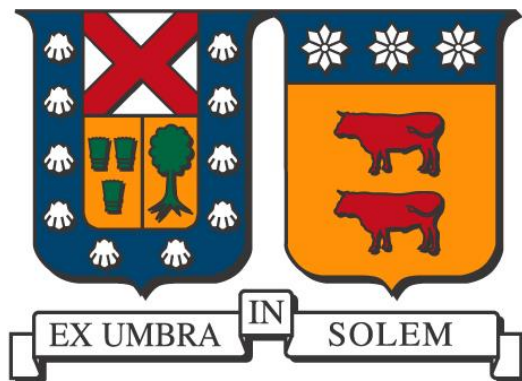


UNIVERSIDAD TÉCNICA FEDERICO SANTA MARÍA
DEPARTAMENTO DE INGENIERÍA QUÍMICA Y AMBIENTAL
VALPARAISO - CHILE



**EXPERIMENTAL MEASUREMENT OF THERMODYNAMIC, TRANSPORT PROPERTIES &
INTERFACIAL PROPERTIES AS WELL AS PHASE BOUNDARIES RELEVANT TO THE CO₂ CAPTURE,
UTILIZATION & SEQUESTRATION**

Rafael Villablanca Ahues

Chemical Engineer degree and Master's in science of the Chemical Engineering thesis.

Advisor: Dr. Juan de la Fuente

Cotutor Professors: Dr. Roberto Canales

Dr. Ing. Philip Jaeger

Dr. Gonzalo Nuñez

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ABSTRACT

Large parts of the industry depend on combustion technologies, not only to satisfy the energy demand but also for production the processes. As a direct consequence Carbon Dioxide (CO_2) has increased its concentration in the atmosphere, interfering with the natural Carbon Cycle. CO_2 is the main contributor to the global warming among the Greenhouse-Effect Gases (water vapor, methane, nitrous oxide among the others). It is accepted by the scientific community (Intergovernmental panel on climate change, 2013) that the increasing concentration of CO_2 in the atmosphere is mainly caused by human activities (anthropogenic) on a direct way e.g., cement production, fossil or high carbon content fuel combustion like power plants or indirect e.g., deforestation.

There are international efforts to decrease CO_2 atmospheric concentration, being the most promising alternative Carbon Capture Utilization & Sequestration (CCUS) technologies. CCUS consist in 4 stages: Capture, Purification, Transport, and Sequestration or Utilization. Two of these stages are crucial for CCUS, transportation and sequestration, where thermodynamic and transport properties are needed in order to achieve them. For the transportation stage, the study of phase behavior of CO_2 rich mixtures containing H_2O and other contaminants becomes necessary. This knowledge regarding CO_2 rich mixtures is also useful for sequestration. There are other properties worth studying for sequestration and transportation such as mutual diffusivities, and interfacial tension (IFT). Given the lack of data regarding these properties available on the literature, simple methods to measure them were used and compared with available literature.

Diffusion coefficient relevant to Sequestration conditions were estimated by three methods, the Stoke-Einstein diffusion coefficient formula is used to estimate pure diffusivities,

statistical methods is proposed and the Fick's second law for longer times at reservoir conditions. The last two models vary between 1.98×10^{-8} and $8.52 \times 10^{-8} \text{ m}^2/\text{s}$, at 40-60°C and 5-20 MPa. The effect of natural convection is observed in view of the effective diffusion coefficient at these conditions and supported by the Rayleigh number.

IFT was measured with a pendant drop method at transport conditions of 5-40°C and 5-20 MPa resulting in values between 9 and 43 mN/m .

Phase behavior of three systems containing CO_2 +Contaminants that represents oxidize, reduce and a real complex mixture were measured to see the influence of different pollutants on the dew and boiling lines. The change in these systems is related to the presence of compounds with critical points at very low temperatures and pressures. This work allows to increase the amount of available data relevant to CCUS technologies and extend the required data base.

NOMENCLATURE

GtC/yr: Giga ton of Carbon per year

GtCO₂/year: Giga ton of Carbon Dioxide per year

Twh: Tera what hour

Gt: Giga ton

°C: Celsius degrees

K: Kelvin

T: temperature

p: pressure

B: capillary constant

F: correction factor

g: gravity constant

R: radius

V: drop volume

X: dimensionless coordinate direction

Z: dimensionless coordinate direction

$\Delta\rho$: density difference between phases, positive.

σ : interfacial tension

ω : angular velocity

T_c : Critical temperature

P_c : Critical pressure

kgCO₂eq/MWh: CO₂ kilograms equivalent per megawatt hour of energy produced

DMC: Dimethyl Carbonate

GPa: Giga Pascal

Q : Rate of transfer per unit area of section

C : Concentration of diffusing substance

D : Diffusion coefficient or diffusivity

M_s : Initial sample weight

M_b : Sample weight in time

m_0 : Apparent interfacial concentration

t_{lag} : Delaying time

ACRONISM

Mwe: Mega watt electrical

CCUS: Carbon Capture, Utilization and Sequestration

CCS: Carbon capture and sequestration

CCU: Carbon capture and utilization

EOR: Enhanced Oil Recovery

IEA: International Energy Agency

MEA: Methyl Ethyl Amine

ECBM: Enhanced Coal Bed Methane

IFT: Interfacial tension

CCD: Charge coupled device

NACE: Statistical classification of economic activities in the European community

IGCC: Integrated Gasification Combined Cycle

CCGT: Combined Cycle Gas Turbine

VdW-EoS: Van der Waals Equation of State

ÍNDEX

ACKNOWLEDGEMENT	2
ABSTRACT	3
NOMENCLATURE	5
ACRONISM	7
ÍNDEX.....	8
TABLE ÍNDEX.....	10
FIGURE ÍNDEX.....	12
CHAPTER 1	15
Introduction.....	15
1.1 Carbon dioxide sources	16
1.2 Effects of high atmospheric carbon.....	20
1.3 Carbon cycle	21
1.4 Mitigation Technologies	24
CHAPTER 2	27
Carbon Capture, Utilization and Sequestration	27
2.1 CCUS potential.....	27
2.2 CCUS stages	30
2.2.1 Source Characterization	32
2.2.2 Capture & Purification	33
2.2.3 CO ₂ rich mixture transport	36
2.2.4 Utilization & Sequestration	42
CHAPTER 3	47
CO ₂ +H ₂ O binary equilibria	47
3.1 Binary equilibria classification and behavior.....	48
CHAPTER 4	52
4.1 Hypothesis	52
4.1.1 Objectives.....	52

4.1.1.1 Main objective	52
4.1.1.2 Secondary objective	52
4.2 Properties on the CO ₂ +H ₂ O system	53
4.2.1 Phase behavior of CO ₂ + impurities.....	55
4.2.1.1 Analytical methods.....	55
4.2.1.2 Synthetic methods:	57
4.2.2 Material and Methods.....	58
4.2.3 Results and discussion.....	61
4.3 Interfacial tension equipment and technique.....	66
4.3.1 Theory.....	69
4.3.2 Materials and Methods	71
4.3.3 Results and discussion	73
4.4 Mutual diffusivity of the binary system CO ₂ +H ₂ O.	77
4.4.1 Theory.....	77
4.4.3 Data Analysis	83
4.4.4 Results and discussion	88
5. Conclusion	98
6. References.....	100
7. Annex.....	111
7.1 Phase equilibria of CO ₂ +H ₂ O relevant to Martian atmosphere.....	111
7.2 Phase boundary data.....	112
7.3 IFT Data Values	115
7.4 Models for diffusivity	118
First model results:	118
Statistical model:	119
Continuous model:	120
Stoke Einstein Equation + Cadogan hydrodynamic Radios	121

TABLE ÍNDEX

Table 1 Fossil-fuel and KgCO ₂ produced per MWh produced. source: Intergovernmental Panel on Climate Change (IPPC, working group III, 2015).....	19
Table 2 Taken from (Li Q, 2015); (Pieri, 2018).....	31
Table 3 Classification of CO ₂ according to different authors.....	33
Table 4 Source classification: "Matching carbon sources and carbon separation technologies" (Pieri, 2018).....	35
Table 5 Scenarios for corrosion on dense phase transportation through pipelines (Lee J. , 2009).....	37
Table 6 Analytical methods classification. Extracted and adapted from Dorhn et al (2012).....	56
Table 7 Synthetic methods with phase transition. Dorhn et al (2012)	57
Table 8 Original characteristic fumes samples.....	59
Table 9 Composition of the oxidize representative mixture fumes.....	59
Table 10 Composition of the reduced representative mixture fumes.....	60
Table 11 Composition of representative of the original mixture.....	60
Table 12 IFT measurement methods adapted from Eurotechnica (2013).	66
Table 13 Rayleigh numbers of each measurement. The result of diffusivity using the statistical method was used to calculate Ra.	91
Table 14 Oxidize mixture phase boundaries data	112
Table 15 Reduced gas mixture phase boundary data	113
Table 16 Real mixture gas system data	114
Table 17 Interfacial tension data. IFT* is the corrected by density IFT values from DSA.	115
Table 18 Diffusivity results for the first model and the respective pressure and temperature of each measurement	118

Table 19 Diffusivity results for the statistical model and the respective pressure and temperature of each measurement	119
Table 20 Diffusivity results for the continuous model and the respective pressure and temperature of each measurement and their nominal length.....	120
Table 21 Mutual diffusivities for CO ₂ +H ₂ O system calculated by Stoke-Einstein Equation, with Cadogan's hydrodynamic radio correlation.....	121

FIGURE ÍNDEX

Figure 1A) World population through the years 1000B.C.- 2100 A.C. B) World population through the years 1600-2100, (OurWorldInData, 2015).....	15
Figure 2 A) CO ₂ atmospheric concentration through the years 0-2016. B) CO ₂ atmospheric concentration through the years 1600-2016, (Ritchie, 2018)	17
Figure 3 Global primary energy consumption. Above: 1800-2012, Bellow: 1959- 2012. (Vaclav Smile 2017).....	18
Figure 4 Temperature deviation, global and by hemisphere. (Ritchie, 2018)	20
Figure 5 Carbon Cycle, source: Biochemical cycles, by OpenStax College, Biology, CC BY 4.0; Modification of work by John M. Evans and Howard Perlman, USGS. Taken from Kahn Academy,	21
Figure 6 Pre-industrial global carbon cycle. Number denote the amount in metric tones per year moved through that system (MGtC/year) (Siegenthaler, 1993)	23
Figure 7 Post-industrial global carbon cycle. Number denote the amount in metric tones per year moved through that system (MGtC/year) (Siegenthaler, 1993)	24
Figure 8 Project Sleipner facilities 2014, Stavanger, Norway. Global CCS institute. (Global CCS institute, 2018).....	28
Figure 9 Cumulative CO ₂ captured 2015-2030 and to 2050 prediction, by region (International energy agency, 2017)	29
<i>Figure 10 The concentration of various species out of H₂O+CO₂ equilibria. (Ivan, 2011)</i>	<i>38</i>
Figure 11 Production of CO ₂ without carbon capture and sequestration and with two technologies of CCS (Cuellar-Franca R. , 2015)	46
Figure 12 Phase diagram behavior. (Coquelet, 2012)	50
Figure 13 Phase equilibria in the H ₂ O–CO ₂ system between 250–330 K and 0–1.7 GPa: Stability of the CO ₂ hydrates and H ₂ O-ice VI at CO ₂ saturation (Bollengier, 2013).....	51

