/\text{m}^3)}{0.0148 \text{Sol (m}^3/\text{m}^3) + 350 \frac{\gamma}{MW}} \right)_{STDC}
\]

\[
\text{Sol. (wt\%)} = \left( \frac{\text{Mol. CO}_2}{1 - \text{Mol. CO}_2} \right) \times \frac{MW_{CO2}}{MW_{oil}}
\]

Using the above equation, all the data gathered from the studies by Maruf (2010), and Mehratra (1984) and Mehratra (1989) were converted to mole fraction. Furthermore, the correlation proposed by Mehratra (1984) returns the value of solubility volumetrically, which were converted to mole fraction based on the equation proposed by Lasater (1958).

### 7.2 Correlating the data available in the literature

In this work, totally one hundred and twenty four data including the data measured in this study were used to generate a proper correlation for \( CO_2 \) solubility in heavy crude oil system. Twenty five data were also gathered from different oil samples with different properties to test the accuracy of the correlation presented in this study. All the data gathered to build and test the correlation presented in Table C.1 in appendix C. The minimum operating pressure was 0.2 MPa, and the maximum pressure used was 16.28 MPa. The lowest temperature selected for this study was 11.9 °C and highest was 121.1
°C. However, at very high temperature, especially higher than 90 °C, some of the heavy oil properties (both chemical and physical) might change, and therefore, correlations above the aforementioned temperature may not be very suitable for heavy oil system. Moreover, wide ranges of molecular weight of heavy crude oil from 236 to 542 gr/mol were used. All of the data is obtained from Canadian heavy oil reservoirs.

7.3 Analysis of the effect of operating conditions using the data in the literature

CO₂ solubility in heavy oil systems are affected mainly by pressure CO₂ and temperature of the system (Mehrotra and Svrcek (1983)). To analyze the effect of these parameters, CO₂ solubility versus temperature and pressure is shown in Figure 7.1 and Figure 7.2. As it can be seen from these figures, CO₂ solubility is decreasing with temperature increase, and this reduction is more sensible at higher temperature. In other words, CO₂ solubility is decreasing logarithmically with temperature. On the other hand, CO₂ solubility increases with pressure increase linearly to a certain point (probably critical pressure of CO₂) and after that, pressure increases effect decreases slightly. Other than these two parameters, molecular weight along with the density of the oil affects the amount of CO₂ solubility inside the oil (Welker and Dunlop (1963), Simon and Graue (1965)). The other factors affecting CO₂ solubility is oil composition distribution. This effect cannot be easily understood because not only the carbon chain in two different heavy oil samples are not similar but also these chains can be assigned to different components in oil samples (i.e., Aromatic, Resins, Asphaltene and etc.). The other parameter that can be included in the CO₂ solubility is the oil viscosity which is highly related to the operating temperature and is usually dropped from the correlations.
Figure 7.1. Effect of temperature on CO$_2$ solubility data.
Figure 7.2. Effect of pressure on CO₂ solubility data.
Based on the above analysis and parametric sensitivity analysis of temperature, pressure, heavy oil molecular weight, and the oil density were considered to be included in the equation. Using the data for training the system (i.e., Table C.1) the following equation was offered to predict the CO₂ solubility in heavy oil system:

\[
\frac{\ln(S \times T/(P \times \rho))}{\ln(MW)} = 0.14254 - 0.02335P^{0.695} + \frac{-0.71879}{T^{0.612}} + \frac{13.267}{\ln(MW)^{1.916}} + \frac{0.006748P^{0.695}}{T^{0.16\ln(MW)^{1.916}}} + \frac{-55.07}{(T^{0.16\ln(MW)^{1.216}})^2}
\]  \quad (5.1)

Based on the above equation a total error of 4.96% was achieved which was calculated by the following equation:

\[
\text{Error} \% = \left( \frac{\text{Abs}(\text{Sol}_{\text{exp}} - \text{Sol}_{\text{Num}})}{\text{Sol}_{\text{exp}}} \right) \times 100
\]

Using the above equation and neglecting two points out of the data (which produced huge amount of error and were deselected from the data), Emera (2006) method generated 12% error, and Mehrotra and Svrcek (1982) produced 150%. Moreover, R-Squared of 0.979 was calculated by the training data. This work shows a better predication of the CO₂ solubility than these two mostly used correlations for CO₂ solubility. The complete comparison among all these three method for the data used in this study is shown in Table C.1.

