

SUSANA VASCONCELOS ARAÚJO

DIFFUSION AND SWELLING OF CO₂/LIGHT OIL MIXTURES USING PRESSURE DECAY AND CT-SCAN

DIFUSÃO E INCHAMENTO DE MISTURAS DE CO₂/ÓLEO LEVE USANDO AS TÉCNICAS DE QUEDA DE PRESSÃO E DE TOMOGRAFIA COMPUTADORIZADA

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UNIVERSIDADE ESTADUAL DE CAMPINAS FACULDADE DE ENGENHARIA MECÂNICA E INSTITUTO DE GEOCIÊNCIAS

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Orientador: Prof. Dr. Osvair Vidal Trevisan

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DISSERTAÇÃO DE MESTRADO ACADÊMICO

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ABSTRACT

 CO_2 -EOR is an important injection agent in oil reservoir due to its miscibility and swelling effects. Concerning the miscibility effect, molecular diffusion is the process describing the natural mixture of miscible fluids, whose main modeling parameter is the molecular diffusion coefficient. The aim of this study is to measure the diffusion coefficient and swelling factor of CO_2 in light crude oil under different experimental conditions concerning pressure, temperature and oil composition. In order to obtain the diffusion coefficient, two experimental techniques were run in parallel: the well-established and so-called pressure decay method and a CT scan method that was still under investigation. The later method was also used to obtain the swelling factor in the selected experimental conditions.

The oil studied was light oil from Brazilian subsalt oil reservoirs. Tests were carried on a specially constructed vertical high pressure cell, from 2.76 MPa to 28.96 MPa (400 psi to 4200 psi) at 293.15 K (20°C) and just 10.34 MPa (1500 psi) at 341.15 K (65°C).

Molecular diffusion is particularly important for miscible gas flooding processes, as diffusion is a key mechanism controlling the miscibility between oil and gas. The diffusion coefficient determines the rate of mass transfer during the diffusive process that will result in a miscible system. The diffusivity of solvents into light oil in porous media has become of great significance in petroleum engineering, since CO_2 injection has been proposed more and more as the enhanced oil recovery method to be applied in the reserves of conventional oils.

The swelling effect of crude oil with CO_2 increases the oil formation volume factor so that residual oil after waterflooding is smaller in volume at surface conditions. The extent of the expansion or swelling is measured by the swelling factor.

While diffusion in CO_2 -heavy oils systems has attracted some attention, the subject in light crude oils is scarcely described in the public literature. Such prospect needs therefore to be thoroughly investigated for the pre-salt reservoirs offshore Brazil, where oil has an API gravity between 28 and 30 and a variable contents of CO_2 . Due to such properties, differences in the models regarding boundary conditions at the interface and in the thermodynamics of the CO_2 -volatile oil must be taken into consideration.

Diffusion coefficients were obtained using only the pressure decay technique throughout Etminan et al. (2013) interface resistance model. The obtained diffusion coefficients were within the ranges previously reported in the literature. Furthermore, another parameter obtained with the model, namely the mass transfer coefficient, allowed identifying that there was almost no mass transfer resistance in the interface in original oil.

Despite the CT limitations to obtain CO_2 concentration, CT investigation could offer an important insight on CO_2 diffusion inside the oil column. In contrast the swelling effect could be clearly observed and characterized through this method.

Key Word: Diffusion, swelling, CO₂, light oil, pressure decay, CT-scan.

RESUMO

O CO₂ utilizado na recuperação avançada em reservatórios de petróleo é um importante agente de injeção devido a suas características de miscibilidade e de inchamento. No que tange a miscibilidade, a difusão molecular é o processo que descreve a mistura natural de fluidos miscíveis, e seu principal parâmetro é o coeficiente de difusão molecular. O objetivo deste estudo é medir o coeficiente de difusão bem como o fator de inchamento do CO₂ em óleos leves em diferentes condições experimentais envolvendo pressão, temperatura e composição do óleo. Com intuito de obter o coeficiente de difusão, duas técnicas experimentais foram realizadas em paralelo: uma primeira técnica conhecida como decaimento de pressão e outra chamada de tomografia computadorizada. Esta última, apesar de ainda estar em processo de investigação, permitiu também a obtenção do fator de inchamento nas condições experimentais selecionadas.

O óleo estudado é um óleo leve proveniente dos reservatórios do pré-sal no Brasil. Os testes foram efetuados em uma célula para altas pressões especialmente desenvolvida para esses ensaios que envolvem tomografia computadorizada. As pressões e temperatura variaram de 2.76 MPa a 28.96 MPa a 293.15 K e somente 10.34 MPa a 341.15 K.

A difusão molecular é considerada um mecanismo chave que controla a miscibilidade entre o óleo e o gás. Sabendo que o coeficiente de difusão determina a taxa de transferência de massa durante o processo, a difusão de solventes em óleo leve dentro de um meio poroso se tornou de grande importância na engenharia de petróleo.

Em paralelo, o inchamento do óleo bruto com CO_2 aumenta o fator de volume de formação do óleo a tal ponto que o óleo residual remanescente após a injeção de água é menor em volume nas condições de superfície. A extensão do aumento ou do inchamento é medida pelo fator de inchamento.

Nos últimos anos a difusão do CO_2 em óleo pesado tem atraído uma maior atenção, enquanto que a difusão em óleo leve tem sido pouco estudada na literatura. Com foco nos reservatórios do pré-sal no litoral brasileiro, onde o óleo tem entre 28 a 30 graus API e concentrações variadas de CO_2 , diferentes modelos de difusão envolvendo as condições de fronteira na interface e a termodinâmica do CO_2 -óleo volátil precisam ser levados em consideração. No presente trabalho, os coeficientes de difusão puderam ser obtidos somente através da técnica experimental de decaimento de pressão por meio do modelo de resistência na interface proposto por Etminan et al. (2013). Os coeficientes de difusão estavam dentro dos intervalos reportados previamente na literatura. Além disso, um outro parâmetro, o coeficiente de transferência de massa, permitiu identificar que a resistência à transferência de massa na interface era praticamente insignificante no óleo original.

Apesar das limitações do método de tomografia computadorizada na obtenção das concentrações de CO_2 no óleo, a investigação desse método ofereceu uma melhor compreensão do fenômeno da difusão do CO_2 dentro da coluna de óleo. Em contrapartida, o inchamento pôde ser claramente observado e caracterizado através desse método.

Palavras Chave: Difusão, inchamento, CO₂, óleo leve, decaimento de pressão, tomografia computadorizada.

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LIST OF ACRONYMS

CAT	Computer-assisted Tomography
CPDGV	Constant Pressure Dissolving Gas Volumes
СТ	Computer Tomography
DPDVA	Dynamic Pendant Drop Volume Analysis
EOR	Enhanced Oil Recovery
EoS	Equation of State
FID	Flame-ionization Detectors
GC	Gas Chromatography
H.U	Hounsfield Unit
ILM	Immobilized Liquid Membrane
IOR	Increased Oil Recovery
kVp	Peak Kilovoltage (radiography)
LCR	Light Components Removed
LM	Levenberg-Marquardt
LPG	Liquid Petroleum Gas
NMR	low-field Nuclear Magnetic Resonance
PD	Pressure Decay
PR-EoS	Peng-Robinson Equation of State
PVT	Pressure/Volume/Temperature
ROI	Region of Interest
SA	Simulated Annealing
SF	Swelling Factor
TCD	Thermal conductivity detector
WAG	Water Alternating Gas
VLE	Vapor Liquid Equilibrium
DICOM	Digital Imaging and Communications in Medicine

LIST SYMBOLS

A	Diffusion cell cross sectional area (m ²)
A _m	Atomic mass of the absorber
b	Constant in eq. 2.1
С	Mass concentration (kg/m ³)
D	Diffusion coefficient (m ² /s)
E	Photon energy (KeV)
$\sigma_{c}E$	Klein-Nishima function
Н	Henry's law constant (MPa/(kg/m ³))
h	Height of oil column (m)
Io	Intensity of the incident x-ray (kV)
Ι	Intensity of the transmitted x-ray (kV)
k	Film mass transfer coefficient (m/s)
М	Group of coefficients
M_w	Molecular weight (kg/kg –mole)
N	Group of coefficients
N_g	Mass electron density $N_g = \frac{N_A Z_e}{A_m}$
N _A	Avogadro's number
р	Pressure (MPa)
R	Universal constant, 8.3144·10 ⁻⁶ (MPa m ³ /kg – mol K)
S	Variable frequency in Laplace domain
Т	Absolute temperature (K)
t	Time (s)
V	Volume (m ³)
Z	Gas compressibility factor
Z_e	Number of electrons per atom
Z.	Vertical spatial coordinate (cm)
Greek letters	
α	Constant for eq. 2.4
β	Constant for eq. 2.4
ζ	Constant for eq. 2.5
θ	Constant for eq. 2.5
λ	Thickness of the penetration material (m)
μ	Attenuation coefficient in Hounsfield units (H.U)
ρ	Density (kg/m ³)

σ_{c}	Cross-section per atom from Compton scattering
Ψ	Constant for eq. 2.5
Superscript	
e	Energy level
t	total
Subscript	
b	bubble
exp	experimental
mix	CO ₂ -oil mixture
sat	saturation
int	interface
eq	equilibrium
d	dimensionless
g	gas
gc	Gas cap
i	initial

1. INTRODUCTION

Oil recovery changes along reservoir producing life. First, it relies on reservoir natural energy (primary recovery) until it is depleted. So additional energy is required throughout physical displacement (secondary recovery) during its viable economic lifetime. A different kind of additional energy (tertiary recovery) enhances fluid flow conditions due to increasing oil mobility by changing oil properties through either the addition of heat, the chemical interaction between the injected fluid and the reservoir oil or the mass transfer.

All information above is described in Figure 1.1, where it is pointed out the difference between IOR (Increased Oil Recovery) and EOR (Enhanced Oil Recovery). The first one still has a wide range of techniques covering, besides water flooding or gas pressure maintenance. The last one comprises only the thermal, the chemical and the gas miscible/immiscible (Stosur et al., 2003).



Figure 1.1 - Proposed definitions of the EOR and IOR terms (Stosur et al., 2003)

Since in 1950, CO_2 -EOR appeared as an important injection agent in oil reservoir due to its high level of solubility in oil and low level in water. This main characteristic leads to the following factors that make CO_2 an effective EOR agent (Carcoana, 1992):

- miscibility effects, given the fact that since CO₂ is not first-contact miscible with reservoir oils, it may develop miscibility through multiple contacts under specific conditions of pressure and temperature and with specific oil compositions;
- swelling of crude oil and reduction in oil density;
- reduction in the water-oil mobility ratio as oil viscosity is reduced expressively when CO₂ is dissolved in crude oil followed by a small increase in water viscosity;
- acid effect on carbonate and shaley rocks.

Within the context of pre-salt reservoirs offshore Brazil, a sustainable hydrocarbon production will require the re-injection of the produced CO_2 -rich stream into the reservoir. During a gas injection operation, the amount of gas to be injected and the time reserved to reach the desired mobility of reservoir fluids are constraints that need to be determined for field design and reservoir simulation. The definition of such constraints requires the provision of data concerning the solubility and diffusivity of the gas in oil under reservoir conditions (Tharanivasan et al., 2006). The definition of the molecular diffusion coefficient in a multicomponent system is for instance very difficult to be determined without experimental measurements. Thus, several methods have been developed to determine the solvent-oil diffusion coefficient. On the other hand, oil swelling increases the recovery factor since, for a given residual oil saturation, the mass of the oil remaining in the reservoir is lower than if the abandoned oil were CO_2 free, as described by Carcoana (1992).

While diffusion in CO_2 -heavy oils systems has attracted some attention, the subject in light crude oils is scarcely described in the public literature (Guo et al., 2009). Such prospect needs therefore to be thoroughly investigated for the above referred pre-salt reservoirs offshore Brazil, where oil has an API gravity between 28 and 30, a gas-oil ratio between 200 and 350 m³/m³ and a variable contents of CO_2 (8 to 15 per cent) (Estrella, 2011). Due to such properties, differences in the models regarding boundary conditions at the interface and in the thermodynamics of the CO_2 -volatile oil must be taken into consideration.

1.1. Objectives

The aim of this study is to measure the diffusion coefficient and swelling factor of CO_2 in light crude oil under different experimental conditions concerning pressure, temperature and oil composition. In order to obtain the diffusion coefficient, two experimental techniques were run in parallel: the well-established and so-called pressure decay method and a CT scan method that was still under investigation. The later method was also used to obtain the swelling factor in the selected experimental conditions.

2. LITERATURE REVIEW

Within the context of miscibility of CO_2 in oil, molecular diffusion figures as the main phenomenon of interest now. In this chapter, the molecular diffusion and its main parameter the diffusion coefficient will be described. One first possible way of obtaining such key parameter is through empirical or theoretical correlations. This offers nevertheless several problems concerning the target system characteristics. Consequently, focus will be given to two experimental methods, namely pressure decay and CT scan, alongside their respective models. Finally a similar analysis will also be performed with swelling.

2.1. Molecular Diffusion

Here it is firstly important to differentiate miscibility from solubility. The first one is valid when two or more fluids form a single homogeneous phase in all mixed proportions while for the last one this happens only for a single level of proportions (Aljarwan, 2012). In addition to this, two miscible fluids will in the case of EOR present no interface and no capillary effect when in contact with porous media.

In 1976, Holm compared CO_2 to other recovery agents in miscible displacement like light hydrocarbons enriched gases and other solvents. CO_2 was for instance the only one to reach miscible displacement at the lowest pressures (6.89 MPa to 20.68 MPa or 1000 psi to 3000 psi), and it was also suitable to reservoirs that have been exhausted of their gas and LPG components. Furthermore, CO_2 presents additional advantages in terms of availability, cost, and operational handling (Holm, 1976).

Such properties make CO_2 the preferred gas in water-alternating-gas (WAG) processes. In such processes, water and CO_2 are alternatively injected until a well-defined volume of last one is attained, being afterwards followed by a continuous water injection. Compared with waterflooding without CO_2 , WAG processes improve mobility ratio and additional recovery.

In order to determine operating constraints for WAG processes, it is necessary to observe conditions that affect the multiple contacts in the miscibility developed by CO₂.

There are several factors that affect CO_2 miscible displacement. In regard to mixing mechanisms, there are three that contribute to this displacement process: microscopic convective

dispersion, macroscopic convective dispersion, and molecular diffusion. The last one has an important role on the recovery of residual oil at pore scale. At low solvent flow rates and long residence time, diffusion between CO_2 and oil interacts effectively to remaining unrecoverable oil, which is subsequently recovered by swelling (Aljarwan, 2012). Furthermore, the diffusion promotes mixing between the injected solvent and the oil, prevents viscous fingering, retards gas breakthrough and therefore improves the sweep efficiency for enhancing oil recovery (Guo et al., 2009).

Complementary to what has been previously mentioned, in the case of gas-based heavy oil recovery, it has been recognized that the molecular diffusion has a significant role during the soaking time while the convective-dispersion is predominant during the time of solvent injection (Tharanivasan et al., 2006).