Figure 14 Experimental Set up for Phase boundaries Measurements.....	58
Figure 15 Phase behavior of simulated oxidize mixture, by REFPROP NIST V.9.1.	61
Figure 16 Comparison between simulated oxidize mixture and actual measurements performed	61
Figure 17 comparison between reduced gas mixture and simulated oxidize mixture.	63
Figure 18 Comparison between real mixture model system and simulated oxidize mixture simulated by REFPROP NIST V.9.1.	64
Figure 19: Pendant drop (left) and the geometry of a two dimensionally projected pendant drop (right). Redrawn from (Sutjiadi-Sia et al. 2007)	70
Figure 20 Experimental Set up for Interfacial Tension measurement	72
Figure 21 IFT values as function of time.....	74
Figure 22 IFT on H ₂ O+CO ₂ system as a function of pressure at 278K. Blue circle shows gas phase for CO ₂ and orange circle shows liquid CO ₂ phase. Blue line shows CO ₂ pure L-V transition at 3,95 MPa	75
Figure 23 IFT on H ₂ O+CO ₂ system as a function of pressure at 313K.	75
Figure 24 Setup for determining the diffusion coefficients of CO ₂ in ionic liquids. Eurotechnica GmbH (2013)	81
Figure 25 Plot of the corrected data from the sample weight during the experiment at 40°C and 5 MPa	82
Figure 26 Considerations for mass transfer	83
Figure 27 Effect separation at 40°C and 5 MPa. A: CO ₂ absorption into H ₂ O rich phase. B: H ₂ O vaporization into CO ₂ rich phase.	86
Figure 28 Diffusion coefficient of CO ₂ into H ₂ O as a temperature function. Stoke-Einstein equation (Δ), Statistical model (-), Continuous model (■), Unver, A. & Hummelblau (1964) (◆), A. Tamimi et al (1994) (●).....	89
Figure 29 Gas-Liquid diffusion scheme for a drop. (Deen, 2004).....	92

Figure 30 CO ₂ diffusion into a H ₂ O sphere at different pressures and temperature. A [40°C-5.5 MPa], B [60°C-11.2 MPa], C [60°C-19.2 MPa]. Comparison of saturation times for different models obtained from Stoke-Einstein model (Blue). Statistic model (Orange) and Continuous model (Grey)	93
Figure 31 Effect of pressure over saturation times with statistic model	94
Figure 32 Carbon dioxide diffusion into a reservoir at different conditions and the impact on saturation times regarding each model. Stoke-Einstein (Blue), Statistic (Orange) and Continuous (Grey).....	95
Figure 33 $DH_2O \rightarrow CO_2$ values as a temperature function. Statistical model (●), Continuous model (-), Stoke-Einstein (▲), Bin Xu, et al (2002) (▲), Gregor Kravanja et al (2018) (◆), J.Wambui Moturi et al (2010) (■)	95
Figure 34 Comparison of saturation times for different p and T. using our diffusivities. Stoke-Einstein (Blue), Statistic (Orange) and Continuous (Grey)	96
Figure 35 Effect of density difference between phases over diffusivity	96
Figure 36 Mutual saturation times into a sphere at two different conditions, diffusivities estimated by Statistical model. $DCO_2 \rightarrow H_2O$ (Blue), $DH_2O \rightarrow CO_2$ (Orange).....	97
Figure 37 Phase equilibrium in the system CO ₂ -H ₂ O: Application to Mars. (Longhi, 2006).....	111

CHAPTER 1

Introduction

Through history, human population remained roughly constant due to equilibrium reached between the birth and death rate, since life quality was different back then, many situations make world population fluctuate, such as sickness, infant mortality, famine and wars, among other causes of mortality (figure 1 A). Improvements on science and other fields allow to us, humans beings, to sustain life longer and therefore, increase population, which had a relatively small and constant growth for many thousands of years. In contrast, a fast growth has been observed through the last 4 centuries, moreover, since the 18th century it started to increase at faster rate, to a point within the 19th century where it showed an exponential growth (OurWorldInData, 2015). Since the 60's the rate of population growth rate decreased, but the overall number of humans on the plane is far from decrease (figure 2 B).

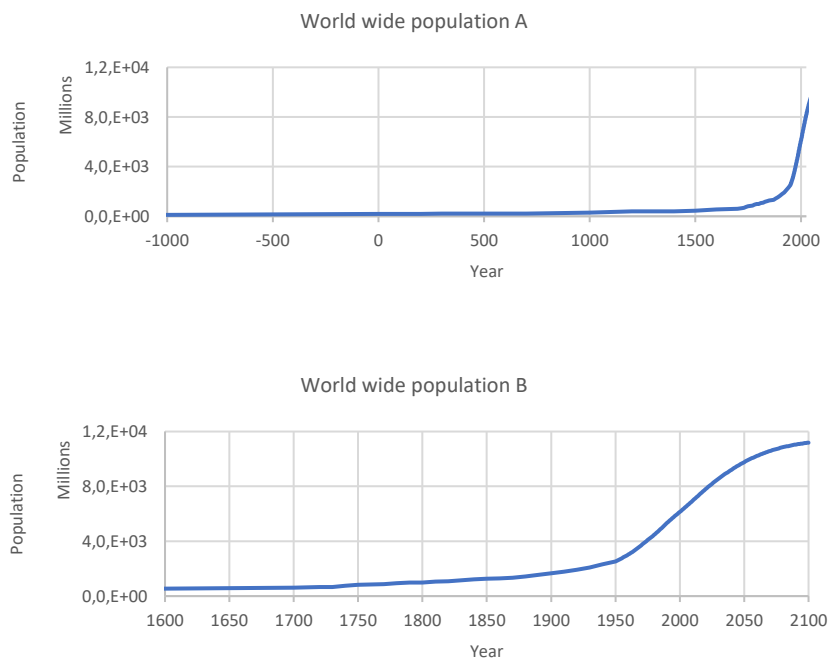


Figure 1A) World population through the years 1000B.C.- 2100 A.C. B) World population through the years 1600-2100, (OurWorldInData, 2015)

Along with the population growth, comes an increase in all activities related to support human kind in areas e.g., food and chemical industry, transport, construction, pharmaceutical products. All industrial activities require a power input, which in modern times is in the form of electricity. That is why power plants, nuclear, thermal, hydroelectric and other source of power used in many countries in the last 50 years increased in number. Global power consumption grew at an average rate of 1.4% per year between 1990 and 1995 which represent the trend to this day.

The dominant power source comes from combustion plants which use mainly hydrocarbons as fuel (85% of all the power plants use fossil-fuel) (Hasana, 2015), or high carbon content fuels, which produce CO₂ as one of outputs of its combustion. As a medium to long-term consequence, it is increasing CO₂ concentration at atmospheric level. Around 75% of the anthropogenic CO₂ released to the atmosphere comes from fossil-fuel burning. An example of this is USA, where it represents around the 60% of all contributions (OurWorldInData, 2015)

By the early 19th century the situation regarding CO₂ atmospheric concentration started to change. Its concentration remained within 280 ± 10 ppm for several thousand years, to a very fast change in the late 19th century (figure 2), due to the use of steam, produced by coal burning during the industrial revolution. Its concentration have been rising continuously since then, reaching 367 ppm in 1999 (Nikicenovic, 2001) and by 2017 the concentration reached around 400 ppm, stablishing the record for highest CO₂ atmospheric concentration ever recorded (NASA, 2018).

1.1 Carbon dioxide sources

The increasing amount of CO₂ in the atmosphere is increased by other activities that contributes indirectly to the CO₂ concentration, and example of this is the tropical deforestation, that represents the main indirect way to contribute to CO₂ concentration since the late 20th century. From 1980 to 1989, atmospheric CO₂ emissions from fossil-fuel burning and tropical deforestation amounted around 7.0 GtC (Giga tons of carbon) (Siegenthaler, 1993), and in 2013, the anthropogenic CO₂ emissions rate emitted globally reached the 34.5 GtCO₂/year (Environmental Assessment Agency, 2013). Power generation

worldwide produce as much CO₂ as the rest of the industrial sectors combined, while the transport sector is the fastest-growing source of CO₂ emissions (airplane and transoceanic ships).