To graphically see the accuracy of this method and the comparison between these methods together, Figures 7.3 and 7.4 are brought here. Figure 7.3 depicts the calculated
data using the correlation generated from this study versus the data experimentally measured. As it can be seen from this figure, the data almost follow the line $y = x$. Figure 7.4 also show the results calculated from this study and the Emera (2006) versus the experimental data. The calculated values of CO$_2$ solubility for Mehrotra and Svreck (1982) are not included in this figure due to high amount of Errors (AARE = 157%).
Figure 7.3. CO₂ solubility in dead oil model prediction results.
Figure 7.4. Comparison of the experimental data and calculated data using the correlation developed in this study and three of the literature correlations.
To evaluate the accuracy of this model for predicting the solubility of CO₂ in other heavy oil samples, 25 data from three different oil sources were selected and the experimental and correlated values for each operating condition were calculated. The results of these analyses are shown in Table 7.1 and the experimental and calculated values are depicted in Figure 7.5. As it can be seen the accuracy of this method for other oil samples are quite acceptable (AARE 6%).
Table 7.1. Data from different works for testing the developed CO₂ solubility correlation in this study

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
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</thead>
<tbody>
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<td>73.89</td>
<td>7.93</td>
<td>246</td>
<td>0.828</td>
<td>0.496</td>
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<td>0.574</td>
<td>0.511</td>
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<td>490</td>
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<td>8</td>
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<td>0.618</td>
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* \( AARE = \frac{(\text{Exp.}-\text{Num.})}{\text{Exp.}} \times 100 \)

Ave. Error = 6%
Figure 7.5. CO$_2$ solubility in dead oil model testing results.
7.4 Summary

In this section, a generalized correlation was suggested to predict CO$_2$ solubility in heavy oil system under different operating conditions. CO$_2$ pressure, system temperature, heavy crude oil molecular weight and its density were used to develop the correlation. Totally, 124 data sets were used to develop the correlation, and afterward 25 data sets were gathered from different heavy oil reservoirs with different properties were used to test the developed correlations. For both the training and testing data, an Average Absolute Relative Error percentage (AARE %) was used to determine the accuracy of the correlations. For the training data sets, a total average error of 4.96%, and for the testing data sets, 6% were achieved using the developed correlation. This correlation was developed for a wide range of pressures (i.e., 0.2–16.3 MPa) and temperatures (12–121 °C). This range of pressures and temperatures usually cover all sorts of heavy oil reservoir conditions. However, this statement does not mean that the correlation will certainly give this value of error for different operating and fluid conditions. It was attempted to consider four of the main parameters that can affect the value of CO$_2$ solubility in heavy oil. However, heavy oil composition distribution can also be a parameter that might influence the CO$_2$ solubility value in heavy crude oil system. In other words, the distribution of the carbon number, for example the percentage of C7–C15 and C16–30 and C30+ or the ratio of these values, can be implemented in the correlation. However, the scarcity of the data regarding these values made it impossible for developing a correlation including these values.
Chapter 8

Conclusions and Recommendations

8.1 Conclusions

A new method was developed involving mathematical models, corresponding analytical and numerical solutions, and a unique experimental design to determine CO$_2$ solubility and diffusion coefficient in heavy oil systems. These efforts were recruited for both bulk and porous model with two different heavy oil samples. The major conclusions drawn of this study are listed as follows:

1. Experimental designs for measuring CO$_2$ solubility in two heavy oil samples under two different oil phase conditions were proposed. The solubility of CO$_2$ in each heavy oil sample was measured at temperatures of 295, 298, 301 and 305 K, and at pressures of 1.73, 3.10, and 4.49 MPa. Mathematical models were developed and solved to determine CO$_2$ diffusion coefficient from the pressure decay data and the measured solubility obtained from the PVT analysis.

2. Mathematical models based on the physical conditions of each experiment were derived, and solved by considering the initial and boundary conditions of the experimental tests. Analytical approach was used to solve the mathematical model at static condition, and numerical method was employed by using PDETW0 routine for dynamic and oil saturated porous media.
3. The experimental results showed that CO₂ diffusion coefficient in bulk and oil saturated porous model increases with pressure and temperature while CO₂ solubility increases with pressure and decreases with temperature increase. In addition, increasing the initial pressure resulted in longer time required for the diffusion process to reach the equilibrium condition. Moreover, CO₂ solubility and diffusion coefficient in heavy oil decreases with viscosity elevation of the heavy oil. The viscosity change has more noticeable impact on CO₂ solubility and diffusion coefficient in oil saturated porous model than oil bulk condition.