Thus, in the succeeding subsections, molecular diffusion and swelling will be detailed in terms of fluid and fluid contact without considering fluid displacement in porous media. In such way dispersion will be ignored.

2.2. Correlations for Molecular Diffusion

It is well established that the diffusion coefficient measured in a two-component system depends on the presence or absence of a chemical concentration gradient (Prager, 1953).

The common theoretical methods that predicts diffusion coefficient are limited, many of them do not interpret adequately the kinetic phenomena because of several assumptions adopted. The Chapman-Enskog theory describes diffusion in low-pressure binary-gas mixtures, but it not applicable for liquids, while the Stokes-Einstein theory is appropriate only to ideal liquid mixtures. Thus, none of them can be used to real liquid mixtures. (Leahy-Dios and Firoozabadi, 2007).

Due to this problem, several semi-empirical equations have been proposed in the literature to estimate these coefficients. The Wilke-Chang correlation is suitable only for diluted systems and at lower viscosities, conditions that are far from oil reservoirs. The Vignes equation is considered a very useful way to calculate the diffusion coefficient as function of the concentration for systems involving hydrocarbons solvent and heavy oil, but it is limited to oil viscosity (Guerrero-Aconcha, 2009).

Concerned about a correlation for non-ideal gas and liquid multicomponent mixtures, Leahy-Dios and Firoozabadi (2007) proposed a unified model to determine D for non-ideal and non-polar multicomponent mixtures. They developed a new correlation based on 889 experimental data for non-polar mixtures and found a general functional form where infinite dilution-diffusion coefficient was dependent on viscosity, reduced temperature, reduced pressure and acentric factor of each component. With the dilution-diffusion coefficient found, the generalized Vignes relation to multicomponent mixtures is used to obtain the Stefan-Maxwell diffusion coefficient. This later coefficient is used to calculate the element of a square matrix which now is used to determine Fickian diffusion (mole based) in a non-ideal multicomponent mixture based on the relationship between Stefan-Maxwell and Fickian diffusive fluxes. In Stefan-Maxwell diffusive flux, the matrix of thermodynamic factor is calculated from PR-EoS, which has high precision for non-ideal hydrocarbon mixtures.

2.3. Experimental Methods

As aforementioned, the molecular diffusion coefficient in a multicomponent system is very difficult to be determined without experimental measurements. Thus, several methods have been developed to determine the solvent-liquid diffusion coefficient. They are split in two conventional techniques: direct and indirect methods. In direct methods, the gas concentration is analyzed with an analytical device. This procedure disturbs the system every time the sample is taken, reducing the accuracy of the measurements. On the other hand, the indirect methods implicate in observing some property of the gas–liquid system which evolves with the gas dissolution.

In order to develop proper gas-injection strategies, accurate values of relevant parameters such as gas-diffusion coefficient, interface mass-transfer coefficient and the liquid swelling coefficient are required for reservoir simulation and prediction of oil recovery by miscible flooding and the optimization of miscibility for best recovery (Civan and Rasmussen, 2006). To properly acquire those parameters experimentally, the indirect methods can be represented by: pressure decay (PD) method, the constant pressure dissolving gas volumes (CPDGV) method, the low-field nuclear magnetic resonance (NMR) spectra change method, the X-ray computer-assisted tomography (CAT) method, the gas permeation through an immobilized liquid

membrane (ILM) method implemented in a diffusion cell, and the dynamic pendant drop volume analysis (DPDVA) method.

With proper description of the dissolution and evaporation process, diffusion coefficient can be inferred from changes in bulk properties. Those properties can be volume, pressure, solute volatilization rate, position of the gas-liquid interface, refraction of electromagnetic radiation, etc. The medium property changed by the diffusing species is correlated with the composition. After the composition of the bulk is established, a mass transfer model as those that will be described later is required to determine diffusivity. Some indirect methods, like NMR and CAT, can estimate diffusivity by measuring the self-diffusion coefficients. Those methods on self-diffusion coefficients are limited by the empirical mixing rules used to calculate the concentrationdependent diffusivity. In general, indirect methods are based on several simplifications, described in the upcoming section.

Next, the experimental methods that were chosen for the present work will be described.

2.3.1. Pressure decay

The pressure decay method is a non-intrusive experimental method, where no compositional measurements are necessary. It starts when a non-equilibrium gas is displaced into a constant-volume constant-temperature PVT cell to remain in contact with a liquid. The gas initial pressure starts decaying as the molecular diffusion of the gas into the liquid proceeds until the system reaches the equilibrium. In other words, it means that the oil interface is entirely saturated with the gas. In a constant temperature, the measured pressure versus time and the proposed model are used to extract a correct value of diffusion coefficient that best represents this diffusion process (Riazi, 1996).

2.3.2. CT scan

2.3.2.1. Principles

This technique, well-known as x-ray tomography, has been widely used in research laboratories for reservoir rock characterization and fluid flow visualization. The fundamentals behind CT scan are that the object internal structure can be reconstructed from its multiple projections. In details, when an X-ray beam traverses an object, its intensity is attenuated as the

X-ray photons are absorbed (photoelectric absorption) or scattered (Compton scattering and Rayleigh scattering). While the photoelectric absorption is a process dependent on the component atomic number and the energy of the X-ray beam, the Compton scattering is influenced by the component bulk density.

The attenuation coefficient represents quantitatively how easily a material or medium can be penetrated by a beam of X-ray. It can be expressed as a function of the X-ray beam photon energy, the atomic number, and the electron density of the substance. Usually, Raleigh scattering is neglected, and then the attenuation coefficient can be expressed as the sum of Compton and photoelectric contributions (Eq. 2.1). When a high-energy X-ray source is used, the contribution from photoelectric absorption can be negligible and the attenuation coefficient μ becomes proportional to the bulk density of the object, as the Compton scattering dominates.

$$\mu = \rho N_g \left(\sigma_C(E) + \frac{b Z_e^{3.8}}{E^{3.2}} \right)$$
 2.1

where ρ is the mass density, N_g is the mass electron density, $\sigma_c(E)$ is the Klein-Nishima function, Z_e is the effective atomic number, E is the photon energy in KeV and b is a constant (Niu, 2010).

The amount that describes how effortlessly an X-ray beam can penetrate in a medium is named linear attenuation coefficient and is a result of the influence of the three different photon interactions cited above.

Lambert-Beer's law is set to measure the intensity of X-ray after it crossed the component:

$$I = I_0 \exp(-\mu\lambda)$$
 2.2

where λ is the thickness of the penetration material, I_o and I are the intensity of the incident x-ray and the transmitted one respectively. This law shows that photons with lower energy are absorbed firstly while the remaining ones are those with higher energy, thus the beam becomes harder. This brings on the total attenuation to change with distance and produce an artifact identified as beam hardening. This artifact and other image quality issues will be discussed in Image quality subsection.

2.3.2.2. Quantitative information

The quantitative information from CT scanning is given by the measured attenuation coefficients changed using the value for pure water as reference, being represented as CT numbers (CTn) in Hounsfield units (H.U),

$$CTn = 1000 \frac{\mu - \mu_{water}}{\mu_{water}}$$
 2.3

where, μ and μ_{water} are the linear attenuation coefficient for the tested material and pure water.

The possibility of obtaining density from the CT number can be employed because x-ray attenuation coefficients are both dependent on bulk density and atomic number (see Eq. 2.1).

For those materials where X-ray attenuation takes place, primarily only due to Compton scattering, there is a linear relationship (Eq. 2.4) between CT number and density (that varies accordingly to CT scanner type used.

$$\rho = \alpha. \operatorname{CTn} + \beta \qquad 2.4$$

where α and β are constants accordantly to the measured energy level and CT-scan employed.

For other materials with atomic numbers that contributes to both Compton scattering and photoelectric attenuation of X-rays, a dual energy measurement should be taken in order to have a correct relationship between CT numbers and densities. The method for determining density of those materials is described in details in the United States Patent Number 5063509 (Coles et al., 1991).

$$\rho = (\Delta CT_t + \zeta CT^{e^1} + \theta)/\psi \qquad 2.5$$

where ζ , θ and ψ are constants accordantly to the measured energy level and CT-scan employed.

To obtain both Eq. 2.4 and Eq. 2.5, a series of calibration tests for liquid and solid samples of known densities need to be accomplished. For the first equation, where only materials with Compton scattering takes place, only a single energy X-ray source is used while for the second equation dual energy source calibration tests are needed (Coles et al., 1991).

With one of those density and CT relationships above, the next step is to obtain solvent concentration in accordance to mixture density obtained.

For liquid solvents in oil, the mixtures rules equation can be used to predict the density of the solvent-oil mixture when there is no volume change after both components are mixed:

$$\rho_{\text{mix}} = (1 - C_{\text{solvent}}) \rho_{\text{oil}} + C_{\text{solvent}} \rho_{\text{solvent}}$$
 2.6

Eq. 2.6 can be rearranged in Eq. 2.7:

$$C_{\rm sol} = \frac{\rho_{\rm mix} - \rho_{\rm oil}}{\rho_{\rm sol} - \rho_{\rm oil}}$$
 2.7

Replacing the densities values in this last equation by Eq. 2.4, Eq. 2.8 is established as the most important relationship employed to find solvent concentration in oil columns after CT numbers are measured. In the case CT number and density that varies according to Eq. 2.4, the following equation can be used:

$$C_{sol} = \frac{CT_{mix} - CT_{oil}}{CT_{sol} - CT_{oil}}$$
2.8

Once, the rule of mixtures cannot be employed for gas solvents in oil, a correlation should be used to obtain solvent concentration in relation to solvent-oil mixture density. Guerrero-Aconcha et al. (2008) had already referred to this issue in their work as it will be detailed in the next section. The work from Emera and Sarma (2008) presented a correlation to predict CO_2 -oil density for dead and live oils over a wider range and conditions. A Genetic Agorithm based correlation accounts for saturation pressure, temperature, oil specific gravity and initial density at the specified temperature.

2.3.2.3. Dopants

When CT numbers of fluids do not differ as much as possible to reduce error, dopants are usually employed to increase CT number in one of the fluids. The majority of dopants applied in liquid phase have halide, which has a high atomic number, producing more attenuation of X-ray and thus requiring dual energy measurement in order to have a good relationship between CTs and density (Eq. 2.5).

So for small difference in attenuation coefficients (CT numbers) between different fluids, sodium bromide or sodium iodide are generally used as water dopants, while bromo-dodecane and iodo-dodecane are employed as oil dopants.

Once the choice of dopants is made, its addition should be done carefully, since they affect the thermodynamic properties of oil phase (viscosity, bubble point and minimum miscibility pressure).

2.3.2.4. Image quality (Niu, 2010).

The term 'Artefact' stands for the difference between the CT number in CT image and the true attenuation coefficient of the objects, which affects the image quality. In CT scan application in core analysis, there are two perceptible and downgrading physical based artifacts: the most noticeable one is called beam hardening and the other one is the photon starvation.

As mentioned previously in this section, beam hardening happens because the low-energy photons are more quickly attenuated than the high-energy photons, which causes the beam to become harder and more penetrating. The quantity of beam hardening rests on the initial X-ray spectrum and the composition of the material crossed. Images affected by the beam hardening are typically characterized with high attenuation coefficients around the periphery of the object and low attenuation coefficients in the center of the object. In practice, a filter can be used to reduce the influence of beam hardening on the image.

Photon starvation on the other hand causes streak artefacts as an insufficient amount of photons passes through the widest part of the materials. This artefacts normally happens when the core or core holder are scanned vertically. In the present work, the diffusion cell is also placed vertically. That is why some considerations have to be made in order to design the cell that will be scanned during the diffusion test. Aluminum and carbon fiber are the materials that can be used in CT scan. Aluminum is used for low pressure conditions while a carbon fiber wrapped aluminum cell is suitable for high pressure conditions. This last combination is done because with the increasing thickness of aluminum cell more photons are absorbed by the cell before enter in the fluid inside it.

Another consideration to avoid artefact is that all objects should have round geometry to reduce photon starvation inside the scanner that is circular. Furthermore, the table should be made of wood and the diameter of the surrounding lines should be as small as possible, to reduce the loss of photons.

Increasing some machine parameters such as the potential difference across the tube (kV) and the output of the tube $(mA \cdot s)$ enabling higher electron speed and also higher energy of the X-ray photons, resulting in improved image quality with less noise in the center of the object.

Increasing the two machine parameters above could therefore prevent several image quality issues – this was nevertheless not possible given the limitations of the here employed medical CT scanner with fixed energy level and care dose limitations.

2.4. Diffusion Models

The classical Fick's law is the most popular diffusion model in reservoir engineering, and it is mainly employed for binary mixtures. Otherwise it can also be used for ideal multicomponent mixture (pseudo-binary) considering that each component diffuses as a result of its own concentration gradient and diffusion coefficients which can be regarded as equal.

Bird et al. (2007) started his diffusivity study with binary diffusion using the onedimensional form of Fick's law of diffusion which defines how the molecular mass flux of species A in vertical direction $z(j_{Az})$ in a binary mixture at a steady-state is transported by means of molecular motions per unit of area. The proportionality factor \mathcal{D}_{AB} below is the diffusivity.

$$j_{Az} = -\rho \mathcal{D}_{AB} \frac{dw_A}{dz}$$
 2.9

where ρ is the density of the system A and B and w_A is the mass fraction of A.

The vector form of the equation above:

$$j_{A} = -\rho \mathcal{D}_{AB} \nabla w_{A} \qquad 2.10$$

As stated before, in addition to transport by molecular motion (j_A) , mass may also be transported by the bulk motion $(\rho_A v)$ of the fluid. Later the molecular mass flux vector and the convective mass flux vector are added together to get the combined mass flux vector (n_A) :

$$n_A = j_A + \rho_A v \tag{2.11}$$

where v is the mass average velocity.

For the fixed volume element considered in this equation, the balance of mass needs to be analyzed assuming the following contributions: rate of increase of mass of species a per unit volume, net rate of addition of mass A per unit volume by convection, net rate of addition of mass of A per unit volume by diffusion, rate of production of mass of A per unit volume by reaction.

All mass flux mentioned before are the combined ones that includes both the molecular flux and the convective flux and results in the equation of continuity for species A that can be put in the equivalent form:

$$\rho\left(\frac{\partial w_{A}}{\partial t} + (v \cdot \nabla w_{A})\right) = -(\nabla \cdot j_{A}) + r_{A}$$
2.12

where r_A represents the rate of production of mass of A per unit volume by reaction.

Considering a binary system with constant ρD_{AB} , Fick's law of diffusion can be used:

$$\rho\left(\frac{\partial w_{A}}{\partial t} + (v \cdot \nabla w_{A})\right) = \rho \mathcal{D}_{AB} \nabla^{2} w_{A} + r_{A}$$
 2.13

If there is no chemical reaction occurring and in addition v is zero and ρ is constant, the diffusion equation is defined as:

$$\frac{\partial c_A}{\partial t} = \mathcal{D}_{AB} \nabla^2 c_A \qquad 2.14$$

This equation represents unsteady-state mass-transfer process where concentration (c_A) at a given point varies with time. It is normally used for diffusion in solids or stationary liquids and for equimolar counter-diffusion in gases, which means that the net molar flux with respect to stationary coordinates is zero.