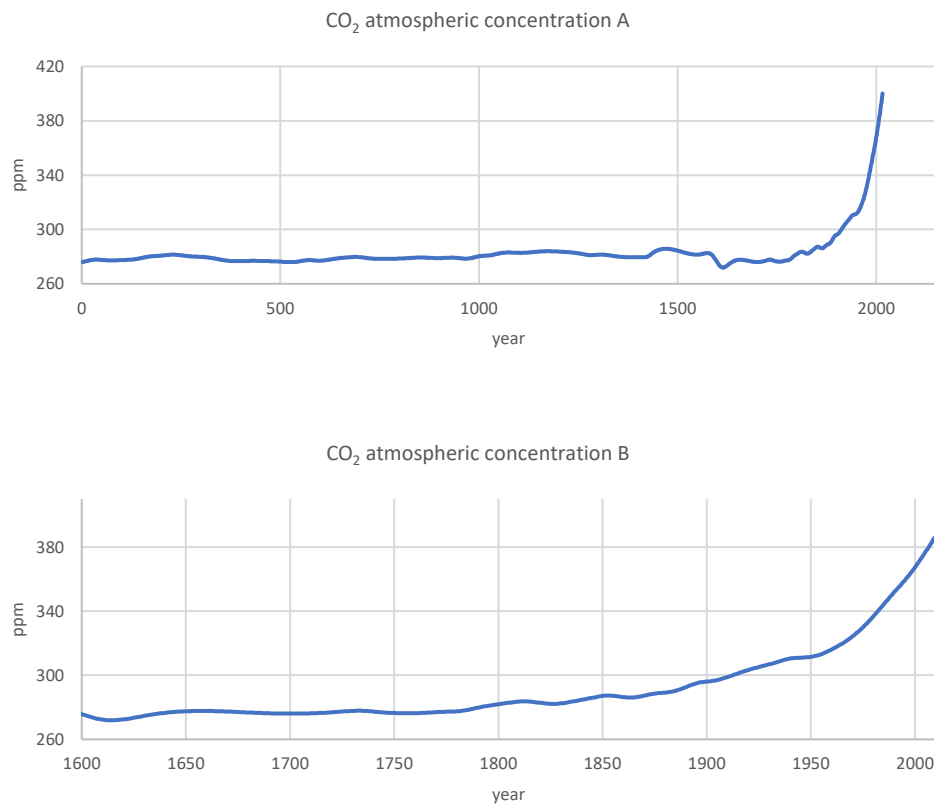


Figure 2 A) CO₂ atmospheric concentration through the years 0-2016. B) CO₂ atmospheric concentration through the years 1600-2016, (Ritchie, 2018)

Comparing the trends on figure 1 and figure 2 is possible to appreciate that CO₂ atmospheric concentration and human population rates are correlated. This is due to power consumption, which take a considerable increased rate during the late 19th century (figure 3) and since it uses mainly fossil-fuel burning to generate power, increase in population means increase in power consumption, therefore, CO₂ emissions augmentation if current power generation technologies remain constant. From the different ways to produce power, coal represent the most used source of carbon through history, followed by crude oil, which becomes an important source of power-generation on the second half of the 21th century. Natural gas consumption showed the same consumption trend as oil, but in lower amounts. Much later in

time comes renewable energies, which have increased their contribution to the total power supply, but it is not yet significant on the overall picture.

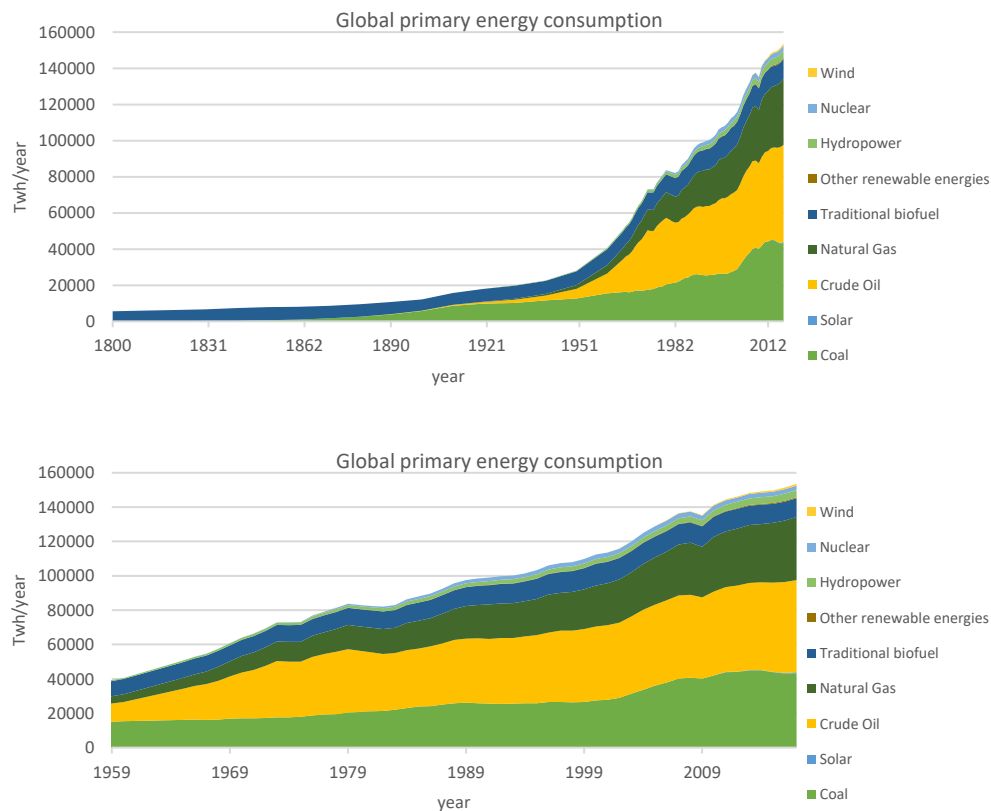


Figure 3 Global primary energy consumption. Above: 1800-2012, Below: 1959- 2012. (Vaclav Smile 2017).

The CO₂ produced by human activities is changing carbon natural balance on planet earth, and as mentioned before, increasing the net amount of CO₂ present in the atmosphere. In other words, the consumption of traditional fossil-fuels is approaching the limit of the carrying capacity of the planet, producing a bottleneck on the carbon cycle, but nature is not able to cope with such large amount of carbon dioxide.

Within the types of fossil-fuel, it is considered a wide variety of burnable material with a high carbon content. It is scientifically agreed that most of the fossil fuel is formed initially by decomposition of organic matter for several thousands of years at high pressure and temperature, producing what is considered today crude oil, carbon and natural gas (Pepper, 1995). With these raw material and posterior

refining or transformation it is possible to obtain other kinds of fuel from the afore mentioned that allow to decrease the carbon emissions compared with energy that is possible to obtain from them (table 1). At the same time this refining increases the production cost.

Table 1 Fossil-fuel and KgCO₂ produced per MWh produced. (IPPC, working group III, 2015)

Fossil-Fuel	KgCO₂/MWe/hour produced
Charcoal	403.2
Coke carbon	385.2
Oil Shale and Tar Sands	385.2
Peat	381.6
Lignite	363.6
Anthracite	353.88
Sub-Bituminous Coal	345.96
Bitumen	290.52
Diesel Oil	266.76
Crude Oil	263.88
Shale Oil	263.88
Jet Gasoline	252
Aviation Gasoline	252
Motor Gasoline	249.48
Natural Gas	201.96

1.2 Effects of high atmospheric carbon

An increasing atmospheric carbon amount in the form of CO₂ is problematic because it has the effect of increase the global average temperature by keeping the sun infrared radiation inside the earth's surface. This is known as Greenhouse Effect and is the way how global warming is caused. The presence of CO₂ and other gases such as nitrous oxide, water vapor and methane in the atmosphere are desirable only in specific concentrations because its presence stabilize earth's superficial temperature. If there were non Greenhouse Effect gases in the atmosphere, earth's average temperature would be -18°C instead of +14°C (Qiancheng, Ma, 1998).

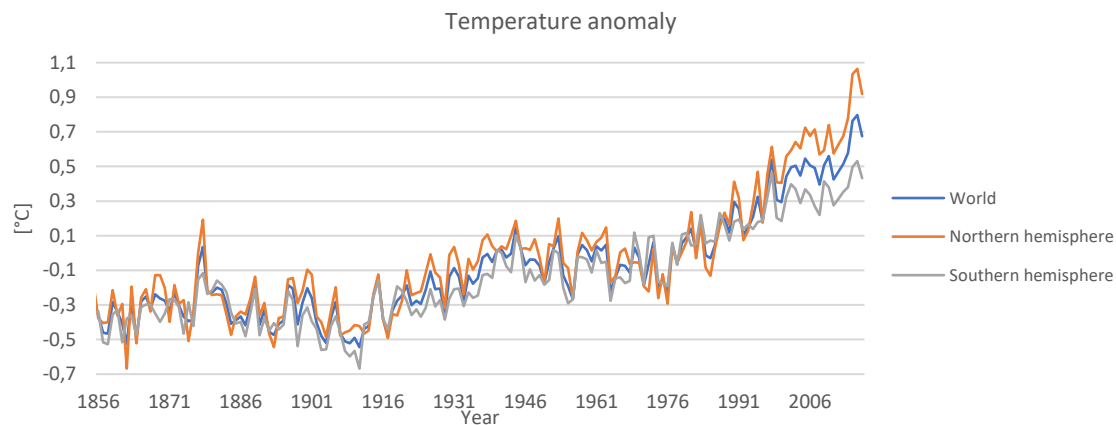


Figure 4 Temperature deviation, global and by hemisphere. (Ritchie, 2018)

Average global temperature has increased in +1.0°C compared with pre industrial periods (figure 4), and an increase of 2.0°C have been settled by more than 100 countries as the limit increase in temperature before it affect human activities and ecosystem in unpredictable ways (Meinshausen, M., 2009). To avoid further damage on the planet's chemical equilibria, a new approach to fossil-fuel consumption and power generation must be considered. This will not only decrease the immediate CO₂ concentrations, but also will allow earth's carbon cycle to take place and capture the excess of CO₂ to equilibrate atmospheric CO₂ concentration to natural levels.

1.3 Carbon cycle

Carbon cycle is the way by which earth moves carbon through different systems and keep balance between each of its parts (figure 5). Carbon is not the only element that cycles around earth's systems but is the one which human altered on a global-scale-consequence manner. This cycle is a complex system that is composed by two sub-cycles that moves carbon in two different time scales. The fast carbon cycle moves carbon between photosynthetic mainly, and heterotroph life forms, which forms the biological compound of this cycle, and the atmosphere and oceanic carbon. The slow or inorganic carbon cycle is formed by ocean and earth. The carbon is moved around this cycle by weather and more important, geological activity, moving carbon on large quantities and time scales (hounded of thousands and millions of years).