4. It was found that at higher temperature, increment of CO₂ initial pressure increased the diffusion coefficient more noticeably compared to lower temperature. The same behaviour was observed when the operational condition changed from bulk oil to oil saturated porous media. Moreover, the effect of temperature on CO₂ solubility in heavy oil was recognized to be more dominant during dynamic oil condition than static one.

5. CO₂ solubility and diffusion coefficient in heavy oil is principally controlled by temperature change rather than the oil viscosity change for the oil in bulk conditions. In addition, the effect of oil viscosity change on CO₂ solubility in heavy oil can be ignored at high operational temperatures and pressures (e.g., at 295 K and 1.73 MPa). However, results of CO₂ solubility and diffusion coefficient in heavy oil saturated porous model showed that viscosity had almost the same contribution as temperature and pressure to CO₂ solubility and diffusion coefficient.

6. The diffusion coefficient under dynamic condition is higher than that of static condition due to the convection exists in the oil phase. Such an effect showed 5–15%
increase on diffusion coefficient at different temperatures and pressures when the operational condition changed from static to dynamic condition.

7. CO\(_2\) solubility in oil saturated porous model were determined to be 3.81–10.42 wt\% for the oil with 5 Pa.s viscosity and 3.57–9.52 wt\% for the oil with the 20 Pa.s viscosity. These values for solubility on average are 2–5\% less than the same values in bulk oil condition.

8. A generalized correlation for CO\(_2\) solubility under different operating conditions was developed. The proposed correlation was based on the several data sets of CO\(_2\) solubility in Canadian heavy oil samples. CO\(_2\) pressure, system temperature, heavy crude oil molecular weight and its density are the training parameters employed to develop the correlation. The simulated CO\(_2\) solubility results obtained from the correlation were found to be in proper agreement (i.e., AARE = 4.96\%) with the measured values.
8.2 Recommendations

This study may be extended by the following recommendations in the future. Main efforts which might be conducted on both experimental and mathematical parts are:

1. A heavy oil-saturated core model with different characteristics can be established to investigate the effect of reservoir characteristic \((k, \Phi)\) on CO\(_2\) diffusion into the heavy oil system.

2. Hydrocarbon solvents can be added to CO\(_2\) to improve heavy oil recovery. For this fact, a mixture of CO\(_2\)-Hydrocarbon can be used to determine the effect of impurities on CO\(_2\) diffusion coefficient. However, it can be very effortful and may include different uncertainty.

3. Since the data for diffusion coefficient of CO\(_2\) in heavy system are scarce, more experiments can be conducted to collect a full set of diffusion coefficient and develop a generalize and applied correlation for this parameter.

4. Different mixing velocity under dynamic condition may be implemented to see the effect of different convection velocities on CO\(_2\) solubility and diffusion coefficient.

5. The velocity field generated by a stirrer inside the reactor can be correctly determined if the Navier-Stokes equations and the continuity equation solve simultaneously. Taking into account the appropriate initial and boundary conditions and numerically solving the Navier-Stokes equations and the continuity equation, the velocity profile can be estimated more accurately. Having the velocity profile and the diffusion equation, the diffusion coefficient can be determined more precisely.
6. To ensure the validity of the research findings, it is recommended that series of similar tests be conducted in a large 3D physical model where mixing velocity is the result of fluids motion in the model.
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Appendix A Experimental results for various pressures and temperatures under static condition