Other additional diffusion models found in the literature alongside the classical Fick's Law are the Maxwell-Stefan, the generalized Fick's law and the irreversible thermodynamics formulation. The three first models are used only for molecular diffusion in single phases, i.e., intra-phase diffusion where diffusion is considered separately only in the gas phase and then only in the oil phase. But when diffusion occurs between components in the gas and oil phases, it is defined as interface mass transfer and the diffusion model that can be used to describe such mass transfer is the irreversible thermodynamic model.
2.5. Diffusion Modeling Assumptions

Since the first mathematical model for pressure-decay experiment was formulated in 1996 by Riazi, the available models are limited by inherent simplifying assumptions. Therefore, before listing the models, it is worthwhile to briefly describe those considerations.

(a) **Pseudo-binary mixtures**

There is an important difference between binary diffusion and multicomponent diffusion In. binary diffusion the movement of species A is always proportional to the negative of the concentration gradient of species A. In multicomponent diffusion, however, other interesting situations can arise: (i) reverse diffusion, in which a species moves against its own concentration gradient; (ii) osmotic diffusion, in which a species diffuses even though its concentration gradient is zero; (iii) diffusion barrier, when a species does not diffuse even though its concentration gradient is nonzero. In addition, the flux of a species is not necessarily collinear with the concentration gradient of that species. (Bird et al., 2007)

(b) Natural Convection

Mass transfer between two fluid phases happens by evaporation and condensation through their interface. As these processes are usually faster than the diffusive and convective time scales in either phase, the rate of mass transfer is controlled by how efficiently mass is transported from the interface and into the bulk. When the density of the heavier (lighter) phase does not increase (decrease) during the mixing process, there will be no natural convection and the rate of mixing is governed by diffusion. No bulk flow is a common assumption in the modeling of PVT cell experiments (Haugen and Firoozabadi, 2009). Natural convection in mixtures in which liquid density increases with dissolution and gas density decreases with evaporation may affect the gasdiffusion rate (Civan and Rasmussen, 2006).

(c) Swelling Effect

When swelling happens in the oil phase, the original capillary equilibrium breaks down, resulting in a pore-scale redistribution of the phases and then in oil mobilization. Thus an important factor is the time required by CO_2 to swell oil significantly (Grogan and Pinczewki, 1987). When swelling is contemplated, it is necessary to consider interface movements. Hence, a

convective term in the diffusion gas continuity equation needs to be incorporated. Swelling will not be taken in consideration during the present diffusion model but it will be described in details in the next section.

(d) Unidirectional diffusion

The non-volatility of oil is verified by a compositional analysis of the solvent phase after the diffusion test. This oil characteristic renders a one-way diffusion of the solvent in oil, assumed as unidirectional diffusion.

(e) Real gas deviation factor

In order to obtain the mass of diffused gas, a constant gas compressibility factor is usually employed in the literature. It is important to mention that the real-gas deviation factor might deviate significantly from the unity at elevated pressures.

(f) Henry's law

Application of Henry's law is questioned by Civan and Rasmussen (2006), when they say that the application of a non-equilibrium boundary condition alleviates the problems concerned by neglecting the oil volume caused by swelling and the pressure dependency of the real gas deviation factor. Once, the majority of methods contemplate dilute solutions to neglect both swelling effect and diffusion coefficient gas concentration dependency, higher concentrations of the dissolved gas in the liquid phase may affect the quality of estimated parameters (Rasmussen and Civan, 2008).

(g) Diffusivity concentration dependency

There are many real systems for which the diffusivity depends upon concentration. Such concentration-dependence exists in most systems, but often, for example in dilute solutions, the dependence is slight and the diffusion coefficient can be assumed constant for practical purposes. A number of methods have been used to obtain numerical solutions, some applicable to any type of concentration-dependent diffusion coefficient, and others restricted to particular types, such as exponential or linear dependence. (Crank, 1975)

As stated by Guerrero-Aconcha (2009), for the diffusion coefficient to be considered constant there are three key factors that have to be achieved:

- diffusing components should have analogous molecular diameters and molecular shape;
- molecular interactions between the diffusion components should be negligible;
- non-reacting components may be part of the system.

(h) Interface boundary condition

After the differential Eq. 2.14 has been integrated, constants of integration appear, and these have to be determined by the use of boundary conditions.

In the beginning of the diffusion test, the concentration of gas in the oil phase is equal to zero. So, the initial condition is assumed to be:

$$c(z,t)|_{t=0} = 0 \quad 0 \le z \le L$$
 2.15

At the bottom of the diffusion cell, the condition satisfying the impermeable boundary is the one which the mass transfer flux at any time is equal to zero (Neumann Boundary Condition):

$$\left. \frac{\partial c}{\partial z} \right|_{t=0} = 0 \quad t > 0 \tag{2.16}$$

Concerning the interface gas-oil, accordingly to Tharanivasan (2006), three boundary conditions have been established for the interface mass transfer model.

The equilibrium boundary condition states that once the system is pressurized at the initial pressure, the interface becomes saturated with gas under the equilibrium pressure (Dirichlet Boundary Condition):

$$c(z, t)|_{z=L} = c_{sat}(P_{eq}) \quad t > 0$$
 2.17

This constant boundary condition is satisfactory only if the pressure decay is small.

For the quasi –equilibrium boundary condition instead of the interface be saturated with gas at equilibrium pressure, it is saturated under the existing pressure. Now the Dirichlet boundary condition is stated in function of time as:

$$c(z, t)|_{z=L} = c_{sat}[P(t)] t > 0$$
 2.18

The third type of boundary condition, the non-equilibrium one specifies that the gas mass flux across the interface is proportional to the difference between the gas concentration at the equilibrium pressure and the gas concentration at the interface. This proportionality in the socalled Robin boundary condition is the mass transfer coefficient at the gas-oil interface. Usually as described by Rasmussen and Civan (2008) most methods ignore film-mass-transfercoefficient.

$$\left. D \frac{\partial c}{\partial z} \right|_{z=L} = k \left[c_{sat} \left(P_{eq} \right) - c(z,t) \right|_{z=L} \right] \quad t > 0$$
 2.19

Another Robin boundary condition, now time dependent, covers the whole range of equilibrium and non-equilibrium behaviors. $c_{int}(t)$ is the concentration in equilibrium with the vapor pressure in the gas cap remote from the surface.

$$\left. D \frac{\partial c}{\partial z} \right|_{z=L} = k \left[c_{int}(t) - c(z,t) \right]_{z=L} =$$

2.5.1. Models Based on Pressure Decay Experiments

As described before, pressure decay is the most used method to obtain data that will be employed in diffusion models. A brief overview of ten models based on pressure decay data will be presented in this segment, followed by a summary in table 2.1. It is important to notice here that most of the discussed models involve solvents in heavy oils, except the ones from Riazi (1996) and Haugen and Firoozabadi (2009).

(a) Riazi (1996)

Riazi was the first in 1996 to present the pressure decay method. His model had as major assumption that equilibrium exists between liquid and gas phases at their interface. Boundary composition changes as pressure changes, so the Dirichlet time dependent boundary condition type was applied (Table 2.1). Once n-pentane was the component used to diffuse methane, swelling effect was considered. The objective of this model was to forecast gas-liquid interface and pressure during diffusion process. The diffusion coefficient was considered dependent on concentration as time elapsed. Another important consideration was the equimolar counter-diffusion, which means that when there is concentration gradient in the gas and liquid phases, diffusion will take place in both phases. In summary, Riazi's model worked into time steps where diffusion coefficient and liquid height inside the cell were constant. For each period, interface concentration was obtained through PR-EoS using the data updated from pressure decay and height of liquid. The final numerical solution of his model provides changes of the average concentration and diffusion coefficient versus time. (Etminan et at., 2013)

(b) Zhang et al. (2000)

Few years after Riazi, Zhang et al. (2000) developed a simplified model. His study was based on gas diffusion in heavy oils, therefore interface position was considered fixed assuming that there was no swelling effect. Furthermore, the diffusion coefficient was also considered constant and diffusion process was considered unidirectional. The compressibility factor was also assumed to be constant since pressure change during the test was small. Zhang considered for their analytical solution a Dirichlet interface boundary condition as constant saturation concentration at interface. To obtain diffusion coefficient, Zhang divided diffusion process in two stages, the first one, the incubation period, where pressure drops expressively and the second one where a straight line is obtained when experimental data is plotted on a semi-logarithm graph. Thus Zhang studied only this second stage and obtained from it the diffusion coefficient.

(c) Upreti and Mehrotra (2000)

After Zhang, Upreti and Mehrotra in 2000 also studied diffusion in heavy oils using pressure decay method with CO_2 . They first determined CO_2 experimental concentration in bitumen using a PVT relationship of the gas and the density of oil after diffusion started. To obtain the density, a correlation was proposed in this work. After experimental concentration is obtained, a numerical minimization of an objective function between experimental concentration and calculated one is used to find gas diffusivity. The calculated data is acquired by means of a mass transfer model, where diffusion coefficient is considered to be a function of gas concentration in oil. Here the heavy oil is also assumed to be non-diffusing, volume change is taken in consideration and concentration at interface varies according to time.

(d) Sheika et al. (2005)

The same experimental data from Upretti and Mehrotra (2000) is used and two different models are developed involving an analogous approach to pressure diffusion behavior in petroleum reservoirs under single-phase flow conditions. So, from the infinite-acting model where diffusion coefficient is achieved, the gas penetration depth never reaches the bottom of the pressure cell, establishing the boundary condition at the bottom. For the interface, the equilibrium between gas and oil is represented by Henry's law and a mass balance of the diffused gas is performed to reach the interface boundary condition that is designated in Table 2.1.. Although, infinite-acting model is valid only for early times, beyond this the model is not valid anymore. To determine this time, finite-acting model is carried out and the boundary condition at the bottom of the cell establishes that there is no mass flux anymore.

Two graphical methods are employed to obtain the relationship between diffusion coefficient and Henry's constant, called combination factor. Those graphical methods are similar to well-testing reservoir permeability determination. After the combination factor is found, the Henry's constant is calculated through a correlation for the volume-basis gas solubility and then diffusion coefficient can be acquired.

The main assumptions of this model are: a constant diffusion coefficient, swelling is negligible, non-volatile oil and a constant gas compressibility factor. Based on those assumptions, the error in estimating diffusion coefficient without swelling and with a constant compressibility factor are also described in this work. An important remark that should be mentioned here is that for CO_2 -heavy oil test the combined relative error in predicting pressures due to neglecting oil swelling and the constant gas compressibility factor was the greatest one (13% - 14%).

(e) Civan and Rasmussen (2001, 2006, 2008)

Since 2001, Civan and Rasmussen developed a mathematically robust diffusion model from Zhang. In 2006, they presented a diffusion model that considered resistance in gas/liquid interface, and had several assumptions such as no swelling effect, incompressible gas/liquid solution and constant diffusion coefficient. With those assumptions, two analytical solutions of

mass accumulation of gas dissolved in liquid phase are proposed. They are based on two types of bottom conditions, namely the semi-infinite (short time) and finite length (long time) approaches. An interpretation methodology is used with experimental data to obtain diffusion coefficient and interface mass transfer coefficient. In 2008, they improved their model interpretation by considering only time-limited data which was independent of equilibrium conditions, being able also to estimate equilibrium pressure and gas solubility. Both long-time and short-time approximations were used to evaluate parameters.

(f) Tharanivasan et al. (2006)

In this work, Zhang experimental data was investigated. The experimental data and theoretically one were compared through a minimum objective function that was used to find the diffusion coefficient. The main focus here was to investigate three kinds of interface boundary conditions that better adjust to each type of solvent interface diffusion conditions (CO_2 , CH_4 and propane). Those boundaries conditions were previously studied by other authors: equilibrium (Zhang), quasi equilibrium (Riazi and Upretti and Mehrotra) and non-equilibrium (Civan and Rasmussen).

Accordingly to Tharanivasan, the assumption of constant diffusion coefficient in the solvent-saturated heavy oil was reasonable, because the solvent concentration in heavy oil is generally low under the test conditions. Furthermore both natural convection and swelling effect were not considered, while unidirectional diffusion was applied.

For each boundary condition, Tharanivasan noticed in reported literature the correspondent solution for solvent concentration distribution in the oil. To obtain diffusion coefficient, a history matching technique between experimental pressures and calculated ones were used. The calculated pressure was established through an EoS for real gas. Lee-Kesler correlation was then used to obtain compressibility factor. The number of moles of solvent dissolved into oil was obtained at any time by numerically integrating the transient solution for each boundary condition found by Tharanivasan.

Before diffusion coefficient determination, equilibrium pressure should be established as it will be used in the boundary conditions. In this work, equilibrium pressure was determined as a result of a vapor-liquid equilibrium apparatus used to measure solubility and hence applying the EoS for the solvent phase at the equilibrium state. To conclude, Tharanivasan noticed that for CO_2 -heavy oil system, the interfacial resistance varies with diffusion time. At early times of diffusion process, interface resistance is significant and non-equilibrium boundary condition can be considered. At large diffusion times, quasi equilibrium conditions are observed when history matching presents the best values.

(g) Haugen and Firoozabadi (2009)

Haugen and Firoozabadi showed with their diffusion numerical model that a purely diffusive model overestimates the liquid diffusion coefficient. Once, no natural convection occurs, the rate of mixing is governed by diffusion. On the other hand, after diffusion induces bulk velocity, convective mass transfer may still be important. This convective mass transport, which results in a local density change, is due to compressibility (dominates gas phase) and non-ideality (dominates liquid phase, once the volume in mixing changes). Thus the two phases exchange mass as they equilibrate and consequently the pressure and liquid level in the PVT cell vary with time. The fact that the interface is moving was also taken in account.

The interface conditions are considered to be in local chemical equilibrium and because there is a jump in composition, fugacity of a component in both phases should be same.

They also reported that to identify the influence from bulk mass transport, it was necessary to use only a constant value of diffusion coefficient. By using variable diffusion coefficients it was difficult to identify bulk mass transport contributions. To complement, they also concluded that non-ideality and gas solubility have a great importance in liquid bulk mass transport. And when a liquid component is nonvolatile there is hardly any diffusion in the gas phase.

(h) Etminan et al. (2013)

In 2013, Etminan et al. published in a review a diffusion model that also considered an interface resistance as Civan and Rasmussen proposed. But instead of having a third type Robin boundary condition based on equilibrium pressure, the present boundary condition was third type Robin time dependent. This time dependence shelters the entire change of equilibrium and non-equilibrium behaviors.

Despite the several assumptions adopted on Etminan et al. (2013) model, this method was the one chosen here as a startup model based on the time-dependent Robin type boundary condition. The mathematical treatment as well as the assumptions will be described and discussed in details in the upcoming sections.