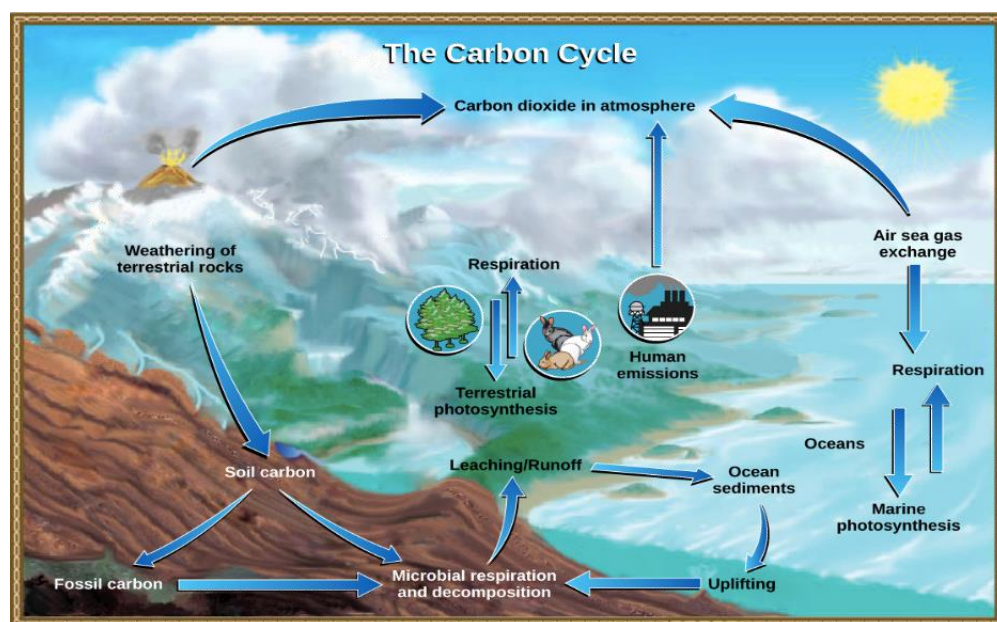
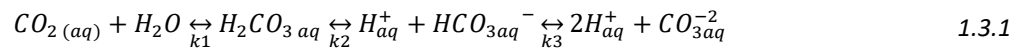


Figure 5 Carbon Cycle, source: Biochemical cycles, by OpenStax College, Biology, CC BY 4.0; Modification of work by John M. Evans and Howard Perlman, USGS. Taken from Kahn Academy,

The common agents between the fast and the slow carbon cycles are the atmosphere and the ocean, where the later one acts as the strongest regulator of carbon in the atmosphere. Through solubility of CO₂ into H₂O a common stage between the atmosphere, biological life forms and geological systems is formed, exchanging carbon between them by storing and releasing CO₂ to keep the balance. Carbon is not just stored there as dissolved CO₂, it is also stored as carbonic acid (H₂CO₃) after reacting with water (equation 1.3.1). This specie can dissociate to form bicarbonate (HCO₃⁻) and carbonate (CO₃⁻²), in this form it can react with calcium ions (Ca⁺²) to form calcium carbonate (CaCO₃), this molecule forms part of many of the shell of aquatic life forms, that after dying, sink into the sea floor and ends up forming geological structures, known as lime stone. This is one of the forms how carbon passes from the fast to the slow carbon cycle. The chemical equilibria between CO₂ and H₂O is defined by different equilibrium constants regarding each stage of dissociation and is strongly dependent on temperature (Goyet, Catherine, 1989) .



The carbon equilibrium between ocean and the atmosphere, since it is an interaction through diffusion, limited by solubility, is strongly dependent on temperature and a weak function of pressure. Higher temperature decrees CO₂ solubility in water and lower temperatures increase CO₂ solubility. Higher pressures increase slightly solubility and lower pressure decrease solubility slightly. In this way, carbon can leave the ocean to the atmosphere as CO₂ or remain on its ionic form (HCO₃⁻, CO₃⁻²) to later be incorporated to geological process by reacting with other molecules. When carbon goes to the atmosphere as CO₂, is then taken by plants and other photosynthetic living forms. When carbon is incorporated into biological forms is denominated “organic carbon”, which is within the fast carbon cycle, more specifically the “organic carbon cycle” which exchange carbon constantly with atmosphere, soil and oceans. Organic carbon goes back to the soil and during millions of years, carbon goes to deep layers of the earth, to go back to the atmosphere through fumes of and blasts from volcanos (Roger Revelle, 1985). During this process limestone is formed, which, along fossil-fuels, are the largest carbon reservoir on earth. Through

a series of chemical reactions and tectonic activity, carbon take between 100 to 200 million years to move between rocks, soil, ocean and atmosphere in the slow inorganic carbon cycle. The amount of carbon going through this cycle per year is around 10 to 100 million metric tons, which seems to make human emissions insignificant. Through the fast cycle (ocean, biota and atmosphere) around 1 to 10 metric tons per year are moved (NASA, Earth Observatory, 2011).

For human time scale, the cycle of interest is the fast carbon cycle (decades to a century), established between the oceans, living creatures and the atmosphere. This fast cycle is the one altered by human activities and the one that is possible to fix in the medium to long-term. A diagram with estimated flows and reservoirs of carbon in MGtC/year before the industrial revolution can be seen on figure 6. (Siegenthaler, 1993). Is possible to appreciate that the different layers of the ocean hold a big portion of carbon, while atmosphere act as the meeting point/common point for each stage of the cycle.

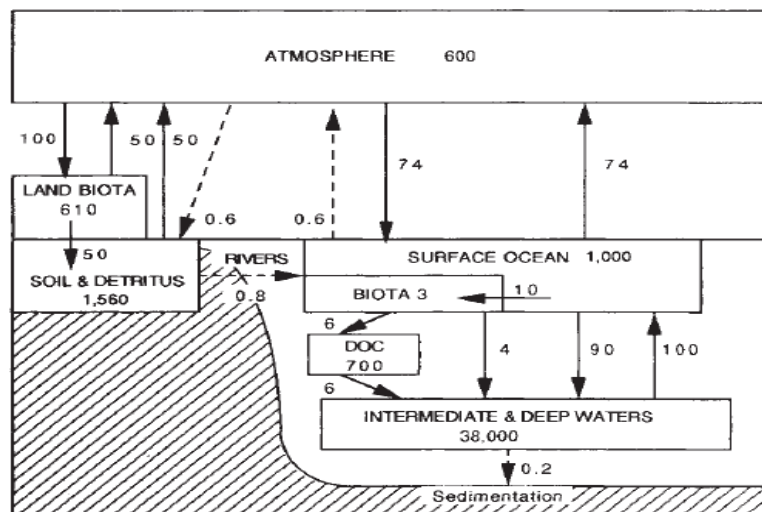


Figure 6 Pre-industrial global carbon cycle. Number denote the amount in metric tones per year moved through that system (MGtC/year) (Siegenthaler, 1993)

The influence of anthropogenic CO₂ in the atmosphere changed the flows, as mention by (Le, Q.C. *et al*, 2013) and (Siegenthaler, 1993). Human CO₂ emissions releases more CO₂ that oceanic water can absorb, soils can move through, and photosynthetic life forms can fix to the ground. This process is then boosting global warming caused by the greenhouse effect of CO₂, warming up the oceans, decreasing

solubility of CO₂ in them. Changes in the CO₂ in oceans affect its pH, which can affect in ways not seen before the ecology of the oceans. As consequence of these changes, the overall cycle is disbalanced, producing a bottle neck in the carbon cycle.

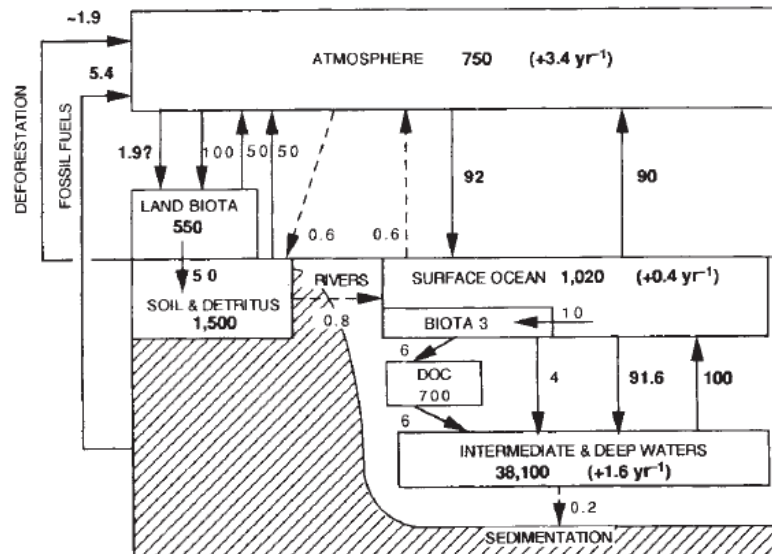


Figure 7 Post-industrial global carbon cycle. Number denote the amount in metric tones per year moved through that system (MGtC/year) (Siegenthaler, 1993)

After the industrial revolution, a new contribution to the carbon cycle was introduced. This is the anthropogenic CO₂ (see figure 7). New sources of carbon start at the source of the emission or fossil fuel burning places (power-plants, cement production, refineries, etc.) and then go to the atmosphere. The problem is that fossil-fuel burning turns carbon from the soil to the atmosphere on an instantaneous way compared with the manner of the nature to do it (through volcanoes and deep ocean fumes). This is the reason of an increase in atmospheric carbon, which is boosting global warming, bringing direct consequences to the ecology of the planet.

1.4 Mitigation Technologies

There is strong evidence that most of the worldwide temperature rising observed over the past 50 years is attributable to human related activities. Extreme climatic events worldwide, such as heat waves, droughts, floods, had increased frequency in the last decades (Li Q, 2015). This temperature rise is caused

by greenhouse effect gases (CO_2 , NO_x , SO_x , CH_4 , H_2O), being the main contributors the CO_2 present in the atmosphere and the one who has increased its amount due to human activities (Intergovernmental panel on climate change, 2013). Although anthropogenic CO_2 emissions are small compared to the amount of carbon exchanged in natural cycles, the discrepancy between the long presence of CO_2 in the atmosphere (50-200) years and the slow rate of natural carbon sequestration processes leads to its accumulation in the atmosphere. IPCC 1995-2017 (Intergovernmental Panel on Climate Change) concluded that *“the balance of evidence suggests a discernible human influence on the global climate change”* (Meira, 1996), (Gupta, 2002). It is then necessary to approach energy production in a new way and develop new technologies or optimize current ones to reduce CO_2 emission to the atmosphere. This is the reason why many countries around the world are opting for investing in the medium-to long-term CO_2 emission mitigation and reduction. An example of this tendency is China, whom endorsed a goal of action to reduce its national CO_2 emissions intensity in 2020 by 45-50% compared to that of 2005. (Li Qi, 2013) also concluded this campaign as a compulsory indicator in its mid- and long- term program for national economic and social development (Li Qi, 2013). Since the last decades of the 20th century an effort to reduce CO_2 emissions by changing the sources of power plants, like green or less contaminating energies, have been made.