Figure A.1. Pressure decay data at pressure of $P = 3.10$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5$ Pa.s at temperature of $T = 295$ K.
Figure A.2. Pressure decay data at pressure of $P = 3.10$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5$ Pa.s at temperature of $T = 298$ K.
Figure A.3. Pressure decay data at pressure of $P = 3.10$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5$ Pa.s at temperature of $T = 301$ K.
Figure A.4. Pressure decay data at pressure of \( P = 3.10 \) MPa and the corresponding mass and concentration of CO\(_2\) in 100 gram of oil with \( \mu = 5 \) Pa.s at temperature of \( T = 305 \) K.
Figure A.5. Pressure decay data at pressure of $P = 4.48$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5$ Pa.s at temperature of $T = 295$ K.
Figure A.6. Pressure decay data at pressure of $P = 4.48$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5$ Pa.s at temperature of $T = 298$ K.
Figure A.7. Pressure decay data at pressure of $P = 4.48$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5$ Pa.s at temperature of $T = 301$ K.
Figure A.8. Pressure decay data at pressure of $P = 4.48$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5$ Pa.s at temperature of $T = 305$ K.
Figure A.9. Pressure decay data at pressure of $P = 1.73$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 295$ K.
Figure A.10. Pressure decay data at pressure of $P = 1.73$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 298$ K.
Figure A.11. Pressure decay data at pressure of $P = 1.73$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 301$ K.
Figure A.12. Pressure decay data at pressure of $P = 1.73$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 305$ K.
Figure A.13. Pressure decay data at pressure of $P = 3.10$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 295$ K.
Figure A.14. Pressure decay data at pressure of $P = 3.10$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 298$ K.
Figure A.15. Pressure decay data at pressure of $P = 3.10$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 301$ K.
Figure A.16. Pressure decay data at pressure of $P = 3.10$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 305$ K.
**Figure A.17.** Pressure decay data at pressure of $P = 4.48$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 295$ K.
Figure A.18. Pressure decay data at pressure of $P = 4.48$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 298$ K.
Figure A.19. Pressure decay data at pressure of $P = 4.48$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 301$ K.
Figure A.20. Pressure decay data at pressure of $P = 4.48$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 305$ K.
Appendix B  Experimental results for various pressures and temperatures under dynamic condition

Figure B.1. Pressure decay data at pressure of $P = 1.73$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 295$ K.
Figure B.2. Pressure decay data at pressure of $P = 1.73$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 298$ K.
Figure B.3. Pressure decay data at pressure of $P = 1.73$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 301$ K.
Figure B.4. Pressure decay data at pressure of $P = 1.73$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 305$ K.
Figure B.5. Pressure decay data at pressure of $P = 3.10$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5$ Pa.s at temperature of $T = 295$ K.
Figure B.6. Pressure decay data at pressure of $P = 3.10$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5$ Pa.s at temperature of $T = 298$ K.
Figure B.7. Pressure decay data at pressure of $P = 3.10$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5$ Pa.s at temperature of $T = 301$ K.
Figure B.8. Pressure decay data at pressure of $P = 3.10$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5$ Pa.s at temperature of $T = 305$ K.
Figure B.9. Pressure decay data at pressure of $P = 3.10$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 295$ K.
Figure B.10. Pressure decay data at pressure of $P = 3.10$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 298$ K.
Figure B.11. Pressure decay data at pressure of $P = 3.10$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 301$ K.
Figure B.12. Pressure decay data at pressure of $P = 3.10$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 305$ K.
Figure B.13. Pressure decay data at pressure of $P = 4.48$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5$ Pa.s at temperature of $T = 295$ K.
Figure B.14. Pressure decay data at pressure of $P = 4.48$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5$ Pa.s at temperature of $T = 298$ K.
Figure B.15. Pressure decay data at pressure of $P = 4.48$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5$ Pa.s at temperature of $T = 301$ K.
Figure B.16. Pressure decay data at pressure of $P = 4.48$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 5$ Pa.s at temperature of $T = 305$ K.
Figure B.17. Pressure decay data at pressure of $P = 4.48$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 295$ K.
Figure B.18. Pressure decay data at pressure of $P = 4.48$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 298$ K.
Figure B.19. Pressure decay data at pressure of $P = 4.48$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 301$ K.
Figure B.20. Pressure decay data at pressure of $P = 4.48$ MPa and the corresponding mass and concentration of CO$_2$ in 100 gram of oil with $\mu = 20$ Pa.s at temperature of $T = 305$ K.
Appendix C  Experimental data used for developing the correlation of CO₂ solubility in dead oil

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237
\*AARE = \((\text{abs (Exp.-Num.)}/\text{Exp.})\)*100

Ave. Error = 4.96%

1–27 Maruf, 

28–35 Mehhrotra (Marguerite Lake Bitumen), 

36–72 Simen et. al., 

73–96 This study, 

97–124 Mehhrotra (Athabasca Bitumen),
Appendix D FORTRAN program for determining CO$_2$ diffusion coefficient