Ref.	Model	Gas/Liquid	p(MPa) / T (K)	Diffusion coefficient	Swelling effect	Z factor	Boundary condition at interface	Calculated parameters
Riazi, 1996	Semi- analytical model	methane with n- pentane	7 / 310.9	Concentrati on dependent	Yes	PR-EoS	Dirichlet time dependent	Diffusion coefficient, swelling factor
Zhang et al., 2000	Analytical model	CO ₂ and heavy oil	2.85 / 294.1	Constant	No	Constant	Dirichlet	Diffusion coefficient, equilibrium molar concentration
Upreti and Mehrotra, 2000	Numerical model	CO ₂ and heavy oil	4 / 298.15 - 363.15	Concentrati on dependent	Yes	PV=nZRT	Dirichlet time dependent	Gas solubility and Diffusion coefficient
Tharanivasan et al., 2006	Analytical model	CO ₂ and bitumen	4.2 / 297.05	Constant	No	Lee- Kesler correlation	Robin	Diffusion coefficient, equilibrium pressure

Table 2.1 - Comparative between pressure decay models reported in literature

Researchers, ref.	Model	Gas/Liquid	p (MPa) /T (K)	Diffusion coefficient	Swelling effect	Z factor	Boundary condition at interface	Calculated parameters
Civan and Rasmussen, 2009	Analytical model	CO ₂ and heavy oil	4 / 348.15	Constant	No	Redlich- Kwong	Robin	gas diffusion, film- mass-transfer Peq
Sheikha et al., 2005	Analytical model	CO ₂ and bitumen	8 / 348.15 - 363.15	Constant	No	Constant	Dirichlet time dependent	Diffusion coefficient
Haugen and Firoozabadi, 2009	Numerical model	methane with n- pentane	7/310.95	Constant	Yes	PR-EoS	Dirichlet time dependent	Diffusion coefficient
Etminan et al., 2013	Semi- analytical model	Bitumen and CO ₂	4 / 348.15	Constant	No	Constant	Robin time dependent	Diffusion coefficient

Cont.Table 2.1 - Comparative between pressure decay models reported in literature

2.5.2. Models Based on CT scan Experiments

Once CT-scan studies were run in parallel to pressure decay, a few of CT-scan models will be described below.

(a) Wen and Kantzas, 2005

In 2005, Wen and Kantzas studied diffusion process using both NMR and CAT techniques. For CAT technique, the change in CT number observed during process delivers the density of the mixture within the oil column as described earlier in Eq. 2.4.

They assumed that the diffusion coefficient of solvent was equal to the diffusion coefficient of the oil, and then called it the overall diffusion coefficient. This overall diffusion coefficient was studied as a constant and as a function of concentration. For constant coefficient study, they realized that it depends on concentration. On the other hand, for a diffusion coefficient dependent on concentration, they used equation of continuity with Fick's law (Eq. 2.14) through the same methodology followed by Oballa and Butler using Boltzmann transformation. This transformation is valid for infinite and semi-infinite boundary conditions, with interface boundary kept at constant concentration. With this transformation, the following equation is obtained as a particular solution of Eq. 2.14.

$$D = \frac{1}{2t} \frac{\partial z}{\partial c} \int_{0}^{c_{1}} z dc$$
 2.21

(b) Guerrero-Aconcha et al., 2008

In this work, the Matano-Boltzmann method is questioned due to the anomalous trend observed for concentration dependent diffusion coefficient. In order to replace this method, they used the "slopes and intercepts" analytical method developed by Sarafianos (1986) to obtain the diffusion coefficient of a liquid solvent (nC_6 , nC_7 and nC_8) in heavy oil. They assumed a constant concentration at the interface along a semi-infinite system.

They proceeded also with a calibration test to obtain a curve (Eq. 2.4) where the densities of the scanned samples can be recalculated.

Despite the "slopes and intercepts" method being appropriately adjusted to liquid solvents diffusion in heavy oil, this analytical method needs the concentration profile information in advance. For diffusion of gas solvents in oil, the acquisition of the solvent concentration data in oil is not an easy task as mentioned by Guerrero-Aconcha, 2009. None of the two Eq. 2.7 and Eq. 2.8 can be used because Eq. 2.6 is not valid to obtain density mixture of gas in oil.

Thus, Guerrero-Aconcha chose to follow a non-iterative finite volume method developed by Chang et al. (2006) which was used by the later one to inverse estimate thermal conductivity in one-dimensional domain. In the case of Guerrero-Aconcha, instead of the thermal conductivity, they wanted to obtain the diffusion coefficient. The differential equation is therefore transformed into a system of linear equations and solved using matrices. To solve these matrices, the density data at discrete points was used.

The choice here to employ density data instead of concentration was justified by the limitations mentioned on the previous paragraph. In order to be able to use density as a replacement for concentration, the equation of continuity with Fick's law was converted in the following form (Eq. 2.22) after the assumption of a lineal approach dependency between concentration and density. This assumption is based on Upreti and Mehrotra (2000) work where the gas-bitumen mixture density was correlated from the experimental data into a linear equation.

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial z} \left(D \frac{\partial \rho}{\partial z} \right)$$
 2.22

2.6. Swelling

The swelling effect of crude oil with CO_2 increases the oil formation volume factor so that residual oil after waterflooding is smaller in volume at surface conditions. Also, oil swelling within the pore spaces displaces water out of the pores, resulting in a decrease in the wetting phase saturation (drainage process). For water-wet porous media, relative permeabilities of the drainage oil are higher than imbibition values, thus favoring additional oil recovery (Carcoana, 1992).

The extent of the expansion or swelling is measured by the "swelling factor", and this is used to calculate other properties of interest in enhanced oil recovery. There are few methods in literature to predict CO_2 solubility and swelling factors of crude. In 1965, Simon and Graue developed empirical correlations in graphical form to obtain CO_2 solubility, fluid swelling, and viscosity data for pure CO_2 -oil mixtures. These correlations have some disadvantages considering the inconvenience for computer calculations and extrapolations out of the range of experiments as they were empirical.

During seventies, Katz and Firoozabadi and other authors treated CO_2 -oil system as a mixture of 10 to 40 recognizable components with known properties and compositions. Despite using a simple equation of state to represent the system, they were able to acquire a complete description of vapor-liquid equilibrium. This multicomponent mixture nevertheless demands a huge amount of computer time becoming quite costly (Teja and Sandler, 1980).

In 1980, Teja proposed an extended corresponding stated method for saturated liquid densities that was later applied to predict oil swelling factor in CO_2 -crude oil systems. In this subsequent work, Teja and Sandler (1980) predicted the swelling factor of CO_2 -crude oil mixtures given the average boiling point or Watson K-factor and specific gravity of the crude and the known properties of two references substances. By now treating the oil as a single pseudo-component, they predicted solubility and swelling factors by using the Peng-Robinson equation of state.

2.6.1. Experimental Methods

Swelling test is a special PVT laboratory test and is the most common multi-contact PVT test (Aljarwan, 2012). During this test, a gas with known composition is injected into the oil at varying proportions (quantified in terms of molar percentage). Then the following data is acquired:

- the relationship between saturation pressures and volume of gas injected;
- the saturation pressure changes after a volume of gas is injected;
- the volume change of the saturated fluid mixture in relation to the volume of the original saturated reservoir oil.

In the present work, the experimental method to measure swelling factor did not use a windowed PVT cell and thus not all the data mentioned above was collected. The only information that was collected was the volume changes after the injection agent was added and measured through CT scan diagnosis. The current adopted methodology will be described in the Methods section.

2.7. Models Optimization

This section will give a brief introduction about the two minimization methods that were applied to obtain the parameters from the chosen model described in Methods section.

As stated in Silva Neto et al. (2010), the problem of parameter identification characterizes a typical inverse problem in engineering. This happens because sometimes developing theoretical models based on physical phenomena and real operating conditions are quite challenging. Thus an inverse mass transfer problem needs to be treated by using different methodologies, such as deterministic, stochastic and hybrid methods. So the inverse problem comprises the determination of the desired parameters through the use of experimental data for minimizing the residue between experimental and calculated values.

Below, two methods that were used in the Results and Discussion section will be quickly described.

2.7.1. Simulated Annealing Method (SA)

The essence of this method is an analogy with thermodynamics from freezing and crystallization of liquids or cooling and annealing of metals. Mainly, the cooling procedure needs to be slow enough in order to reach the minimum energy level. For each iteration of this method, a new point is randomly generated. The extend of the search is based on the so-called Boltzmann probability distribution. As this algorithm admits additional points that raise the objective function, it avoids being stuck in local minima in early iterations and is also capable of exploring globally for better solutions.

2.7.2. Levenberg-Marquardt Method (LM)

This method is used to solve non-linear least square problems, especially in least squares curve fitting. LM method is basically a combination between the Gauss-Newton algorithm and the method of gradient descent, but it finds only a local minimum, not a global minimum.

In order to keep the best features of each method, Silva Neto et al. (2010) proposed a combination of different methods, using SA as the global optimizer. In the case of LM and SA combination, once LM reached a point of minimum, SA was placed to run. If the same solution was found, it means that a global minimum has been reached and the iterative procedure was

finished. Although if a different solution was obtained from SA, it meant that the solution found in LM was not a global but rather a local minimum. Consequently, both methods were run again until the global minimum was reached.

3. MATERIALS AND METHOD

The following chapter will describe all the equipment and materials employed during the tests as well as the experimental methods from the two selected techniques.

3.1. Materials

The materials listed in Table 3.1 enabled the experimental assembly to simultaneously perform pressure decay and CT scan experiments.

EQUIPMENT	SPECIFICATIONS		
CT scan	Siemens Spirit Somaton		
Pressure recorder	nVision Intrinsically safe, Crystal engineering corporation (Pressure Module 103.42 MPa or 15000 psi)		
Diffusion Cell	Detailed description bellow		
Pump to pressurize CO ₂ bottles	Quizix Q5000		
Pump to inject oil	Jasco PU-2086i		
Thermocouple	Omega Part #JQIN-116U-12		
Density meter	Anton Paar DMA 4500		
MATERIALS	SPECIFICATIONS		
Pressure bottles	Usiesp usinagens especiais ltda (1000 mL and 15000 psi)		
Valves	Needle valves for high pressure		
Crude dead oil	density = 0.876 g/cm3 @ 20°C and atmospheric pressure. Further information Attachment B.		
CO_2	Air Liquid with purity levels of 99.995%		
Dopant	98% 1-Iododecane (Sigma-Aldrich, product reference 238252)		
Thermal blanket	PET wool-type fibres and Kevlar® aramid fiber blanket		

Table 3.1 - Equipment, Materials and Specifications

Experiments were conducted in an apparatus mounted according to the setup shown in Figure 3.1.



Figure 3.1 - Experimental Setup

The pressure cell used in both experiments was properly designed to be used inside the CT scanner and to hold high-pressure levels. Once it needed to be used inside a CT scanner, it was constructed with x-ray transparent material, such as aluminum, and had a cylindrical shape to minimize CT reconstruction errors.

As detailed in Figure 3.2 the aluminum diffusion cell was designed with the specifications found in Table 3.2.





Figure 3.2 - Diffusion cell special design

SPECIFICATIONS	VALUE
Internal diameter	38.1 mm
External diameter	300 mm
Internal height	114.7 ± 0.3 mm
Material	Duralumin (AA2024, which contains 4.4% copper, 1.5% magnesium, 0.6% manganese and 93.5% aluminum by weight)
Working pressure	41.37 MPa or 6000 psi
O-ring type used	Buna-N Nitrile Duro 90 Hard - Parker®

Table 3.2 - Diffusion Cell Specifications

As depicted in Figure 3.3, the diffusion cell was mounted over an acrylic base and then the whole assembly was installed on a fixed position over a wood table attached to CT bed. This entire installation allowed each CT image taken to be positioned in the same cross-sectional region of interest (ROI) inside the diffusion cell.



Figure 3.3 - Diffusion cell positioned inside CT gantry

3.1. Experimental methods

As depicted in experimental setup, the diffusion process was monitored using both pressure transducer and Siemens CT scanner. The pressure decay technique registered the pressure drop inside the cell at a constant temperature as gas diffused and dissolved into the oil column until the system reached the equilibrium. A diffusion cell was connected at the top and at the bottom to two pressure bottles, from where the fluids were admitted. The pressure transducer apparatus was calibrated and tested by manufacturer, so that no further calibration of the pressure sensor was performed. This pressure sensor has a 103.42 MPa or 15000 psi pressure module. With this model, accuracy of operational range is illustrated in Table 3.3 (Online Crystal Engineering data sheet source). Once, this equipment was not appropriate to the pressure operational range, there was a significant chance that measurement results could be affected by this level of error.

 OPERATIONAL RANGE
 ACCURACY

 0.10 to 31.13 MPa / 15 to 4515 psi
 ± 0.035 MPa / ± 5 psi

 31.13 to 103.52 MPa / 4515 to 15015 psi
 ± 0.1% of reading

Table 3.3 – 103.42 MPa Pressure Module Accuracy

Simultaneously to pressure decay measurement, CT-scan techniques were used to generate 2D images of the CO₂-oil mixture. As CO₂ diffuses into oil, the concentration gradient distribution with distance can be acquired because the CT number varies during the process and relates to the concentration of CO₂ in the mixture. To directly relate CT with concentration, firstly a relationship between CT number and densities need to be established, with this relation being defined by building a calibration curve with known densities. Afterward CT profile was related to density values, the next step was to obtain the correspondent CO₂ concentration is obtained over the length of the oil column. This was made possible through CT scan image taken at each fixed interval during diffusion process. A region of interest (ROI) close to the CO₂-oil interface was designated inside the CT scan (See Figure 3.4). An average of horizontal CT numbers generates a vertical profile that represents CT numbers change throughout the ROI at X-ray image.



Figure 3.4 - Diffusion cell with ROI

As the used CT scanner was a medical one, there was no protocol available to be used in the present work conditions. It was necessary to develop a special CT scan protocol to scan this aluminum cell and enhance image quality as much as possible. The following table summarizes the CT scan protocol parameters employed for the current measurements at 130 kV.

PARAMETERS	OBSERVATIONS
Protocol Name	'Cal_fluid_diff'
Format	DICOM
Width	512
Height	512
BitDepth	12
ColorType	grayscale
Body Part Examined	ABDOMEN
SliceThickness	10
kVp	130
ReconstructionDiameter	60
DistanceSourceToDetector	940
DistanceSourceToPatient	535
GantryDetectorTilt	0
TableHeight	155
XrayTubeCurrent	160
ConvolutionKernel	B30s

 Table 3.4 - Protocol Parameters

The calibration curve, CO_2 concentration relationship with mixture density and CT-scan data treatment will be subject of further discussion in the Results and Discussion subsection for CT scan method investigation.