Other ways to reduce CO_2 emissions must be considered and further investigated to allow the natural processes to take part and stabilize the current excess of atmospheric carbon. Technological options for reducing net CO_2 emissions to the atmosphere includes reduction on energy demands and/or utilization, switching to less carbon content fuels, increase the use of renewable energy sources or nuclear energy, each of which emits little or no net CO_2 , sequestering CO_2 by enhancing biological absorption capacity in forest and soils or capturing and storing CO_2 chemically or physically. Carbon Capture Utilization and Sequestration (CCUS) is a suitable way to deal with this challenge. It is a technological option for reducing immediate contact of CO_2 with the atmosphere from human activities. It does not mean CO_2 will

not be produce, but it will be relocated or used for further processing to avoid a direct contribution and giving more time to natural system to take the carbon to other system of the cycle. This concept means that CO₂ produced will be captured and stored away from the atmosphere for a very long time. Many entities trust and support the development of CCUS technologies as one of the main tools towards global warming mitigation, such as the European Union, EEUU, China, and others (Prier, 2018) . The worlds first commercial-scale CO₂ Sequestration facility, which begun operation in 1996, makes use of a deep saline formation under the North Sea (Korbøl, R, 1996). The concept of CO₂ capture and Sequestration is therefore based on a combination of known technologies applied to the new purpose of mitigate climate change. The economic potential of this technique to enable deep reduction un emissions was examined by Edmonds (Edmonds, 2001). Based on the different technologies for CO₂ reduction, such as an increase in efficiency, use of renewable energies, fuel switching, nuclear plants and CCUS, it is forecasted that by 2060 CCUS will account for the 32% of the reduced carbon emissions, 1% Nuclear, 18% fuel switching, 15% renewable energies and 34% by an increase in process efficiency. (International energy agency, 2017).

Carbon Capture, Utilization and Sequestration

Carbon Capture, Utilization and Sequestration aims to reduce net carbon emissions as CO₂ to the atmosphere by sequestering it underground, in locations such as deep saline reservoir, depleted oil reservoir, geological formation, among others. Also, CCUS can be used in other processes instead of sequestration, converting a waste into a commodity. In general terms, these technologies are composed by four basic steps. Once CO₂ is produced as part of a complex gases mixture from industrial and power-generation processes, purification and separation of CO₂ must take place, followed by transport to a Sequestration location and long-term isolation from the atmosphere, known as injection, thus achieving long term isolation of CO₂ from the atmosphere or instead, further use to a wide range of applications (King, 2013).

2.1 CCUS potential

CCUS has the potential of reducing the greenhouse effect, reduce the overall operation costs and increase flexibility in achieving carbon dioxide emission reductions. It has been determined that the worldwide potential for greenhouse gases reduction using technological improvement and CCUS is between 6900 and 9500 MtCO₂/year, equivalent to 25 to 40% of global emissions respectively. By 2017, there are 21 large scale CCUS projects in operation or under construction globally, with a carbon capture capacity of 40 MtCO₂/year, 6 projects being constructed with 8 MtCO₂/year and there are 11 more large-scale CCUS projects in early stages of planning adding 21 MtCO₂/year Sequestration capacity. More specifically, examples of countries and companies using CCUS concept around the world are USA, with *Kemper County Energy Facility* and *Air Products Steam Methane-Reformer EOR Project* (by 2016 had already capture 4 million tones of CO₂ for later use in EOR), in Canada is located *Boundary Dam 3* (2015) with over 1.6 MtCO₂ already captured and 100.000 MtCO₂ captured in deep saline formations and used

for enhanced oil recovery (EOR), this facilities has also a capacity to retrofit 120 MWe using CO₂ and *Quest* (2015) with over 2.6 MtCO₂ captured. Norway is currently the best example of CCUS implementation with *Sleipner* (figure 8), the first CO₂ injection project plant that operate since 1996, with over 20 years of successful operation and more than 16 million MtCO₂ stored (by 2016) (Global CCS Institute, 2016).



Figure 8 Project Sleipner facilities 2014, Stavanger, Norway. Global CCS institute. (Global CCS institute, 2018)

The potential for CO₂ mitigation using CCUS technologies in China is expected to be hundred million tons per year (Forbes, 2013) and for already operating plants there, *Jilin Oil Field EOR Demonstration Project*, with more than 1 million MtCO₂ injected into reservoir. In Brazil, *Petrobras Santos Basin Pre-Salt Oil Field CCS Project* is operating, with over 3 million MtCO₂ injected into reservoirs (Global CCS Institute, 2016). New projects are being planned, like *Emirates Steel Project* in United Arab Emirates (UAE) which started in November 2016th, CO₂ comes from a Direct Reduced Iron (DRI) steel plant that uses Amine capture for purifying the fumes. This project has 800.000 MtCO₂ Sequestration capacity expected. In the USA, *Petra Nova Project* started in January 2017 with an expected capture rate of 1.4 MtCO₂/year and it is aimed to sell CO₂ for EOR as a costs reduction measure. Also, in the USA, *Illinois Industrial Carbon Capture Project* started in April 2017, it will produce 1 MtCO₂/year from a bioethanol plant by dehydrated gases aimed to stored them in deep saline formation. In japan is the project *TOMAKOMAI*, which started in April 2016th, which is a test plant and its aimed to store 100 000 MtCO₂/year for two years into deep saline formation.

It is worth mentioning that CCUS technologies remains in the stage of exploration and demonstration, which means that CCUS will not be able to solve completely the health, safety and environment issues in a short term, therefore, more data and experience is needed (Global CCS Institute, 2016). It is forecasted that CCUS will be an important way to handle CO₂ after it is produced in the next 20 to 30 years (Forbes, 2013). The volumes of CO₂ expected to Sequestration estimated by the International Energy Agency (IEA) can be seeing in figure 9, showing a promising Sequestration capacity scenario for CCUS technologies.

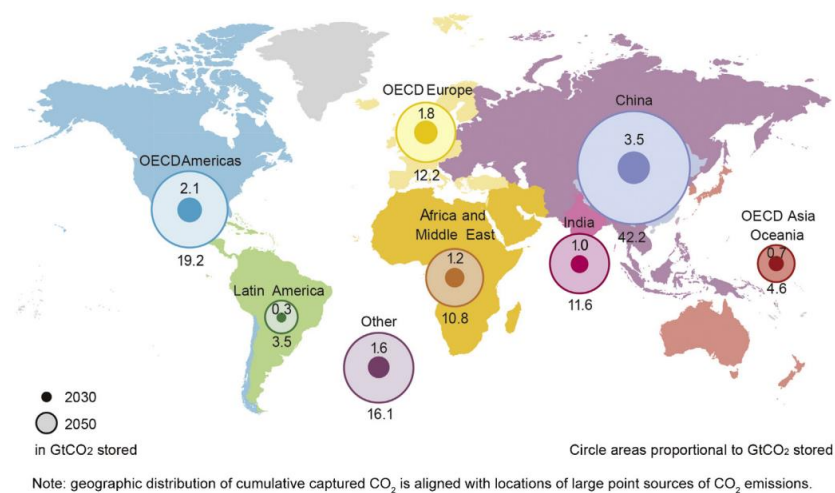


Figure 9 Cumulative CO₂ captured 2015-2030 and to 2050 prediction, by region (International energy agency, 2017)

Li *et al* (2013) (Li Qi, 2013) estimate that the effective theoretical carbon dioxide Sequestration capacity for China is 3.088 Giga MtCO₂, from which around 99% will be injected within a saline aquifer, and the rest include Oil reservoir, Gas reservoir and Coal Seam as a sequestration site. The use of other types of sequestration sites allows not only injection to be stored, but also to use carbon dioxide for some yield improvement techniques, such as extraction of natural gas and hydrocarbons.

It is very important that the place for storing chosen, known as reservoir, is able to hold orders of gigatons of CO₂ per year to make a significant contribution to the mitigation of atmospheric CO₂ production, although the capture of smaller amounts would also be an useful contribution to lowering

emissions. There are several types of reservoir that provides Sequestration capacities of this magnitude, some examples of this is the injection of CO₂ into oil and gas fields (EOR). This option is attractive because the costs of CCUS could reduce the cost of this technology and can increase oil recovery by as much as 15% of the original oil in place (National energy technology laboratory, 2010)

Even though there seems to be several reasons to implement this technology, it has been found some resistance among governments. The widespread application and operation of CCUS technologies depends on several factors, besides technical knowledge. To list few factors to have in mind:

- *Initial operation costs*
- *Overall potential for use and/or storing*
- *Diffusion and transfer of technology*
- *Regulatory and legal aspects*
- *Environmental issues and public perception*
- *Scientific knowledge*
- *Understanding about the phenomena occurring in each stage of CCUS*

The reasons afore mentioned shows that research, funding and development are still needed to be able to apply CCUS technologies on large scale.

2.2 CCUS stages

According to (Li Qi, 2013) and (Pieri, 2018) the steps and suitable technologies that can be applied to the different stages of a CCUS facility can be summarized in the following steps: Source characterization, Capture-purification, Transport and Sequestration or Utilization.

Table 2 Taken from (Li Q, 2015); (Pieri, 2018)

Stage	Category
Source characterization	<p>By Industry</p> <ul style="list-style-type: none"> ▪ Energy Sector ▪ Oil refineries ▪ Cement industry ▪ Iron & Steel industry ▪ Biogas sweetening ▪ Chemical Sector <p>By Purity</p> <p>By Cost of purifying</p>
Capture-Purification	<p>Post-combustion</p> <ul style="list-style-type: none"> ▪ Absorption by chemical solvents ▪ Cryogenic separation ▪ Adsorption by solid sorbents ▪ Pressure / vacuum swing adsorption ▪ Membrane separation <p>Pre-combustion</p> <ul style="list-style-type: none"> ▪ Absorption by chemical solvents ▪ Absorption by physical solvents <p>Oxy-fuel</p> <p>Chemical Looping</p> <p>Combustion in pure oxygen</p> <p>Chemical looping reforming</p>
Transport	<p>Pipeline</p> <p>Truck</p> <p>Shipping</p>
Sequestration	<p>Geological Sequestration</p> <p>Enhanced Oil Recovery</p> <p>Saline Formations</p> <p>Enhanced Coal Bed</p> <p>Methane Recovery</p> <p>Ocean Sequestration</p>
Utilization	<p>Energy production</p> <p>Chemical production</p> <p>Materials</p> <p>Energy</p> <p>Organic Chemicals</p> <p>Inorganic chemicals</p> <p>Energy and feed additives</p> <p>Fertilizer</p> <p>Fuel production</p> <p>Direct use</p> <p>Mineral carbonation</p> <p>Mineral resources</p>

2.2.1 Source Characterization

Sources of carbon nowadays are plenty and vary widely according to the classification criteria, such as purity, kind of contaminants, geographical location, quantity produced and impact, activity from where it is produced, among others (table 3). Therefore, standardization of its sources is an useful way to establish optimal paths for CCUS implementation according to the particularities of each emission and the final reservoir or use chosen. In the early stages of development, an initial useful criterion for carbon sources classification was proposed by the (IPPC, working group III, 2015) which considered the content of CO₂ and its available quantity for the major worldwide CO₂ stationary sources. (Patricio, 2017) classify extensively CO₂ sources and related them to the industrial activity they were produce from, referred to them by its corresponding NACE code (NACE, 2008). In their classification, they also listed common impurities found in each category by its NACE code as well as the typical magnitude of the CO₂-rich mixture fumes. Another classification was done by (Zakkour, 2010), who focus on the high purity carbon sources (>80% CO₂), from which included a summary of the different industrial activity within the high purity sector. (Fennel, 2012) have also presented a detailed list of industrial and power-generation sectors, focusing on the CO₂ partial pressure content and the cost associated with its removal from the gas stream/ the purifying process. (Jin, 2012) classify the sources into four categories (high >90% , secondary higher 50-90%, moderate 20-50% and low <20%). The Centre for Low Carbon Futures (Styring, 2011) has also classified CO₂ sources in four categories based on the impact of the CO₂ concentration on the energy requirements and the corresponding cost for separating CO₂ from the gas stream, whereas (Angelisk-Dimakis, 2016) and (Cuellar-Franca R. , 2015) proposed three classification criteria, based on the purity of the CO₂ content (High>90%, moderate 20-90% and low <20%).