SUBROUTINE F(T,X,Y,U,UX,UY,DUXX,DUYY,DUDT,NPDE)
    USE DATATYPES
!
! DEFINE THE PDE !
!
REAL T,U,X,Y,UX,UY,DUXX,DUYY,DUDT,EXP
INTEGER NPDE
!COMMON /PROB/ DL,DLI,KODE
DIMENSION U(NPDE),UX(NPDE),UY(NPDE),DUXX(NPDE,NPDE),
&       DUYY(NPDE,NPDE),DUDT(NPDE)
REAL V,Vbar,r
REAL term1,term2,term3,term4
r=X*RPnow%R
! V=RPnow%m*(RPnow%Omega*RPnow%Omega)*(RPnow%R*RPnow%R-r*r)
! V=V/(RPnow%mu*2.0*Pi*RPnow%L)
V=RPnow%Vz
Vbar=(RPnow%R/RPnow%Diff)*V
IF (X>0.0) THEN
    term1= DUXX(1,1)
    term2=(1.0/X)*UX(1)
    term3=-Vbar*UY(1)
    term4=(RPnow%sigma*RPnow%sigma)*DUYY(1,1)
    !DUDT(1)=term1+term2+term3+term4
    DUDT(1) = (DUXX(1,1)+(1/X)*UX(1))+(Vbar)*UY(1)+ DUYY(1,1)
!ORIGINAL
!DUDT(1) = 2.0*DUXX(1,1)+(1.0/X-Vbar)*UX(1)+(RPnow%sigma*RPnow%sigma)*DUYY(1,1)
ELSE
    term1= DUXX(1,1)
    term2=DUXX(1,1)
    term3=-Vbar*UY(1)
    term4=DUYY(1,1)
    !DUDT(1)=term1+term2+term3+term4
    DUDT(1) = DUXX(1,1)+(Vbar)*UY(1)+ DUYY(1,1)
!ORIGINAL
! DUDT(1) = 2.0*DUXX(1,1)+(-Vbar)*UX(1)+(RPnow%sigma*RPnow%sigma)*DUYY(1,1)
END IF
RETURN
END
SUBROUTINE BNDRYH (T,X,Y,U,AH,BH,CH,NPDE)
  USE DATATYPES
!*********************************************************************7
2
! DEFINE THE HORIZONTAL BOUNDARY CONDITIONS
!
  REAL T,U,X,Y,BH,AH,CH
  INTEGER NPDE
! COMMON /PROB/ DL,DLI,KODE
  DIMENSION U(NPDE),AH(NPDE),BH(NPDE),CH(NPDE)

IF (y==0.0) THEN
  !ORIGINAL DC/DX=0.0
  AH(1)=0.0
  BH(1)=1.0
  CH(1)=0.0
  RETURN
  AH(1)=0.0
  BH(1)=1.0
  CH(1)=0.0
ELSE
  AH(1)=1.0
  BH(1)=0.0
  CH(1)=1.0
END IF
!!! REVERSING B.Cs
RETURN
END

SUBROUTINE BNDRYV (T,X,Y,U,AV,BV,CV,NPDE)
  USE DATATYPES
!*********************************************************************7
2
! DEFINE THE VERTICAL BOUNDARY CONDITIONS
!
  REAL T,U,X,Y,BV,AV,CV
  INTEGER NPDE
! COMMON /PROB/ DL,DLI,KODE
  DIMENSION U(NPDE),AV(NPDE),BV(NPDE),CV(NPDE)

!############################ ALTERED
IF (x==0.0) THEN
  AV(1) = 0.0
  BV(1) = 1.0
  CV(1) = 0.0
ELSE
  AV(1) = 1.0
  BV(1) = 0.0
  CV(1) = 0.0
END IF
!RETURN
SUBROUTINE DIFFH (T,X,Y,U,DH,NPDE)

!**********************************************************************
2
! DEFINE THE HORIZONTAL DIFFUSION COEFFICIENTS
!
REAL  T,U,X,Y,DH
INTEGER NPDE
! COMMON /PROB/ DL,DLI,KODE
DIMENSION U(NPDE),DH(NPDE,NPDE)

DH(1,1) = 1.0
RETURN
END

SUBROUTINE DIFFV (T,X,Y,U,DV,NPDE)

!**********************************************************************
2
! DEFINE THE VERTICAL DIFFUSION COEFFICIENTS
!
REAL  T,U,X,Y,DV
INTEGER NPDE
! COMMON /PROB/ DL,DLI,KODE
DIMENSION U(NPDE),DV(NPDE,NPDE)

DV(1,1) = 1.0
RETURN
END

program main
USE PUBLICVARFORMAIN
USE IO
USE INIT
USE INTEGRATOR
IMPLICIT NONE
REAL H,TFStep,tnow,tbarnow,dtbar
REAL TEnd,TEndbar,tDL,tbar0,massNum,timenow,chktime,MSE,jval
INTEGER*4 I,NRun,NOUT,OUTPUTINTERVALS
INTEGER*4  curEXP, icntrDiff
LOGICAL*1  flagreach
CHARACTER*30 zoneTitle