Before starting all the experiments, the diffusion cell assembly was pressured tested with nitrogen at 1.38 MPa (2000 psi) and at room temperature 293.15 K (20° C) inside a water bath. And before each experiment, the diffusion cell and lines were cleaned with kerosene, with alcohol and vented with compressed air. Later, CO₂ was vented from top to the bottom of the cell and a small amount of pressure (0.013 - 0.027 MPa / 2 - 4 psi) was left inside the cell chamber. After this "atmosphere" of CO₂ was left inside the cell, crude oil was injected from the bottom cell entrance until it reaches around 60 mL of pumped oil, rigorously checked through a beaker before and after oil injection started. A rate of 5mL/min oil injection was chosen to minimize CO₂ convective forced mass transfer into oil due to fluid movement. CT scans were taken during oil pumping to check for any modification in oil CT numbers.

Immediately after the column of oil was pumped inside the cell, the CO_2 was injected from the top entrance until it reached the desired initial pressure. Here, the CO_2 pump injection rate was controlled to be around 0.023 MPa/s (200 psi/min) remaining with the same purpose to prevent forced convection mentioned in the paragraph above. Right after the CO_2 injection was finished, the first scan was taken and this image represented the CT number at the initial pressure (p_i) and initial time (t=0). The end of the diffusion process was here defined as when a variation of no more than 0.007 MPa (1 psi) could be observed every 30 minutes during the following three hours. The entire process of filling the cell is short compared with the duration of the experiment, and hence it is assumed that mass transfer between the phases during the injection of both fluids is negligible.

3.1.1. Experiments at 293.15 K (20°C)

Almost all the tests were performed at the room temperature of 293.15 K (20°C). A thermocouple was attached close to the cell to be able to verify the stability of room temperature (see Figure 3.3). Only the last test was executed at 338.15 K (65° C), where thermal blankets were used to maintain temperature in the diffusion cell and in the pressure bottle where the CO₂ was pressurized.

The first two tests at 293.15 K (20° C) were done with dead oil in its original composition. The initial pressures applied to each test were 5.31 MPa (770 psi) and 6.89 MPa (1000 psi). In the former, CO₂ was still in its gas phase while in the latter test CO₂ was already in the liquid phase (see Attachment A for isothermal properties for CO₂ from NIST). Although in both experiments, the diffusion process end up in equilibrium pressure, CT attenuation values were not able to identify the CO₂ concentration in oil.

(a) Using original oil

Thus, for the next steps the crude dead oil was doped with iododecane (4% in volume) to enhance CT attenuation in order to detect the CO_2 dissolution in oil. Other amounts of iododecane were tested (1% and 10%), but the one with 4% showed to be the optimal concentration of dopant that on one hand will not significantly change the oil composition (density = 0.893 g/cm³ @ 20°C and atmospheric pressure) and on the other hand will still enable CT attenuation identification along the diffusion process.

(b) Using doped oil

So, after oil was doped, experiments were performed at 3.03, 5.31, 9.65 and 28.96 MPa (440, 770, 1400 and 4200 psi). For the first three pressure levels, CO_2 is lighter than the oil and therefore it was injected through the top after the oil was pumped through the bottom, and pressure was also monitored in the upper cell connection. As for the 28.96 MPa (4200 psi) level, CO_2 is heavier than the oil so that, at this pressure level, the fluid was firstly injected and then the system was filled with oil from the top. The pressure in this case was monitored in the lower cell connection. The doped oil experiments presented a limitation that will be further subject of discussion in section 5. The last goal was to perform diffusion test under a similar reservoir conditions.

3.1.2. Experiments at 338.15 K (65°C)

The pressure chosen a close to reservoir condition was 10.36 MPa (1500 psi) and the temperature was 338.15 K (65° C). In such levels, CO₂ was on its supercritical condition. The dead oil used was from the same original samples taken for experiments performed at 293.15 K before the doped oil was used.

4. THEORETICAL MODELING

4.1. Pressure Decay

As stated earlier, the pressure-decay technique used in the present work follows Etminan et al. (2013) procedure. The next theoretical model presented was a short-term summary, for supplementary information address to Etminan et al. (2013) and Etminan (2012).

For the diffusion model with interface resistance in isothermal conditions throughout the pressure-decay experiment, the use of Fick's law is reasonable just after some assumptions are applied, as presented in the work from Etminan et al. (2013):

(i) No chemical reaction between the oil and the gas;

- (ii) No natural convection;
- (iii) Swelling is negligible;
- (iv) Gas diffusion is unidirectional;
- (v) Diffusion coefficient is constant;
- (vi) Gas compressibility factor is constant;
- (vii) Solution density remains constant.

Considering the geometry of the cell depicted in Figure 4.1 and the mentioned hypothesis, diffusion was modeled as:

Fick's law
$$\frac{\partial^2 C_g}{\partial z^2} = \frac{1}{D} \frac{\partial C_g}{\partial t}$$
 4.1

Initial condition
$$C_g(z, t = 0) = 0$$
 4.2

Boundary condition at bottom $\frac{\partial C_g}{\partial z}\Big|_{z=h} = 0$ 4.3

Boundary condition at interface
$$-D\frac{\partial C_g}{\partial z} = k (C_{g-int}(t) - C_g(z = 0, t))$$
 4.4



Figure 4.1 - Diffusion cell

The boundary condition at the interface represents the non-instantaneous thermodynamic equilibrium. As the gas concentration in vapor pressure equilibrium $(C_{g-int}(t))$ is not the same as the gas concentration below the interface $(C_g(z = 0, t))$, a resistance to the mass transfer is represented by the film mass transfer resistance coefficient (1/k).

The gas concentration in equilibrium above the interface is given by Henry's law:

$$C_{g-int}(t) = \frac{p(t)}{H}$$
 4.5

The boundary condition at interface presented in Eq. 4.4 is modified into Eq. 4.6 to be used in the next diffusion equation solution (Etminan et al., 2013).

$$\frac{\partial C_g}{\partial z} = M \frac{\partial C_g}{\partial t} - N \left[\frac{\partial^2 C_g}{\partial t \partial z} \right], \qquad z = 0$$
4.6

Where M and N are identified as:

$$M = \frac{V_{gc}M_{w}H}{AZRTD}$$
4.7

$$N = \frac{V_{gc}M_{w}H}{AZRTk}$$
 4.8

By connecting the rate of mass transfer from the gas cap to the pressure decay with the rate of gas dissolution into the oil system, it is possible to obtain the solution of the diffusion equation in Laplace domain:

$$\bar{C}_{g}(z,s) = \frac{Mp_{i}[e^{((z-2h)\sqrt{s/D})} + e^{(-z\sqrt{s/D})}]}{H[(Ms + (1+Ns)\sqrt{s/D}) + e^{(-2h\sqrt{s/D})}(Ms - (1+Ns)\sqrt{s/D})]}$$
4.9

Afterwards by using Henry's law constant to replace concentration by pressure it is also possible to have the pressure calculated with the equation in Laplace space (Etminan et al., 2013):

$$\bar{p}_{\text{computed}}(s) = \frac{Mp_{i}[(e^{(-2h\sqrt{s/D})} + 1) - D/K(\sqrt{s/D}e^{(-2h\sqrt{s/D})} - \sqrt{s/D})]}{[(Ms + (1 + Ns)\sqrt{s/D}) + e^{(-2h\sqrt{s/D})}(Ms - (1 + Ns)\sqrt{s/D})]}$$

$$4.10$$

Pressure variation with time can be calculated from Eq. 4.10 by using numerical methods such as Stehfest algorithm to invert the Laplace transform. The results are the theoretical values rendered by the diffusion model. Results are affected by the parameters of mass transfer coefficient (k), Henry constant (H) and diffusion coefficient (D).

An objective function was used to obtain the best values of parameters:

Squared Error =
$$\sum_{i=1}^{n} (p_{exp}(t) - p_{computed}(t))^{2}$$
 4.1

An elaborated method of fitting is necessary to render the optimum set of parameters for the large amount of data collected. The minimization method used to obtain the global minimum was the simulated annealing. This method was used to define the following three unknown values: mass transfer coefficient (k), Henry constant (H) and diffusion coefficient (D). The combination of two minimization methods will be later elucidated during Result and Discussion for Pressure Decay subsection.

5. **RESULTS AND DISCUSSION**

At this chapter, the results from pressure decay and CT scan are presented. The obtained data in both experiments is analyzed in order to evaluate its accuracy to be adjusted to a theoretical model to generate diffusion parameters. CT scan is also used to collect data from swelling effect. By the end of this chapter, a brief GC analysis is performed with the aim to detect mass transfer process in the opposite path of CO_2 diffusion.

5.1. Pressure Decay

In a first step here, the pressure decay data quality is examined during Preliminary Analysis. Afterwards the diffusion coefficient and other parameters are obtained from model adjustment with these records and are illustrated in Data Analysis. Later, a sensitivity analysis is also developed considering the model. Finally, from those parameters, a CO_2 concentration study inside the oil column is performed using also concentration solution for the chosen model.

5.1.1. Preliminary Analysis

The table in the next page summarizes all tests accomplished in the sequence they were performed. Such order was in fact established during the CT scan investigation and the differences between them were oil type, the way oil was added inside the diffusion cell and the initial conditions of each experiment (temperature and pressure).

No.	OIL TYPE	OIL ADDED INSIDE THE CELL	ТЕМР. (К)	INITIAL PRESSURE (p _i) (MPa)	FINAL PRESSURE (p _f) (MPa)	FINAL TIME (h)
1	Original	Pump	293.15	5.31	3.57	49.14
2	Original	Beaker	293.15	5.28	4.43	47.23
3	Original	Pump	293.15	6.94	5.51	50.59
4	Light components removed (LCR)	Pump	293.15	5.29	4.29	161.16
5	LCR doped 4%	Beaker	293.15	5.31	4.94	69.41
6	Doped 1%	Beaker	293.15	5.25	4.32	250.68
7	Doped 10%	Beaker	293.15	5.24	4.78	52.69
8	Doped 4%	Pump	293.15	2.81	1.72	43.51
9	Doped 4%	Pump	293.15	5.26	3.89	19.79
10	Doped 4% (Dupli.)	Pump	293.15	5.27	3.99	41.80
11	Doped 4% (Tripli.)	Pump	293.15	5.31	3.77	40.36
12	Doped 4%	Pump	293.15	9.95	6.90	63.80
13	Doped 4%	Pump	293.15	28.96	27.85	21.97
14	Original	Pump	338.15	10.36	9.03	74.73

Table 5.1 – Experimental Data for Pressure Decay

With the purpose of understanding the pressure decay behavior according to the different scenarios enumerated above, pressure curves versus time are plotted in the next figure. In a first step, experimental data obtained with an initial pressure of 5.31 MPa (770 psi) is analyzed, as depicted in the next figure.



Figure 5.1 - Pressure decay profiles for 5.31 MPa initial pressure scenarios

Some of the pressure decay experiments presented in Figure 5.1 may not have reached the equilibrium pressure, namely experiments 1, 7 and 9. Once the saturation pressure was not attained, experimental results were probably affected as well as parameters modeling reliability. Other experiments may not present the same pressure decay trend profile, like experiments 4 and 5, where a different profile is noticed after each curve is plotted. This different profile may represent a leak.

It is noticed that oil on its original composition has the highest pressure drop since it has the lower density value. So doped oil has lower pressure decay if compared to non-doped oil. So the denser the oil is, like experiments 5 and 7, the smallest is the pressure drop, with less diffusion of CO_2 into oil.

The conditions under which oil was added inside the cell were also checked, with oil being added in two different ways inside the diffusion cell. The first one consists of pumping oil into one of cell's entries and the other by pouring oil with a beaker. The aim here was to analyze if pumping oil inside the cell with a CO_2 atmosphere changed the oil composition. It is detected

that without pumping the oil, the pressure drop was less than the expected (experiments 2, 6 and 7).

Repeatability was only checked for experiments with doped oil at 5 MPa range (experiments 9, 10 and 11) where pressure profiles observed during diffusion process follow the same qualitative trend.

For pressures where CO_2 is already on its liquid phase (CO_2 pressure @ 293.15 K or 20°C > 5.73 MPa or 831 psi), pressure profiles are extremely sensitive to temperature variations (see Figure 5.2). At this temperature and higher pressures, CO_2 is closer to its critical point ($T_c = 304.1$ K and $p_c = 7.38$ MPa – See Attachment A). Consequently, minor temperature variations may lead here to major pressure changes. It is important to mention here that the thermocouple used in the temperature measurement was attached to external diffusion cell wall.



Figure 5.2 - Pressure decay profiles instabilities for high pressures

With the aim of reducing temperature variations during 293.15 K (20° C) tests, the whole system was placed inside a heating thermal blanket, while the room temperature was set to lower value and monitored with the thermocouple. Such conditions were valid for the test performed at

10.34 MPa (1500 psi) and 338.15 K (65° C). Thus as seen in Figure 5.3, if experiment 12 at 293.15 K (20° C) is compared with the one at 338.15 K (65° C), it is clear that the latter one produces more reliable and stable data.



Figure 5.3 - Pressure decay profiles for experiments 12 and 14 scenarios

Another observation that can be extracted from Figure 5.3 is that the pressure drop in 10.34 MPa (1500 psi) and 338.15 K (65° C) test is smaller than that one with 9.95 MPa (1443 psi), 293.15 K (20° C). This may have happened because of high temperature 338.15 K (65° C) and also because during the experiment, oil was left 24h inside the diffusion cell to stabilize temperature.

5.1.2. Data Analysis

It is worthwhile to mention that Etminan et al. (2013) diffusion model, chosen to be applied here, has several limitations concerning the here presented experimental conditions, such as high pressures and light crude oils.

With pressure data presented in the previous section, experimental profiles were adjusted to the model for obtaining the desired parameters using a routine implemented in Matlab® (see code

in Appendix A). Firstly Levenberg-Maquardt (LM) was utilized as an initial minimization method to find local minimum. For experiments with higher pressure, the convergence of the three parameters could nevertheless not be achieved. Besides this, as LM method has no boundary restrictions, during some 5.31 MPa experiments, the obtained mass transfer coefficient values were out of the expected range. In regard to this last issue, a sensitivity analysis is performed by the end of this section.

The present minimization method choice was the Simulated Annealing, which requires setting a range of initial parameters to start the algorithm. Once it randomly investigates the values inside the selected range to identify the global minimum; it attempts to improve the global minimum obtained earlier, by narrowing the range.

Besides the experimental pressure profile, other experimental information is demanded as input values in order to the calculate diffusion coefficient, mass transfer coefficient and Henry constant. Such inputs are the gas cap volume, height of oil column and compressibility factor. Once the diffusion cell was not windowed, the first two input factors were obtained using CT-scan, with details presented in the upcoming swelling subsection. On the other hand the compressibility factor is considered constant and was found using PR-EoS with initial pressure and constant temperature as EoS entry variables.

Figure 5.4 and Figure 5.5 illustrate experimental data adjustment, through simulated annealing, using Etminan et al. (2013) model. Figure 5.4 is better suited for experimental data once after equilibrium pressure was reached; it was also maintained for a while. The other experiments adjustment figures is listed in Appendix B.



Figure 5.4 – Experiment 8 adjustment to model (2.81 MPa)



Figure 5.5 – Experiment 12 adjustment to model (9.95 MPa)

Hereafter, the estimated parameters that best fit Etminan model with experimental data are described in Table 5.2 and Table 5.3 with literature parameters for comparison purpose.