Table 3 Classification of CO₂ according to different authors

Autor	Criteria
IPPC	Purity and available quantity of the mayor worldwide large CO ₂ stationary sources
Patricio et al	Type of industrial activity and the corresponding NACE code. Mention potential impurities of each source
Zakkour and Cook	From sources with more than 80% CO ₂ , they classified according to the level of industrial activity
Fennel et al	Classify with CO ₂ partial pressure according to the industrial and power generation sector and the cost of purification
Jin et al	Purity range, four categories
Centre for low carbon future	Purity range, four categories
Angelis-Dimakis and Castillo	Purity range, three categories

While there have been many attempts to standardize sources classification based on purity and other criteria, there are no national or international unified classification. The overlapping of the proposed categories and the inconsistencies among researchers makes the purpose of source characterization for CCUS an unclear improvement.

2.2.2 Capture & Purification

Carbon dioxide is captured from sources such as power plants, oil refineries, biogas sweetening, ammonia production plants, ethylene oxide, cement, iron and steel industry can be used as source of CO₂ rich emissions, being power plants the responsible of most of the anthropogenic CO₂ production. The aim of this stage is to leave CO₂ at high concentration, cleaning it from other large contaminants, depending on the source. There are three conceptual paths for capture the carbon emissions: *Post-conversion* carbon capture, *Pre-conversion* carbon capture and *Oxyfuel combustion* carbon capture (Cuellar-Franca R. , 2015).

Post-conversion carbon capture consists in separating CO₂ after combustion or digestion of waste water sludge. The most used technique within the post-conversion capture is chemical absorption using monoethanolamine (MEA).

Pre-conversion carbon capture is the technique of separating carbon from streams containing CO₂ as an undesirable product or impurity from conversion reactions, very common in Natural Gas Reforming where the produced synthesis gas (syngas) reacts with H₂ through a H₂O gas shift reaction to produce a mixture of CO₂ and H₂, it is also the case of ammonia production plants.

Oxy-fuel combustion carbon capture consist in performing the combustion using pure oxygen as an oxidant media, separating it from air. This is essentially the same as *Post-conversion* carbon capture, but in this situation, many impurities can be avoided due to oxygen being pure, without the impurities contained in the usual oxidant media, which is air, containing only around 21% of oxygen (Cuellar-Franca R. , 2015).

Another criterion for classification was established by (Spigarelli, 2013), who categorized capture technologies according to the CO₂ partial pressure, classified as high, medium and low partial pressure technologies. (Prier, 2018) proposed a very useful method of classification for carbon capture techniques that match with the purification methods. The categories proposed are “*General gas conditioning and removal of common impurities NO_x, SO_x, dust and H₂O*”, “*Absorption with chemical solvents or combustion using pure oxygen*” and “*absorption with physical solvents*”. According to this classification, done with information provided by several researcher’s work (Cuellar-Franca R. , 2015), (IPPC, working group III, 2015), (Patricio, 2017), (Porter, 2015), (European technology platform for zero emission fossil fuel power plants, 2011), the scenario up to 2018 was described by (Prier, 2018) are summarized in table 4.

Table 4 Source classification: "Matching carbon sources and carbon separation technologies" (Pieri, 2018)

Capture technique	High CO ₂ % purity	Medium CO ₂ % purity	Low CO ₂ % purity
General Gas Conditioning	Fermentation processes such as Beer (100%) Wine (100%) Bioethanol (100%) Biogas production (99%) Refineries gas sweetening (96-99%)		
Absorption with chemical solvents or combustion using pure oxygen		Iron and steel industries Corex (30%) TGRBF (22-38%) Blast furnace (22%) Lime production Combustion of fuels in lime kilns (24-32%) Cement industries: Cement kilns (22%) Oil refineries (8-24%)	Pulp industry Recovery boiler (13%) Paper industry Energy production (13%) Power generation Oil fired boilers Coal fired boilers (11%) Natural gas fired boilers (7-10%) Incineration of waste (10%) Glass industries (10%) Aluminium production (3-10%) Polyethylene production Cracker furnaces (5%) Gas turbines (3-4%) Carbon black manufacturing (2-5%) Brick dryers and kilns (1.5-4)%
Absorption with physical solvents	Hydrogen production (100%) Ammonia production Haber-Bosch process (30-99%) Ethylene oxide production (30-100%) Natural gas processing (2-70%)	Integrated gasification combined cycles (12-14%)	

Regarding the technologies used for purification. (Cuellar-Franca R. , 2015) concluded that from all the CCUS options studied, considering only sequestration option and as source power-plants, carbon contamination can be reduced between 63-82% (referred to mass production), with the greatest reductions achieved by *Oxyfuel Combustion* with pulverised coal and Integrated Gasification Combined

Cycle (IGCC) plants, the smaller reduction was by post-combustion capture in combined cycle gas turbine (CCGT).

2.2.3 CO₂ rich mixture transport

After the capture, purification must be performed, which includes water removal and compression that sets the gas stream up for transport in dense phase for a later sequestration or utilization (Abbas, 2013), (Aspelund, 2007), (Lee, 2009). This stage is crucial due to the consequences that a poor cleaning may cause on later stages of a CCUS facility. These consequences include corrosion, poisoning of the soils, risk of explosion, to name a few. *Wetenhall, B.* (Wetenhall, 2014) and *Ivan, S.* (Ivan, 2011) identified and analyzed the effect of impurities in the stream on the equipment during transportation such as corrosion.

These impurities change the physical properties of the CO₂ rich stream being transported such as phase behavior, density and viscosity, which affect transportation conditions (p & T) and design parameters. Their work shows that impurities in the mixture increases the required pressure (mixture critical pressure) to keep the mixture at supercritical phase ($T_c > 31.1^\circ\text{C}$, $P_c > 73.8$ bar for pure CO₂). It is also mentioned that the presence of pollutants such as H₂S, SO₂, and NO₂ increase viscosity while decreasing density, compromising pipeline capacity. Not only the fluid properties change, also the presence of H₂S, SO₃ and NO₂, but mainly H₂O cause corrosion.

To transport CO₂ to sequestration or use sites, first it must be compressed to reduce its volume. At dense conditions CO₂ occupies around 0,2% of the volume of the gas at standard temperature and pressure. Several million tonnes per year of CO₂ are transported nowadays around the world by different techniques, depending on the geographical location and the end goal of the transported CO₂. The most common methods for transporting are by pipeline, by ship, by road tanker, railroad tanker (Skovholt, 1993).

The preferred method for CO₂ rich mixture transportation is through pipelines in dense or supercritical phase (Carter, 2010). Impurity levels on the stream are not well specified, but it is known that if H₂O content on the CO₂-rich mixture exceeds the solubility limit, a second aqueous phase will be observed. The aqueous phase will condense on any surface able for nucleation, which will be certainly the inner walls of the pipelines. Depending on the source, flue gas from power plants can contain between 5-15% H₂O (Ivan, 2011). An examples of typical contamination content from fumes of a coal-fired power plant are shown in table 5 (Lee J. , 2009).

Table 5 Scenarios for corrosion on dense phase transportation through pipelines (Lee J. , 2009)

Situation	Description	Contaminants level
1	No contaminant control.	SO ₂ 0.6-4.4 wt%, SO ₃ 42-579 ppmv, NO ₂ 24-111 ppm, HCl 36-835 ppmv, Hg ²⁺ 23-261 ppmv
2	SO ₂ control by wet flue gas desulfurization.	SO ₂ 337-2403 ppmv, SO ₃ 21-302 ppmv, NO ₂ 18-87 ppm, HCl 2-44, Hg ²⁺ 2-27 ppmv
3	NO _x control by low NO _x burner/Selective catalytic reduction.	SO ₂ 0.6-4.4 wt%, SO ₃ 42-579 ppmv, NO ₂ 10-44 ppm, HCl 36-835 ppmv,
4	NO _x control by low NO _x burner/Selective catalytic reduction plus SO ₂ control by a wet flue gas desulfurization scrubber	SO ₂ 337-2403 ppmv, SO ₃ 21-302 ppmv, NO ₂ 7-35 ppm, HCl 2-44 ppmv, Hg ²⁺ 2-27 ppmv
5	Adding to case 4 a CO ₂ trap.	SO ₂ 34-135 ppmw, SO ₃ <21-<302 ppmw, NO ₂ <7-<35 ppmw, HCl <2-<44 ppmw, Hg ²⁺ <2-<27 ppbw

Pipeline transportation, which is the most used (Gale, 2004), takes place in the dense phase, which can be liquid or supercritical state. Usual pressures are above 5 and 8 MPa respectively, temperatures must be low for CO₂ rich mixtures to assure a low mixture molar volume, being the most used around 0-5°C, depending on the purity of the stream (Ivan, 2011). Transportation through pipelines is the most used method for transporting CO₂ rich mixtures, just in the USA for EOR, the total length used for transporting CO₂ through pipelines reach around 5000 km (Gale, 2004). The quality of the gas stream depends on pollutant control measures at the carbon source emission site and by the gas conditioning before the pipelines. Pipelines for EOR had been used under very restrictive specifications on the amount and nature of pollutants presents such as H₂O, H₂S, S compounds and oxygen to name a few (Carter, 2010).