CALL  READPARAM()
CALL  READEXP()

OPEN (UNIT=70,FILE="MASS.PLT")
WRITE (70,*) "VARIABLES=time massEXP massNum"
OPEN (UNIT=90,FILE="MeanSquareError.PLT")
WRITE (90,*) "VARIABLES=Diffusion MSE"
OPEN (UNIT=30,FILE="DOMAIN.PLT",ACTION="WRITE",STATUS="REPLACE")
CLOSE (30)
DO  icntrDiff=0,RP0%NDiff
   CALL  INITIALIZE()
   MSE=0.0;
   RPnow=RP0
   TEnd=DATAEXP (NODATA,1)
   dtbar=RP0%H
   H=dtbar
   RPnow%Diff=RPnow%Diffflow+FLOAT (icntrDiff)*RPnow%DDiff
   WRITE (zoneTitle,*),'ZONE ',
   WRITE (70,*) zoneTitle
   tDL=RPnow%Diff/(RPnow%R*RPnow%R)
   jval=  dtbar/tDL
   TEndbar=tDL*TEnd
   tbarnow=0.0
   tbar0=0.0
   curEXP=1;
   timenow=0.0
DO  WHILE (timenow<TEnd)
   IF (DATAEXP(curEXP,1)*tDL>(tbarnow+dtbar)) THEN
      tbarnow=tbarnow+dtbar
      flagreach=.false.
   ELSE
      curEXP=curEXP+1
      tbarnow=DATAEXP (curEXP,1)*tDL
      flagreach=.true.
   END IF
   CALL  DRIVEP
   (NODE,tbar0,H,U,tbarnow,EPS,INDEX,WORK,IWORK,X,Y)
   timenow=tbarnow/tDL
   IF (INDEX<0) THEN
      WRITE (*,*), "ERROR",INDEX
      EXIT
   END IF
   IF (flagreach) THEN
      CALL  INTEGRATE(massNum)
      IF (icntrDiff==RP0%NDiff) THEN
         CALL  WRITEGRID()
      END IF
   DATANUM(curEXP,1)=tbarnow/tDL
END IF
END DO
MSE=MSE/FLOAT(NODATA)
MSE=SQRT(MSE)
!MSE=100.0*MSE/FLOAT(NODATA)
WRITE(90,*) RPnow%Diff,MSE
WRITE(*,200) icntrDiff,RP0%NDiff,RPnow%Diff,MSE,RP0%Vz
END DO
END PROGRAM

*********************************************************************
MODULE INIT
USE PUBLICVARFORMAIN
IMPLICIT NONE
CONTAINS
SUBROUTINE INITIALIZE()
INTEGER I,J
REAL tmpM,jval1,jval2
! DIMENSIONLESS NUMBERS AND OTHER INITIALIZATION
RP0%sigma=RP0%R/RP0%L
NPDE=1
MF=22
!! X--> R
!! Y--> Z
NX=RP0%NR
NY=RP0%NZ
NODE=NPDE*NX*NY
INDEX=1
IWORK(1) = NPDE
IWORK(2) = NX
IWORK(3) = NY
IWORK(4) = 12
IWORK(5) = 28500000
IWORK(6) = 28500000

DX=1.0D0/(FLOAT(NX)-1.0D0)
DY=1.0D0/(FLOAT(NY)-1.0D0)
RP0%dr=DX
RP0%dz=DY
RP0%dDiff=(RP0%Diffhigh-RP0%Difflow)/FLOAT(RP0%NDiff)
IF(ALLOCATED(U)) THEN
    DEALLOCATE(U)
END IF
ALLOCATE(U(NPDE,NX,NY))

UTOT=>U
IF(ALLOCATED(UTOT0)) THEN
    DEALLOCATE(UTOT0)
END IF
ALLOCATE(UTOT0(NPDE,NX,NY))
IF(ALLOCATED(X)) THEN
    DEALLOCATE(X,Y)
END IF
ALLOCATE(X(NX),Y(NY))
DO I=1,NX
    X(I)=FLOAT(I)*DX-DX
END DO
DO I=1,NY
    Y(I)=FLOAT(I)*DY-DY
END DO
EPS=1.0D-7

!INITIAL CONDITION FOR U
DO I=1,NX
    DO J=1,NY
        U(I,J)=0.0
    END DO
END DO
UTOT=U
! CLEAR THE OUTPUT FILE

END SUBROUTINE

END MODULE INIT