No.	OIL TYPE	T (K)	p _i (MPa)	D (m ² /s)	k (m/s)	H (MPa/(kg/m ³))	SQUARED ERROR
1	Original	293.15	5.31	1.41 x 10 ⁻⁸	9.48 x 10 ⁻⁴	2.72 x 10 ⁻²	9.86 x 10 ⁻²
2	Original	293.15	5.28	2.82 x 10 ⁻⁸	1.69 x 10 ⁻⁴	8.10 x 10 ⁻²	6.23 x 10 ⁻²
3	Original	293.15	6.94	1.68 x 10 ⁻⁸	8.79 x 10 ⁻⁴	$1.58 \ge 10^{-2}$	3.20 x 10 ⁻²
4	LCR	293.15	5.29	4.10 x 10 ⁻⁹	8.36 x 10 ⁻⁵	4.75 x 10 ⁻²	7.48 x 10 ⁻²
5	LCR doped 4%	293.15	5.31	7.88 x 10 ⁻⁹	9.89 x 10 ⁻⁵	1.54 x 10 ⁻¹	3.40 x 10 ⁻²
6	Doped 1%	293.15	5.25	4.28 x 10 ⁻⁸	1.06 x 10 ⁻⁵	7.98 x 10 ⁻²	5.70 x 10 ⁻²
7	Doped 10%	293.15	5.24	7.73 x 10 ⁻⁹	1.50 x 10 ⁻⁵	1.65 x 10 ⁻¹	3.59 x 10 ⁻³
8	Doped 4%	293.15	2.81	6.40 x 10 ⁻⁸	7.44 x 10 ⁻⁶	5.26 x 10 ⁻²	2.70 x 10 ⁻³
9	Doped 4%	293.15	5.26	7.96 x 10 ⁻⁷	3.71 x 10 ⁻⁶	6.71 x 10 ⁻²	7.79 x 10 ⁻³
10	Doped 4% (Dupli.)	293.15	5.27	9.53 x 10 ⁻⁷	3.94 x 10 ⁻⁶	7.35 x 10 ⁻²	1.30 x 10 ⁻²
11	Doped 4% (Tripli.)	293.15	5.31	1.22 x 10 ⁻⁷	5.74 x 10 ⁻⁶	6.03 x 10 ⁻²	1.86 x 10 ⁻²
12	Doped 4%	293.15	9.95	5.37 x 10 ⁻⁸	8.62 x 10 ⁻⁴	2.05 x 10 ⁻²	1.79 x 10 ⁻¹
13	Doped 4%	293.15	28.96	2.50 x 10 ⁻⁸	6.71 x 10 ⁻⁴	2.18×10^{-1}	6.26 x 10 ⁻²
14	Original	338.15	10.36	3.09×10^{-8}	9.27 x 10 ⁻⁴	2.20×10^{-1}	4.85 x 10 ⁻²

Table 5.2 – Estimated parameters obtained from Pressure Decay Data

Table 5.3 - Estimated parameters in Etminan analysis used for comparison purpose

WORKS	p _i (MPa) / T (K)	D (m ² /s)	k (m/s)	H (MPa/(kg/m ³))
Riazi, 1996	10.20 / 310.95	1.12 x 10 ^{-8 a}	9.2 x 10 ^{-6 a}	0.1097 ^a
Haugen and Firoozabadi, 2009	10.20 / 310.95	1.30 x 10 ⁻⁸	-	-
Ghaderi et al., 2011	8 / 348.15	1 x 10 ⁻⁹	-	10
Guo et al., 2009	20/333.15	1.87e x 10 ⁻¹¹	-	-
Etminan et al., 2013	4 / 348.15	$5.00 \ge 10^{-10}$	1.50 x 10 ⁻⁶	0.11

^a calculated by Etminan et al. (2013)
Even though the experimental conditions used in the present work have never been tested before in literature, the estimated diffusion coefficients have the same order of magnitude of those presented in Table 5.3 and are similar to those ones from Riazi (1996) and Haugen and Firoozabadi (2009) once both experiments also used lighter components than heavy oil, as employed by Etminan et al. (2013).

Almost all the adjustments presented in Table 5.2 are quite accurate as illustrated by the squared errors oscillation in the range of 1×10^{-2} .

For experimental conditions with 2.81 MPa (440 psi) and 5.31 MPa (770 psi) initial pressures, Etminan Model is well suited as those pressures fall in a similar pressure range of Etminan analysis. Consequently, they are still at VLE and then Henry law can be employed if mixture is considered sufficiently diluted. But since the swelling effect is noticed, in some way it may affect the adjustment with experimental data.

Once the diffusion coefficient represents how smoothly the solvent can diffuse into oil body; it is noticed, according to Table 5.2, that heavier oils (experiments 4, 5 and 7) are the only ones with diffusion coefficients in the order of magnitude of 1×10^{-9} which means that for denser oils CO₂ propagates in the oil column slowly than in lighter oils.

Regarding the mass transfer coefficient (k), 1/k is defined as the interfacial resistance against the gas molecular diffusion. Half of them have an order of magnitude of 1×10^{-4} , and almost all doped oil experiments presented in the range of 1×10^{-5} and 1×10^{-6} . Relating these orders of magnitude to those ones obtained by Etminan et al. (2013), the resistance at the interface may be neglected for all practical purposes when larger than 1×10^{-4} . Thus including mass transfer coefficient into the model for such values may not necessarily and physically represent interface resistance.

For relatively low pressures and dilute solutions, ideal gas phase behavior can be assumed and then Henry constant is inversely proportional to the equilibrium concentration at a given pressure. Consequently, as Henry's constant increases (solubility decreases), the gas pressure drops at a lower rate. For pressures up to 5 MPa, the effects of pressure on Henry's constant are quite small and it can be considered that it is solely a function of temperature. For higher values of Henry's law constant, it is expected that solubility decreases and then the predicted gas cap pressure decay is shorter, as demonstrated in the Table 5.4.

No.	OIL TYPE	T (K)	p _i (MPa)	PRESSURE DROP (MPa)	HENRY CONSTANT (MPa/(kg/m ³))
5	LCR doped 4%	293.15	5.31	0.37	1.72 x 10 ⁻¹
7	Doped oil 10%	293.15	5.24	0.46	1.65 x 10 ⁻¹
2	Original	293.15	5.28	0.85	8.10 x 10 ⁻²
6	Doped oil 1%	293.15	5.25	0.93	7.98 x 10 ⁻²
10	Doped oil 4% (2)	293.15	5.27	1.28	7.35 x 10 ⁻²
9	Doped oil 4%	293.15	5.26	1.37	6.71 x 10 ⁻²
11	Doped oil 4% (3)	293.15	5.31	1.54	6.03 x 10 ⁻²
1	Original	293.15	5.31	1.74	2.72 x 10 ⁻²

Table 5.4 – Pressure drop increases and Henry constant decreases tendency

As mentioned previously, Henry's Law can just be satisfactorily used to express solubility for dilute solutions, and then it is limited by the thermodynamics of the system. On the other hand, for mixtures that largely deviate from the ideal behavior, EoS models are used to represent phase equilibria and then are applied for solubility calculations. In this sense, rather than have Henry's constant as a third parameter in the diffusion model, it would be better to estimate it by using an EoS. Under these circumstances, the other two missing parameters from the model, D and k, could be evaluated more precisely.

An acceptable adjustment to Etminan Model requires pressure saturation to be well established. If the theoretical curve for each experiment is extrapolated and the final pressure is far from the one at theoretical equilibrium, those experiments have their parameters reliability affected. In Table 5.5, next page, the difference between the final pressure reached at each experiment and the expected one from Etminan model are illustrated.

No.	OIL TYPE	T (K)	p _i (MPa)	p _f (MPa)	THEORETICAL p _{eq} (MPa)	FINAL TIME (h)
1	Original	293.15	5.31	3.57	3.93	49.14
2	Original	293.15	5.28	4.43	4.44	47.23
3	Original	293.15	6.94	5.51	5.71	50.59
4	LCR	293.15	5.29	4.29	4.30	161.16
5	LCR doped 4%	293.15	5.31	4.94	4.99	69.41
6	Doped 1%	293.15	5.25	4.32	4.31	250.68
7	Doped 10%	293.15	5.24	4.78	4.76	52.69
8	Doped 4%	293.15	2.81	1.72	1.72	43.51
9	Doped 4%	293.15	5.26	3.89	3.92	19.79
10	Doped 4% (Dupli.)	293.15	5.27	3.99	4.00	41.80
11	Doped 4% (Tripli.)	293.15	5.31	3.77	3.64	40.36
12	Doped 4%	293.15	9.95	6.90	7.32	63.80
13	Doped 4%	293.15	28.96	27.85	27.90	32.11
14	Original	338.15	10.36	9.03	9.07	74.73

Table 5.5 – Theoretical Equilibrium Pressure versus Final Pressure

The effect of such adjustment can be noticed when comparing in next page the following Figure 5.6 and Figure 5.7, as for the first one the adjustment is not precise given the fact that the equilibrium pressure is not reached; while this is corrected for the second one.



Figure 5.6 – Experiment 1 experimental curve and model adjustment to equilibrium



Figure 5.7 - Experiment 2 experimental curve and model adjustment to equilibrium

Another study using the present model can be performed using Eq. 4.9 and the three obtained parameters from Table 5.2. This study determines CO_2 concentration variation along oil column either at a fixed time or in a fixed position with varying time. In Figure 5.8 and Figure 5.9, the CO_2 concentration distribution during time and along oil column is illustrated for experiment 1 with original oil at 5.31 MPa (770 psi) and 293.15 K (20°C).



Figure 5.8 – CO₂ concentration at a fixed position in oil column during time



Figure 5.9 – CO₂ concentration at a fixed time varying along oil column

Accordingly to Figure 5.8, at early times, it seems that the CO_2 concentration close to the interface is higher than the equilibrium concentration. As diffusion progresses, pressure decreases, and this concentration tends to equilibrium. At Figure 5.9, it is clear that CO_2 reached the cell bottom. In both studies (Figure 5.8 and Figure 5.9), concentration values higher than saturation may happen due to the absence of swelling in the model, meaning that the transition zone, where the amount of CO2 should be dissolved, is underestimated in its size. All the other experiments have similar curves, only concentration values change, as showed in next page in Table 5.6.

No	OIL TYPE	T (K)	p _i (MPa)	p _f (MPa)	FINAL TIME (h)	FINAL CO ₂ CONCENTRATION (kg/m ³)	OIL DENSITY (kg/m ³)	CO ₂ (% in mass)
1	Original	293.15	5.31	3.57	49.14	134.5	876	15.01
2	Original	293.15	5.28	4.43	47.23	54.8	876	6.82
3	Original	293.15	6.94	5.51	50.59	339.5	876	30.08
4	LCR	293.15	5.29	4.29	161.16	93.38	886	11.23
5	LCR doped 4%	293.15	5.31	4.94	69.41	31.64	903	4.10
6	Doped 1%	293.15	5.25	4.32	250.68	52.44	882	6.45
8	Doped 10%	293.15	2.81	1.72	43.51	33.7	893	3.78
9	Doped 4%	293.15	5.26	3.89	19.79	57.33	893	6.87
10	Doped 4%	293.15	5.27	3.99	41.8	55.92	893	6.72
11	Doped 4% (Dupli.)	293.15	5.31	3.77	40.36	70.17	893	8.22
12	Doped 4% (Tripli.)	293.15	9.95	6.90	63.8	355.58	893	31.03
13	Doped 4%	293.15	28.96	27.85	32.11	123.52	893	12.89
14	Doped 4%	338.15	10.36	9.03	74.73	40.84	876	5.17

Table 5.6 – CO $_2~\%$ in mass in oil column at the end of each experiment

5.1.3. Sensitivity analysis

The sensitivity analysis of parameters is motivated by the fact that the obtained mass transfer coefficients (1 x 10^{-4} m/s < k) are out of the expected range (1 x 10^{-4} m/s > k > 1 x 10^{-8} m/s) of values using the LM method for experiment 1 data.

To better comprehend what was noticed above, a sensitivity analysis of the effect from those three parameters (k, H and D) on the behavior of the analytical solution is examined. All data obtained for the predicted gas cap pressure versus time for each case is compared to the base case parameters obtained for experiment 1.

In Table 5.7, the base case parameters and value of each case are listed.

PARAMETERS	k EFFECT (m/s)	D EFFECT (m ² /s)	H EFFECT (MPa/(kg/m ³))
1	1.00 x 10 ⁻⁷	1.00 x 10 ⁻⁹	1.00 x 10 ⁻²
2	1.00 x 10 ⁻⁶	9.00 x 10 ⁻⁹	2.00 x 10 ⁻²
Base Case Experiment 1	9.48 x 10 ⁻⁴	1.41 x 10 ⁻⁸	2.72 x 10 ⁻²
4	1.00 x 10 ⁻²	1.00 x 10 ⁻⁷	3.00 x 10 ⁻²
5	$1.00 \ge 10^2$	1.00 x 10 ⁻⁶	4.00 x 10 ⁻¹

Table 5.7 – Base case for experiment 1 and values for each case for sensitive analysis

As it was mentioned earlier, when mass transfer coefficient is larger, resistance at the interface becomes insignificant. For mass transfer coefficients higher than the one from the base case, it can be noticed that the squared error is very close to the best case and will remain the same for values higher than the base case (see Figure 5.10). Physically, it is possible to say that diffusion is dominant over interface resistance, so that CO_2 diffuses into oil almost instantaneously.



Figure 5.10 – Effect of mass transfer coefficient on predicted gas cap pressure

Performing an analogy to heat transfer, diffusion coefficient can be compared to the conductance resistance of oil column towards CO_2 molecules' diffusion. So for reduced values of diffusion coefficient, concentration saturation takes longer to be reached along the oil column and then equilibrium time will become also longer, as seen by magenta profile in Figure 5.11.



Figure 5.11 - Effect of diffusion coefficient on predicted gas cap pressure

The results in Figure 5.12 illustrate that the gas pressure drop is lower as Henry's constant increases. So for smaller values of Henry's constant, a larger amount of CO_2 is dissolved into oil.



Figure 5.12 - Effect of Henry's constant on predicted gas cap pressure

5.2. CT scan

5.2.1. Data treatment

After a special protocol was created to scan the diffusion cell with oil inside, each image exported from CT scan software was opened in Matlab as a 512 x 512 matrix. Figure 5.13 describes the area inside the cell where CT scan acquires the image and how the image is visualized in Matlab.



Figure 5.13 – Image scanned from CT to Matlab

First a conversion of the original file from the CT-scan software in DICOM (Digital Imaging and Communications in Medicine) format was performed. A couple of pixel transformations were required to convert pixel value in the file to Hounsfield units (H.U).

As previously explained, after a ROI area close to the CO_2 -oil interface was selected, a vertical profile was generated to be compared to other images profiles as is demonstrated in the next picture.



Figure 5.14 – Diffusion cell zones and CT number vertical profile

When focusing the analysis only on the oil column, it is possible to observe significant artifact effects on image quality. One possible assumption here is that this error was mainly induced by aluminum walls thickness and by the vertical positioning of the cell. Further data treatment is therefore required to minimize such error.