When H_2O is present on the CO_2 stream as impurity, since the solubility of H_2O in CO_2 at transportation conditions is very low, the amount of H_2O will separate and form another fluid phase that will be saturated with CO_2 , reacting and producing carbonic acid (H_2CO_3), with corrosive properties (pH around 3) for most of the steel alloys used for piping manufacture. If temperatures are lower than $0-5^\circ\text{C}$, risk of hydrate formation is also present. Not only water means a problem for pipelines regarding the phase behavior of the mixture, a fundamental aspect of CCUS transport systems is that the prescience of pollutants, such as H_2S , SO_3 and NO_3 will segregate on the H_2O rich phase formed, decreasing pH even further by the formation of H_2SO_4 (sulphuric acid) and HNO_3 (nitric acid) in addition to the already present H_2CO_3 (carbonic acid) (Ayello, 2010). As consequence of the pH decreasing, a significant increment of the corrosion rate on the pipelines steels will occur. Furthermore, Russick *et al* (Russick, 1996) reported no corrosion when transporting pure CO_2 at supercritical conditions through stainless steel (304L and 316) and carbon steel (1018). Corrosion was only observed when traces of H_2O contaminated the CO_2 stream. In figure 10 is possible to appreciate the changes in the equilibria of the species resulting from the reaction of CO_2 and H_2O . This means that pH also affects the solubility of CO_2 , this shows the importance of a proper cleaning before transportations according to the particularities of each project.

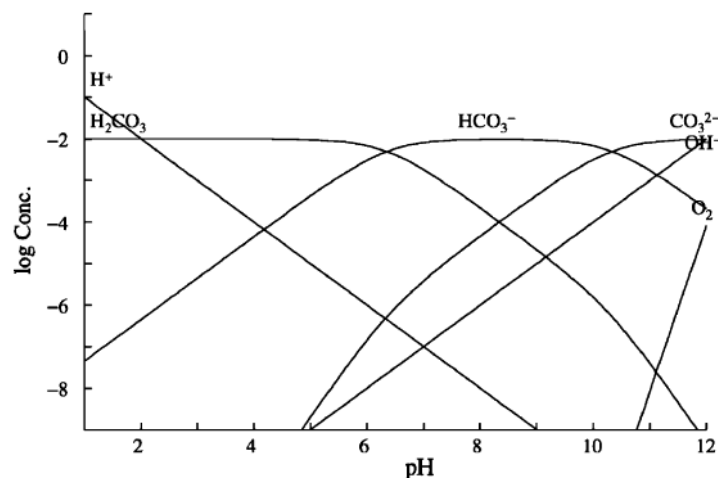
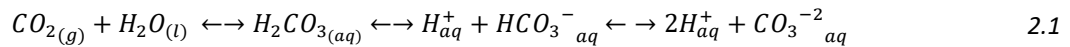


Figure 10 The concentration of various species out of $\text{H}_2\text{O}+\text{CO}_2$ equilibria. (Ivan, 2011)

Regarding pH changes, (Choi, 2010) found that the aqueous phase in equilibria with CO₂-rich phase has a pH between 3.1 and 3.2 in the pressure range 5-15 MPa and temperatures range of 32-42°C (relevant to sequestration conditions). To have some perspective of the influence of contaminant on the pH, 1 grHCl/kgCO₂ would drop the pH to -4.1 while 1 grHNO₃/kgCO₂ would result on a pH of -3.1 (Ayello, 2010), even though the concentration just mentioned are higher than the ones present on usual contaminants in the streams reported by (Lee J. , 2009), it reflects the effects of impurities over pH values.

(Choi, 2010) also mentioned that corrosion rates of steel can vary from 0.2 mm/year to 20 mm/year as the CO₂ goes from high purity to H₂O saturated CO₂ stream. At the same time, (Ayello, 2010) reported that 3.6x10⁻⁵ grHCl/kgCO₂ and presence of H₂O at a concentration of 1000 ppm would result into a corrosion rate of 5.6 mm/year, which is around 20 times faster compared with a high purity CO₂ stream. There are three main reactions that can happen in the presence of a H₂O rich phase (Ivan, 2011) that influence corrosion:

- Absorption of gaseous CO₂ and acidification of the condense water phase over the pipe inner walls due to carbonic acid formation and further dissociation:



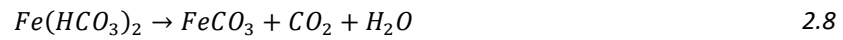
- After the acidification of the condense water, further cathodic reaction could take place by direct reduction of hydrogen ions or through carbonate:



- The anodic reaction happens through the oxidation of iron from the pipeline wall:



- Once these different species are found in the pipeline, oxides may form either by one stage reaction with carbonates, or via a two-stage reaction with bicarbonates:



All these reactions are consequence of a low pH value over the walls of the pipelines, therefore, transport of CO₂ with small impurities (if phase behavior is not under consideration and proper control) condensation can significantly increase the corrosion rates, decreasing the life span of the pipelines, increasing operational costs (Ivan, 2011).

According to (Cole, 2012) there are 4 categories of classification or regimes with different risk of corrosion for dense phase CO₂ streams transportation.

- 1) Very low contaminant levels and extremely low water content.
- 2) Low contaminant levels and water content below the solubility content.
- 3) Low contaminant levels and water content above the solubility content.
- 4) Moderate contaminant levels and water content above the solubility limit.

Regime (1) is typical of CO₂ transport in EOR in the USA (Carter L. , 2010) and would prevail in other places if CO₂ were extracted using MEA in a plant with strong pollution control measures and gas conditioning to lower the H₂O content below the maximum solubility, depending on temperature and pressure. Regime (2) would occur if gas conditioning was limited or there was a limited source of H₂O into the pipeline. Regime (3) could occur in the absence of gas conditioning, or with additional sources of H₂O, while regime (4) would occur without gas conditioning and limited cleaning of the gas mixture at the sources. (Cole, 2012).

The purity that needs to be achieved mainly depends on the technical constraints of the equipment involved and with health and safety considerations. “*Dynamis*” project, presented recommendations for the impurity content level of gas streams containing mainly CO₂ for CCUS, primarily from a transport point of view and with less detail, for sequestration (De Visser, 2008). The study examined oxyfuel, pre and post-combustion-electricity-production processes utilising different types of coal and Natural Gas Combined Cycle Gas Turbines to include a wide range of usual pollutants (Global CCS institute, 2018). After considering the safety and toxicity of impurities, avoidance of free water formation, avoidance of hydrate formation, avoidance of corrosion, reduction of CO₂ volume, a list of recommendations for the concentration of various impurities was summarized by (De Visser, 2008). Based on that report, the maximum concentration of some of the key impurities are H₂O (500 ppm), H₂S (200 ppm), SO_x (100 ppm), NO_x (100 ppm), and the minimum concentration of CO₂ is 95.5%.

There are many ways to avoid the corrosion such as improved and more resistant metals alloys (which increase the cost of pipelines); addition of reducing chemicals agents is also an option (which would cause contamination of the reservoir or interfere to later uses). Another way avoid corrosion is to know under which pressure and temperature conditions different phase behavior of model systems for CO₂ rich mixtures changes and to know how drops nucleate over different metal alloys and different atmospheres.

2.2.4 Utilization & Sequestration

To make a significant contribution to reduce atmospheric greenhouse gases, the amount of CO₂ that would be needed to store or use would have to be significant compared to the amount of CO₂ currently produced, in the order of gigatons of CO₂ per year. The only potential Sequestration sites with the capacity for such quantities are natural reservoirs. Reservoir are natural underground formations that allows the capture of CO₂ through many mechanisms, such chemical reaction, solubility and trapping mainly. The capacity of European formations was first assessed by (Holloway, 1997) and the deep ocean sequestration by (Cole C. , 1993).

The first proposal of sequestration was done by Marchetti, C. *et al* (Marchetti, 1977) suggesting the injection of CO₂ into the ocean, with the aim that it would be carried out into deep water, where it was thought, it would remain for hundreds of years through phase equilibria with the marine system. Carbon dioxide underground injection would involve similar technology to the ones employed in oil and gas industry for the extraction and production of hydrocarbons, it means to drill into geological formations and then CO₂ would be injected in the same way as CO₂ has been injected for enhanced oil recovery since 1970 (Blunt, 1993), (Stevens, 2000). An extension of this idea involves injection of CO₂ into saline formations (Koide, 1992) or into an unamenable coal seams as mention (Gunter, 1997). Carbon injection into coal seams can also be used for the displacement of methane, which could be used as a fuel, reducing operation costs, further promoting its use.

Sequestration options can be classified as: Underground, Ocean and Mineral Sequestration. Underground Sequestration, also known as geological Sequestration, consist into the injection of the CO₂ into geological formations filled with a fluid-phase (gas, liquid or supercritical) where CO₂ can form phase equilibrium, solubilize or stay as a differentiated phase for long periods of time (Cuellar-Franca R. , 2015), the success of this technique depends on the solubility and the effective diffusion rates of CO₂ into the fluid and the rocks porosity that forms the diffusion barrier. Examples of Geological formations for

sequestration are depleted oil and gas reservoirs, deep saline aquifers and coal bed formation. The depths of this reservoir may vary widely, but usually within the range of 800 to 1000 m (Metz, 2005). Pressure and temperature are vital parameters to consider for Sequestration conditions since considerable amount of transport and thermodynamic properties are strong functions of these two parameters. Storing CO₂ as a supercritical fluid improves the sequestration capacity of the chosen reservoir by increasing the diffusion resistance through the rocks pores due to a higher viscosity and density compared with the gas state, resulting in longer Sequestration times (Wei-Wei, 2014). The goal in this stage is get a very low effective diffusion coefficient, high viscosity and high solubility. To set proper conditions to achieve the properties described, the depth of the aquifer must be adequately chosen to get suitable pressure and temperature.

Deep saline aquifer formation is also an attractive option for Sequestration with a considerable Sequestration capacity, estimated between 700-900 Giga MtCO₂ (Metz, 2005). The main concerns with CO₂ Sequestration are its possible leaks and the related damage that concentrated CO₂ stream would cause if it escapes to the environment.

Carbon dioxide utilization constitute the main objective of the mitigation methods creating a more circular process design, this allows not just a reduction on carbon emissions, but also gives value to a current waste that can diminish operation cost and increasing the value of these technologies. Depending on the final porpouse, there are four categories defined: *Direct use*, *Mineral carbonation*, *Fuel production* and *Chemical production*.