In a first step, the optimal area of the ROI inside the cell is selected in order to be narrow enough to reduce aluminum wall effect and sufficiently large to increase the data range used in each horizontal average. Below is depicted the delimitation of such area.



Figure 5.15 – ROI selection 62

Due to observed artifacts near the bottom of the cell, an additional error compensation is performed, namely subtracting the original obtained matrix from a correction matrix. Such correction matrix in turn is calculated by subtracting the matrix result with the cell filled with air from the CT values from the air alone. In Figure 5.16, the green line represents the original measured profile while the green blue one illustrates the result of the data treatment.



Figure 5.16 – Error removal of CT profile in oil column experiment 1

Finally, all images exported from CT-scan software are treated using a code to generate the desired profile. This process is detailed in a Matlab® code described in Appendix C.

5.2.2. Data Analysis

The first two experiments were performed with dead oil at initial pressure of 5.31 MPa (770 psi) (with CO_2 in gas phase) and 6.94 MPa (1006 psi) (with CO_2 in liquid phase), both at 293.15 K.

In Figure 5.17, the plot represents each scan vertical profile of the CO_2 gas and oil phases during diffusion process. It is possible to observe at each profile the interface displacement

caused by swelling effect. Once all interfaces are aligned, Figure 5.18 is plotted. There the increase of the CT-number of CO_2 phase can be clearly observed due to the increase of pressure.



Figure 5.17 – Profiles of gas cap, interface and oil column of experiment 1



Figure 5.18 – Experiment 1 with interfaces aligned

Zooming in the area inside oil column, without interface alignment, Figure 5.19 is generated. Those CT peaks represent when two components density values are very distinct.



Figure 5.19 – Experiment 1 profiles with original oil at initial pressure of 5.31 MPa.

From Figure 5.19, it is not possible to notice a representative CT variance that shows density decay due to CO_2 dissolution in oil. Each profile above also presents a different value for its random error. For this experiment the average error was around 18 H.U without considering the peak at top of the oil column and the CT numbers decrease at the bottom of the cell.

In the case of the experiment with 6.94 MPa (1006 psi), as depicted next, the random error was higher at around 10 H.U. At the beginning of this experiment when cell was pressurized at initial pressure, the peaks observed in the previous figure were reduced. Additionally, in Figure 5.20, it is possible to observe a slight increment in CT number profiles as the process takes place. This last observation is the opposite from what was expected, while the diffusion process is occurring.



Figure 5.20 - Experiment 3 profiles with original oil at initial pressure of 6.94 MPa.

While the interface movement in both experiments can be clearly noticed, the expected CT profile decrease during diffusion process caused by density reduction is not noticed in both experiments with original oil.

Before moving to another alternative to detect a reasonable CT number variation, it is necessary to investigate the relationship between the expected CT variation due to density decrease and the random error. Thus, in the next figure, a calibration curve at an energy level of 130 kV is plotted with the present Siemens Spirit Somaton scanner in use.



Figure 5.21 – Calibration curve at 130 kV for Siemens CT-scan

Afterwards, using a multiphase equilibrium package called MULTIFLASHTM from Infochem software, it is possible to detect the expected CO₂-oil mixture density variation as CO₂ dissolves according to different concentrations (see Figure 5.22), considering the present oil characteristics (Attachment B).



Figure 5.22 - Expected oil mixture density %CO₂ variation at 293.15 K

For an exemplary situation at 293.15 K (20°C), if the initial pressure were 6.89 MPa (1000 psi) ($\rho_{oil} = 873.5 \text{ kg/m}^3$), the final pressure would be at most 3.45 MPa (500 psi) and the amount of CO₂ dissolved would correspond to 40% ($\rho_{mix} = 866.0 \text{ kg/m}^3$). Under such conditions representing a best case scenario for detection, the expected CT number variation would be only 7 H.U.

In reality, the expected pressure variation is much smaller and hence also the level of CT number variation to be measured. From the observed random errors presented in Figure 5.23 and Figure 5.24, it is possible to conclude under those conditions (oil 5.31 MPa or 770 psi and 6.94 MPa or 1006 psi at 293.15 K or 20°C) that the level of precision required to perform the analysis is not attainable.



Figure 5.23 – Total error for experiment 1 profile at p_i: 5.31MPa



Figure 5.24 - Total error for experiment 3 profile at $p_i{:}\ 6.94\ \text{MPa}$

A feasible alternative to increase the difference in attenuation coefficients (CT number) between fluids (CO₂ and oil) above the referred error levels was adding dopant to crude oil. Three diffusion tests were performed for each dopant concentration (1%, 4% and 10%) with initial pressure at the range of 5.31 MPa (770 psi) and 293.15 K (20°C). From the obtained results, it is possible to identify that the optimum dopant concentration that allowed a substantial CT number variation was 4% volume in oil.

Afterwards, four experiments were performed with doped oil (4% iododecane) at the following initial pressures: 2.81 MPa, 5.26 MPa, 9.95 MPa and 28.96 MPa (407 psi, 757 psi, 1406 psi and 4185 psi); all at 293.15 K (20° C).

In Figure 5.25, Figure 5.26 and Figure 5.27, it is possible to observe a certain CT profile decrease during diffusion process, though the random error makes the analysis of CT values deviation for each profile a challenging task.



Figure 5.25 – Experiment 8 profiles with doped oil at initial pressure of 2.81 MPa.



Figure 5.26 - Experiment 9 profiles with doped oil at initial pressure of 5.26 MPa.



Figure 5.27 - Experiment 12 profiles with doped oil at initial pressure of 9.95 MPa.

During experiment 13, CO_2 was heavier than oil. That is why it is noticed in Figure 5.28, that oil is placed in the top of the diffusion cell.



Figure 5.28 - Experiment 13 profiles with doped oil at initial pressure of 28.96 MPa.

Once it is possible to perceive CT profile difference during diffusion process, the forthcoming step is to obtain the density value for each CT number through a calibration curve.

As mentioned in previous subsection, for materials with atomic numbers that contributes to both Compton scattering and photoelectric attenuation of X-rays such as the doped oil, a dual energy measurement shall be taken in order to have a correct relationship between CT numbers and densities. In Coles et al. (1991), it was explained that two series of measurements of material with known densities should be performed in two levels of CT-scan energy. The present CT-scan in use has only 130 kV and 80 kV levels of energy. At this lower energy level of 80 kV and due to care dose limitations, it was not possible to increase output of the tube (mA.s) in order to improve image quality. Thus, at 80 kV level a very poor image quality was attained, making it impossible to obtain a relationship between CT number and densities with an acceptable standard deviation. This limitation with doped oil in obtaining a calibration curve at lower energy level hindered all possible attempts to detect a reasonable CT number variation during diffusion experiments at the temperature of 293.15 K. The last resort was to perform diffusion test under a similar reservoir conditions. The initial pressure chosen was 10.36 MPa (1500 psi) and temperature was 338.15 K (65° C). In such conditions, CO₂ was on its supercritical phase. The next figure shows CO₂-oil mixture density variation according to CO₂ dissolution in the mixture at 338.15 K (65° C) (MULTIFLASHTM).



Figure 5.29- Expected oil mixture density %CO₂ variation at 338.15 K

As depicted in Figure 5.30, the major difference on the CT number profile happens after the cell was heated for 24 hours at 338.15 K (65° C), with such oil density decrease happening because of temperature increase. When the diffusion process takes place, a minor difference between the profiles can only be observed near the interface. The random error is still noticeable as depicted in Figure 5.31.



Figure 5.30 - Experiment 14 profiles during heating and diffusion process



Figure 5.31- Total error for experiment 14 profile at Pi: 10.36 MPa.

5.2.3. Swelling

As previously stated, the pressure diffusion cell employed in this work was not windowed. Thus to obtain swelling factor, CT scan was used to acquire CO_2 -oil interface height variation.

To measure CO_2 -oil interface height variation for each experiment, CT profiles are plotted accordingly to Figure 5.32 where interfaces are highlighted inside a dashed red box.

The cell height values depicted in the next figures represent the matrix's lines. Thus each line has the length of 0.011719 cm.



Figure 5.32 – CT profiles for experiment 1

After zooming in (see Figure 5.33), the interface variation is measured in the dashed vertical line, and from now on it is possible to measure the difference between the height where system was not pressurized and system with saturation pressure.



Figure 5.33 – Interface position variation indicating swelling

The Simon and Graue (1965) definition of a dimensionless swelling factor is used to calculate a value from the experimental data:

$$SF = \frac{\text{oil volume at } P_{\text{sat}} \text{ and } T}{\text{oil volume at } 1 \text{ atm and } T}$$
5.1

According to the description above, consistent values for SF can be obtained only after saturation pressure of each experiment was reached. This was nevertheless not the case for some experiments, where equilibrium time was not attained.

In Table 5.8, SFs are obtained for each experiment. In terms of accuracy, those ones that have the final pressure closer to the equilibrium one have more reliable factor.

No.	OIL TYPE	T (K)	p _i (MPa)	p _f (MPa)	THEORETICAL p _{eq} (MPa)	DIMENSIONLESS SWELLING FACTOR	OIL COLUMN HEIGHT (cm)
1	Original	293.15	5.31	3.57	3.93	1.15	3.02
2	Original	293.15	5.28	4.43	4.44	1.17	3.95
3	Original	293.15	6.94	5.51	5.71	1.11	2.74
4	LCR	293.15	5.29	4.29	4.30	1.20	3.06
5	LCR doped 4%	293.15	5.31	4.94	4.99	1.22	3.12
6	Doped 1%	293.15	5.25	4.32	4.31	1.16	4.00
7	Doped 10%	293.15	5.24	4.78	4.76	1.14	3.69
8	Doped 4%	293.15	2.81	1.72	1.72	1.04	4.72
9	Doped 4%	293.15	5.26	3.89	3.92	1.15	4.69
10	Doped 4% (Dupli.)	293.15	5.27	3.99	4.00	1.15	4.64
11	Doped 4% (Tripli.)	293.15	5.31	3.77	3.64	1.14	4.64
12	Doped 4%	293.15	9.95	6.90	7.32	1.13	4.35
13	Doped 4%	293.15	28.96	27.85	27.90	1.07	2.63
14	Original	338.15	10.36	9.03	9.07	1.17	5.03

Table 5.8 – Swelling factor for each experiment

For almost all 5 MPa experiments, SF range is between 1.14 and 1.17; except for those ones that have their light components removed: experiments 4 and 5. A reason for this may be due to light components extraction during CO_2 pressurization. Thus, once light components have been already removed previously to CO_2 pressurization, there was no volume reduction after CO_2 pumping and consequently oil volume immediately started to swell from its height at atmospheric pressure.

This light components extraction during CO_2 pressurization is observed during three experiments (2, 7 and 8), while few scans were taken during CO_2 pumping. This phenomenon of light component extraction is very quick, occurring just in the beginning of the experiment and may not be detectable in all of them.

As depicted in Figure 5.34, it is possible to see the interface height position slight reduction during CO_2 pumping due to oil light components extraction.



Figure 5.34 – Volume reduction in the beginning of 2.81MPa test, test 8

Once initial pressure of the experiment increased, as observed in experiments 8 to 9, SF correspondently increased. In contrast, when CO_2 changes from gas to liquid phase, SF decreases as noticed in experiments 2 to 3 and experiments 11 to 12.

For experiments 3 and 12, the interface position during CO_2 injection changed when CO_2 started changing into liquid phase. As depicted in Figure 5.35, when CO_2 injection is still taking place, two interfaces can be clearly noticeable at 5.47 MPa, 5.54 MPa and 5.71 MPa (793 psi, 804 psi and 827 psi) profiles, The first interface is between CO_2 gas phase and CO_2 liquid phase and the other one is between CO_2 liquid phase and oil. After CO_2 injection continued until initial

pressure was reached, CO_2 became solely liquid and just one interface is seen (6.92 MPa or 1004 psi profile).



Figure 5.35 – Interface position during CO₂ injection for test 3

As also noticed in Figure 5.36, in a moment during diffusion process (after 6.46 MPa or 937 psi), the interface height starts reducing until system reaches equilibrium, from 6.17 MPa (895 psi) until 5.54 MPa (804 psi). This phenomenon is also noticed for experiments 1, 3 and 12.



Figure 5.36- Interface position during test 3 diffusion process

5.3. GC analysis

At the end of 10.36 MPa (1500 psi) and 338.15 K (65° C) experiment, a collection device was connected to the top entry of the diffusion cell. The fluid was then collected inside a gas sampling bag (Tedlar®) at room temperature of 293.15 K (20° C) and GC (gas chromatography) was performed with this fluid. Figure 5.37 shows the results of the two GC analyses accomplished: thermal conductivity detector (TCD) and flame-ionization detectors (FID).



COMPOSIÇÃO DA AMOSTRA

Componente	(% molar)
N2	2.16
CO	
C1	
CO2	96.92



COMPOSIÇÃO DA AMOSTRA						
Componente	(% molar)					
C1	0.00041					
C2	0.00852					
C3	0.11469					
NC4	0.16261					
NC5	0.08628					
NC6	0.07249					

Figure 5.37- TCD and FID GC analysis from gas sample at the end of test 14

As noticed from GC analysis, a very small amount of light oil components is found inside the fluid zone where only CO_2 were supposed to be placed. Those light oil components extraction from oil may be caused by the CO_2 supercritical extraction. This assumption as well as counter diffusion hypothesis need to be further investigated and better quantified in order to determine if diffusion model needs to be adjusted to this new observation.

6. FINAL REMARKS

The original focus of this work was to identify the diffusion coefficient and swelling factor for CO_2 in light oils through CT scans. Such method was preferred as the density concentration profile could be directly obtained through measurements, instead of indirect calculations using pressure values. Consequently all measurements were accordantly planned, including doping the oil. On the course of the measurements, it was nevertheless observed that random error at both measurements with original and doped oil (respectively at energy levels of 130 kV and 80 kV) was far higher than the required precision to detect the expected density reduction as CO_2 diffused.

One possible solution to decrease such random error would be reducing the aluminum cell wall thickness, though this could directly lead to lower working pressure levels. Another alternative would be using a CT scan capable of operating with higher energy levels and without the observed limitations from the employed medical model.

Despite the above referred problematic, CT investigation could offer an important insight on CO_2 diffusion inside the oil column. Not only could a significant swelling effect could be measured, but also CO_2 displacement down to the bottom of the cell was identified. Those two conditions were not reported in the literature so far, as the diffusion of CO_2 in light oil is not yet well documented and might be taken into account for further diffusion models boundary conditions.

In contrast the swelling effect could be clearly observed and characterized with such a precision level that even volume reduction during both CO_2 injection and at the end of some tests could be identified.

Simultaneously to the CT approach, the pressure decay technique was also employed, directly leading to the selection of the diffusion model. The choice of the model from Etminan et al., (2013) was justified by its interface boundary condition that considered both equilibrium and non-equilibrium conditions. Nevertheless, this model was valid for some assumptions (Henry's law, non-volatile oil, neglected swelling, constant gas compressibility factor) that did not partially match the present experimental conditions (higher pressure and light oil). In addition to this, such model was better suited for experimental data obtained after equilibrium pressure was reached

and then maintained for a while. However, the non-insolation of diffusion cell during tests at 293.15 K (20° C) and near to supercritical conditions generated experimental data that compromised model adjustment.

Despite such limitations, the obtained diffusion coefficients were within the ranges previously reported in the literature. Furthermore, another parameter obtained with the model, namely the mass transfer coefficient, allowed identifying that there was almost no mass transfer resistance in the interface for original oil.

For further studies, the choice of a model that represents more closely the noticed phenomena will help obtaining more reliable parameters, such as a diffusion model considering a diffusion coefficient dependent on concentration. It is also recommended to compare obtained experimental swelling factor to existing correlations in such conditions. About CT scan, once almost all tests were performed at 293.15 K (20° C), it is highly suggested to perform additional tests at experimental settings as near as possible to reservoir conditions, namely at higher pressure and temperature, in order to obtain information more suitable for CO₂-EOR projects.

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APPENDIX A – Code to obtain model parameters

Matlab® code to obtain three parameters (D, k and H) from Etminan et al. (2013) through Simulated Annealing adjustment Model.

```
function []=principal()
disp('****Menu****');
disp('1.- Calculate global minimum);
disp('2.- Exit');
op=input('Choose your option:');
****
contit=2;
while op~=2
    if op==1
      D=input('Estimate diffusion coefficient value:');
      k=input('Estimate mass transfer coefficient value:');
      H=input('Estimate Henry constant value:');
      par=[k, D, H];
      CC=sprintf('%s%d%s%d%s%d%s%d%s%d%s','C:\Users\TEMP.SCI.003\Desktop\SA -
770 - 4% iodo\SA\ParameterInitial', contit, '.txt');
      C=sprintf('%s%d%s%d%s%d%s%d%s','C:\Users\TEMP.SCI.003\Desktop\SA -
770 - 4% iodo\SA\ParameterFinal', contit, '.txt');
      save(CC, 'par', '-ASCII');
        lb=[1e-3,1e-9,0.01];
        ub=[1e-1, 1e-7, 0.1];
        options =
saoptimset('PlotFcns', {@saplotbestx,@saplotbestf,@saplotx,@saplotf});
[parameter,fobj,exitFlag,output]=simulannealbnd(@func,par,lb,ub,options)
        save(C, 'parameter', 'fobj', 'output', '-ASCII');
        disp(parameter);
        disp(fobj);
        fprintf('Iterations number: %d\n', output.iterations);
        fprintf('Number of times function was evaluated: %d\n',
output.funccount);
        fprintf('Best function value : %g\n', fobj);
        sum_error=0;
        [T,Mw,Vgc,Z,A,R,h,Pi,Pexp,time] = dados();
        [m,n]=size(Pexp);
        F=PressureDecayModel();
        for i=1:m
        M = (Vgc*Mw*parameter(3) / (A*Z*R*T*parameter(2)));
        N=(Vgc*Mw*parameter(3)/(A*Z*R*T*parameter(1)));
P_t(i,1)=qavstehPD(F,time(i,1),16,h,M,N,parameter(2),parameter(1),Pi,Vqc,Mw,A,
Z, R, T, parameter(3));
        error=(Pexp(i,1)-P_t(i,1))^2;
        sum_error=sum_error+error;
```

```
end
%%%%Grafico de comparação dos valores experimentais e teoricos%%%%%
hh=figure,plot(time,Pexp,'r+-',time,P t,'b*-')
grid on
nome_title=sprintf('%s%d%s%d', 'k=', parameter(1), 'D=', parameter(2), 'H=', par
ameter(3));
title(nome_title);
legend('Experimental', 'Teorico', -1);
xlabel('Time');
ylabel('Pressao');
graf=sprintf('%s%d%s%d%s','C:\Users\TEMP.SCI.003\Desktop\SA - 770 - 4%
iodo\SA\ModelodePressureDecay',Pi,'Iteração-',contit,'.fig');
saveas(hh,graf);
H=parameter(3);
D=parameter(2);
k=parameter(1);
parameters=sprintf('%s%d%s%d%s','C:\Users\TEMP.SCI.003\Desktop\SA - 770 - 4%
iodo\SA\ModelodePressureDecay',Pi, 'Parameters-Iteração-',contit,'.txt');
save(parameters, 'k', 'D', 'H', 'sum_error', '-ASCII');
disp('Diffusion coefficient value is:');
disp(parameter(2));
disp('Mass transfer coefficient value is:');
disp(parameter(1));
disp('Henry constant value is:');
disp(parameter(3));
disp('****Menu****');
disp('1.- Calculate global minimum ');
disp('2.- Exit');
op=input('Choose your option:');
end
end
```

```
function[F]=PressureDecayModel()
syms M Pi h s D N Pexp kk H Vgc Mw A Z R T
%%%%Presão calculada=Pcomputed%%%
M=(Vgc*Mw*H/(A*Z*R*T*D));
N=(Vgc*Mw*H/(A*Z*R*T*kk));
F=M*Pi*([exp(-2*h*sqrt(s/D))+1]-D/kk*[sqrt(s/D)*exp(-2*h*sqrt(s/D))-
sqrt(s/D)])/[(M*s+(1+N*s)*sqrt(s/D))+exp(-2*sqrt(s/D)*h)*(M*s-
(1+N*s)*sqrt(s/D))];
end
```

```
function ilt=gavstehPD(funname,t,L,h,M,N,D,kk,Pi,Vgc,Mw,A,Z,R,T,H)
nn2 = L/2;
nn21= nn2+1;
for n = 1:L
    z = 0.0;
    for k = floor((n + 1) / 2):min(n,nn2)
        z = z + ((k^nn2)*factorial(2*k))/ ...
        (factorial(nn2-k)*factorial(k)*factorial(k-1)* ...
```

```
factorial(n-k)*factorial(2*k - n));
end
v(n)=(-1)^(n+nn2)*z;
end
sum = 0.0;
ln2_on_t = log(2.0) / t;
for n = 1:L
s = n * ln2_on_t;
sum = sum + v(n) * subs(funname);
end
ilt = sum * ln2_on
```

```
function [feval]=func(par)
F=PressureDecayModel();
sum_error=0;
*****
[T,Mw,Vgc,Z,A,R,h,Pi,Pexp,time] = dados();
[m,n]=size(Pexp);
 for i=1:m
        M = (Vgc*Mw*par(3) / (A*Z*R*T*par(2)));
        N = (Vgc*Mw*par(3) / (A*Z*R*T*par(1)));
P_t(i,1) = gavstehPD(F,time(i,1),16,h,M,N,par(2),par(1),Pi,Vgc,Mw,A,Z,R,T,par(3)
);
        error=(Pexp(i,1)-P_t(i,1))^2;
        sum_error=sum_error+error;
 end
feval=sum_error
disp(par(1));
disp(par(2));
disp(par(3));
end
```

```
function [T,Mw,Vgc,Z,A,R,h,Pi,Pexp,time] = dados()
nome_prop=sprintf('%s','C:\Users\TEMP.SCI.003\Desktop\SA - 770 - 4%
iodo\SA\prop.xls');
prop=xlsread(nome_prop);
T=prop(1,1); %temperature K
Mw=prop(1,5);%molecular weight g/mol
Vgc=prop(1,3);%gas cap volume
Z=prop(1,7);%compressibility factor
A=prop(1,4);%area
R=prop(1,8);% gas constant
h=prop(1,6);%cell height
Pi=prop(1,2);
nome_pressao=sprintf('%s','C:\Users\TEMP.SCI.003\Desktop\SA - 770 - 4%
iodo\SA\pressao.xls');
pres_t=xlsread(nome_pressao);
[m,n]=size(pres_t);
%sum_z=Z0;
cont=6;
```

```
for i=1:m
    Pexp(i,1)=pres_t(i,2);
    time(i,1)=pres_t(i,1);
% [ZZ]=Preos(Pexp(i,1),T);
% Z(i,1)=ZZ;
% sum_z=sum_z+Z(i,1);
end
%Z=sum_z/(m+1);
end
```

APPENDIX B - Experiments adjustment to Etminan et al. (2013) Model



Figure (a) – Adjustment to experiment 1





Figure (c) – Adjustment to experiment 3



Figure (e) – Adjustment to experiment 5



Figure (g) – Adjustment to experiment 7



Figure (h) – Adjustment to experiment 9



Figure (i) – Adjustment to experiment 10



Figure (k) – Adjustment to experiment 13



Figure (1) – Adjustment to experiment 14

APPENDIX C – Image Treatment

Matlab code example for image treatment and to obtain CT profile from each ROI.

[W11,w11]=dicomread('01875118'); %choose scan image without anything inside gantry W12=int32(W11); w12 = dicominfo('01875118'); W13 = W12 * w12.RescaleSlope + w12.RescaleIntercept; W14=W13((1:512),(220:350));

[Y11,y11]=dicomread('80514074'); % diffusion cell with air inside Y12=int32(Y11); y12 = dicominfo('80514074'); Y13 = Y12 * y12.RescaleSlope + y12.RescaleIntercept; Y14=Y13((1:512),(220:350));

ERROR= Y14-W14; % matrix that represents error

[A,a]=dicomread('80392775'); %selected matrix to perform error removal A1=int32(A); a1 = dicominfo('80392775'); A2 = A1 * a1.RescaleSlope + a1.RescaleIntercept; A3=A2((1:512),(220:350));

A4=A3-ERROR; A5=A4'; A6=mean(A5); a2=mean(A6);

ATTACHMENT A – CO₂ properties

- Critical temperature (T_c)
 304.1282 K
 373.946°C

 Critical pressure (p_c)
 7.3773 MPa
 3200.11 psia

 Critical density (D_c)
 467.600 kg/m³
 322.00000 kg/m³

 Acentric factor
 0.22394
 0.3443

 Normal boiling point
 194.75 K
 99.9743 C
- Fluid properties for CO₂

•	Isothermal <i>a</i>	data for	CO_{2}	293.15 K	or 20°C
•	150ther mar y	uata 101	$\mathbf{U}\mathbf{U}_2$	4/J.13 h	

Temperature (K)	Pressure (MPa)	Temperature (°C)	Pressure (psia)	Density (kg/m ³)	Phase
293.15	1.3790	20.000	200.00	26.962	vapor
293.15	2.7579	20.000	400.00	59.579	vapor
293.15	4.1369	20.000	600.00	102.48	vapor
293.15	5.5158	20.000	800.00	174.20	vapor
293.15	5.7291	20.000	830.93	194.20	vapor
293.15	5.7291	20.000	830.93	773.39	liquid
293.15	6.8948	20.000	1000.0	806.28	liquid
293.15	8.2737	20.000	1200.0	832.23	liquid
293.15	9.6527	20.000	1400.0	851.96	liquid
293.15	11.032	20.000	1600.0	868.16	liquid
293.15	12.411	20.000	1800.0	882.04	liquid
293.15	13.790	20.000	2000.0	894.26	liquid
293.15	15.168	20.000	2200.0	905.24	liquid
293.15	16.547	20.000	2400.0	915.23	liquid
293.15	17.926	20.000	2600.0	924.43	liquid
293.15	19.305	20.000	2800.0	932.96	liquid
293.15	20.684	20.000	3000.0	940.93	liquid
293.15	22.063	20.000	3200.0	948.42	liquid
293.15	23.442	20.000	3400.0	955.49	liquid
293.15	24.821	20.000	3600.0	962.20	liquid
293.15	26.200	20.000	3800.0	968.57	liquid
293.15	27.579	20.000	4000.0	974.66	liquid
293.15	28.958	20.000	4200.0	980.48	liquid

Temperature (K)	Pressure (MPa)	Temperature (°C)	Pressure (psia)	Density (kg/m3)	Phase
338.15	13.790	65.000	200.00	22.627	vapor
338.15	27.579	65.000	400.00	47.682	vapor
338.15	41.369	65.000	600.00	75.839	vapor
338.15	55.158	65.000	800.00	108.09	vapor
338.15	68.948	65.000	1000.0	145.93	vapor
338.15	82.737	65.000	1200.0	191.72	vapor
338.15	82.737	65.000	1200.0	191.72	supercritical
338.15	82.737	65.000	1200.0	191.72	supercritical
338.15	96.527	65.000	1400.0	249.05	supercritical
338.15	11.032	65.000	1600.0	322.22	supercritical
338.15	12.411	65.000	1800.0	409.64	supercritical
338.15	13.790	65.000	2000.0	494.28	supercritical
338.15	15.168	65.000	2200.0	560.85	supercritical
338.15	16.547	65.000	2400.0	610.37	supercritical
338.15	17.926	65.000	2600.0	648.27	supercritical
338.15	19.305	65.000	2800.0	678.54	supercritical
338.15	20.684	65.000	3000.0	703.60	supercritical
338.15	22.063	65.000	3200.0	724.95	supercritical
338.15	23.442	65.000	3400.0	743.51	supercritical
338.15	24.821	65.000	3600.0	759.94	supercritical
338.15	26.200	65.000	3800.0	774.69	supercritical
338.15	27.579	65.000	4000.0	788.07	supercritical
338.15	28.958	65.000	4200.0	800.32	supercritical

• Isothermal data for CO_2 @ 338.15 K or $65^{\circ}C$

ATTACHMENT B – Oil characteristics

COMPONENTS	DEAD OIL	FLASH GAS	RESERVOIR FLUID		
CO ₂	0.00	16.42	12.17		
N_2	0.00	0.64	0.48		
C_1	0.00	62.55	46.38		
C_2	0.00	9.04	6.70		
C_3	0.44	6.34	4.81		
IC_4	0.29	1.02	0.83		
NC_4	1.19	2.15	1.90		
IC_5	0.65	0.51	0.55		
NC_5	3.62	0.70	1.45		
C_6	3.81	0.42	1.29		
C_7	7.35	0.14	2.00		
\mathbf{C}_{8}	6.15	0.07	1.65		
C ₉	6.41	0.01	1.66		
\mathbf{C}_{10}	5.50	0.00	1.42		
C_{11}	4.76	0.00	1.23		
C_{12}	4.10	0.00	1.06		
C ₁₃	3.55	0.00	0.92		
C_{14}	3.12	0.00	0.81		
C ₁₅	2.70	0.00	0.70		
C_{16}	2.39	0.00	0.62		
C ₁₇	2.08	0.00	0.54		
C_{18}	1.88	0.00	0.48		
C_{19}	1.73	0.00	0.45		
C ₂₀ +	38.28	0.00	9.90		
total	100.00	100.01	100.00		
Gas density		0.9063			
Total molar mass	270	26.25	89		
Molar mass C ₂₀₊		478			
Density C ₂₀₊		0.9509			
GOR from flash	224.06 m ³ std/ m	³ std			
API 27.33					
Content of original contamination 2.84 (mass%) 3.86 (mol%)					

• Flash expansion of oil sample at 313.15 K – fluids composition (mol%)