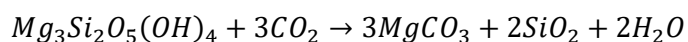
When CO₂ is used without chemical modifications is called *direct use*. Some direct applications are found on the food industry, cooling units, inert gas for food preserving, like the ones used in modified atmosphere packing technologies. The specifications in these direct applications are such that purity must be higher than 99%, moisture content less than 52 vppm, CO less than 10 vppm, total hydrocarbons less than 50 vppm, oil less than 10 ppmw, and pass a test for acidity and red substances (Girdon, 2006). In food applications, CO₂ can be used for carbonated drink and in many applications related to extraction of

valuable or undesirable compounds through supercritical extraction. An example of this is the decaffeination process of coffee. An important user of CO₂ is the metallurgic sector, where CO₂ is used for cooling parts for shrink fitting, hardening of sand cores, and moulds, as a shrouding gas to prevent oxidation in a welding process, or in a minority of basic oxygen furnaces as a bottom stirring agent or dust suppression. In the paper industry, CO₂ is used to reduce pH during pulp cleaning in the paper industry. Another usual and interesting use of CO₂ is the use of it in greenhouse to create an enhanced atmosphere for plant growing.

For fuels production, a variety of fuels can be produced using CO₂ stream as feedstock. Methanol, for example, can be produced out of CO₂ and H₂, the latter one coming from water electrolysis. Then CO₂ and H₂ can be compressed (Linde, 2018). Formic Acid (CH₂O₂) can be produced by electrochemical reduction of CO₂, by combining concentrated CO₂ and H₂O. CO₂ also can be used as an external carbon source in algae cultivation, which can then be used to produce biodiesel or a variety of oils. The process Fischer-Tropsch can use CO₂ feedstock to produce fuels (Staynberg, 2006).

Chemical production is one of the biggest industries worldwide and from the chemical production, organic chemistry is crucial for other sub industries, such as polymer and pharmaceutical. For organic chemistry, the basic block molecule is carbon, followed by hydrogen and oxygen. That is why the use of CO₂ as carbon source could promote CCU in production of chemicals as organic acids, alcohols, esters, and sugars.

Mineral carbonation or mineral sequestration involves reacting CO₂ with metal oxides (magnesium and calcium), to form carbonates. This option can be considered as both Sequestration and utilisation option due to the possibility of later mining of the minerals formed as raw materials. Similarly, EOR and ECBM (Enhanced Coal Bed Methane) recovery can be considered sequestration and utilization technique. Direct carbonation takes place under high pressure conditions in either dry or aqueous media (Huijgen, 2007). An example of this reactions is the carbonation reaction at 375°C and a CO₂ partial pressure of 20 atm:



2.9

For mineral carbonation, purity of CO₂ is not essential, in consequence, this option is suitable for capture and purification methods that are not very effective or can be even omitted if the source of CO₂ does not include toxic materials that could leak to the surface system.

The average impact of different methods of capture are evident, for a pulverized coal power plant, without CCUS is 876 kgCO₂eq/MWh, while it can be reduced to 203 kgCO₂eq/MWh if post conversion, captured by MEA is applied, this amount decreases to 154 kgCO₂eq/MWh if oxyfuel combustion is used (Cuellar-Franca R. , 2015). Considering the option of utilization, the amount of emissions varies widely depending on the on the utilization option, Mineral Carbonation can reduce emissions from 4 to 48% compared with no utilization. Application of CCUS in the chemical industry, specifically from the production of DMC (dimethyl carbonate) reduces emissions 4.3 times if it is compared with the standard way of production. EOR has Carbon emission reduction of 2.3 times lower compared to a direct CO₂ discharge to the atmosphere. Is then possible to stablish that Sequestration has significantly lower CO₂ emission reduction than utilization options. (Cuellar-Franca R. , 2015). According to different authors, the potential of carbon emission reduction is considerable. In figure 11 is possible to appreciate that the potential of reduction just by capturing CO₂ from the fumes for further use can decrease the amount of CO₂ to less than half of the one without extraction.

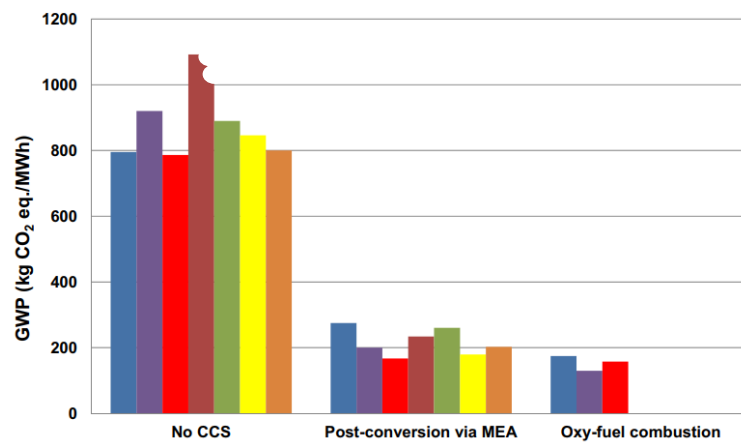


Figure 11 Production of CO₂ without carbon capture and sequestration and with two technologies of CCS (Cuellar-Franca R. , 2015)

CHAPTER 3

CO₂+H₂O binary equilibria

The CO₂+H₂O system is of great interest around scientific and engineering community and present in oceans, atmosphere and soils. For geological studies, this system is of great interest for hydrothermal processes, representing an initial model to compare and study before more complex ones (Spycher, 2003). Compounds present at the reservoir and the ones present on the CO₂-rich mixture to be injected usually contains acid gases that cause corrosion problems when transporting them and could cause undesirables phase behavior and reactions at the reservoir. Therefore, is important to make efforts to reduce their concentration or if it is feasible, removed them completely (Valtza, 2004). The injection of CO₂ to be Sequestration underground at reservoir conditions requires good knowledge and reliable data of solubility of CO₂ into aqueous phase as an initial model system for a first approach to more complex models. There is a lack of experimental data for the [CO₂+H₂O] system available for public use, and even more for multicomponent mixtures of interest for related uses of CO₂ and their systems (EOR as an example of CCUS) such as [CO₂+H₂O+Hydrocarbons], [CO₂+Brine+Hydrocarbons], [CO₂+Contaminants+H₂O], and others. Many of the experimental data published are for low pressures (bellow 10 MPa) and most of them does not have compositional analysis. There have been many experimental studies, made by the private sector, of this system and some literature reviews, but still uncertainty regarding the results is considerable, especially at elevated temperature and pressures, resulting on large discrepancies (Shu-Xin, 2012). Some literature shows some agreement between works of certain constants of this system, such as the Henry's constant in temperatures within (273-353) K. Data reviewed by (Crovetto, 1992). shows that Henrys constant could be estimated with relative uncertainty of 1% and between (353-600) K could be estimated with (5–10) % uncertainty.

3.1 Binary equilibria classification and behavior

Scott and Konynenburg in 1968, using the Van der Waals Equation of State (VdW-EoS, 1873, eq. 3.1) proposed five fluid-fluid phase binary systems types to develop a classification method. The type number six was later added to classify those systems that VdW-EoS was not able to predict. Van der Waals equation of state takes the following form:

$$p = \frac{RT}{\tilde{V} - b_m} - \frac{a_m}{\tilde{V}^2} \quad 3.1$$

Where p is the pressure of the system, $\tilde{V}$ is the molar volume, b_m is the co-volume (space not available for the molecules to move) and a_m is the energetic factor, R is the molar gas constant and T is the absolute temperature. After the application of VdW-EoS to pure compounds, the parameters a_m and b_m were adapted as a function of the pure component parameters (a , b) and the molar composition of the mixture (x_1 , x_2) to predict binary mixture parameters. For a binary mixture, this is:

$$a_m = x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22} \quad 3.2$$

$$b_m = x_1^2 b_{11} + 2x_1 x_2 b_{12} + x_2^2 b_{22} \quad 3.3$$

The sub index 11 and 22 in eq 3.2 and 3.3. denotes the pure compound parameter and the sub index 12 denotes an hypothetical hybrid molecule that represent the contribution of the mixing on the pure compound properties. This consideration comes from the fact that mixing substances generates changes on the behavior of each compounds due to interaction between them, resulting on a phase

behavior that differs to the linear combination of the pure compound properties. For chain molecules and not spherical, the original form of b_m can be reduced to:

$$b_m = x_1 b_{11} + x_2 b_{22} \quad 3.4$$

From eq 3.1 chemical potential can be calculated and describe the phase equilibria. The advantages of using VdW-EoS is that it is simple and gives qualitatively good/reasonable results over the entire range of temperature and pressures, including an estimation of the critical points (Scott, 1970).

The category system proposed by Scott and Konynenburg was based on the presence or absence of three phase lines, presence or absence of azeotrope lines and by the critical lines connect with these. Critical lines may end in various ways, at a one-component gas-liquid critical point C_1 (T_{1c} , p_{1c} , $x_2=0$) or C_2 (T_{2c} , p_{2c} , $x_2=1$), at the limiting upper critical solution point C_m (T_m , $p = \text{infinity}$, x_m) in a close-packed ($\tilde{V}$ approximating b_m) system, at the end of a three-phase line (L_1 , L_2 , G) with an upper or lower critical end point (UCEP or LCEP). Azeotrope lines, if present, end tangentially on critical lines. Types were described as follow:

- Type I: One critical line (G-L), C_1 or C_2 , (CO_2 +n-Buthane).
- Type I-A: Same as I, with the addition of a negative azeotrope,
- Type II: Two critical lines, C_1 to C_2 (G-L), C_m to UCEP (L-L). (CO_2 +n-Octane)
- Type II-A: Same as II, with the addition of a positive azeotrope.
- Type III: Two critical lines, C_1 to UCEP (G-L), C_m to C_2 (L-L to G-L)., (CO_2 +Squalane)
- Type III-HA: Same as III, except that the three-phase line lies at lower pressure than either pure component, producing a “heteroazeotrope” type diagram.
- Type IV: Three critical lines, C_1 to UCEP (essentially G-L), LCEP to C_2 (L-L) to (G-L), C_m to UCEP (L-L), (CO_2 +Nitrobenzene)

- Type V: two critical lines, C_1 to UCEP (essentially G-L), LCEP to C_2 (L-L to G-L) (Ethane+Ethanol, $C_2H_6 + C_2H_4OH$)
- Type V-A: Same as V with addition of a negative azeotrope.
- Type VI: All that are not predicted by this equation, like $CO_2 + \text{Naphthalene}$.

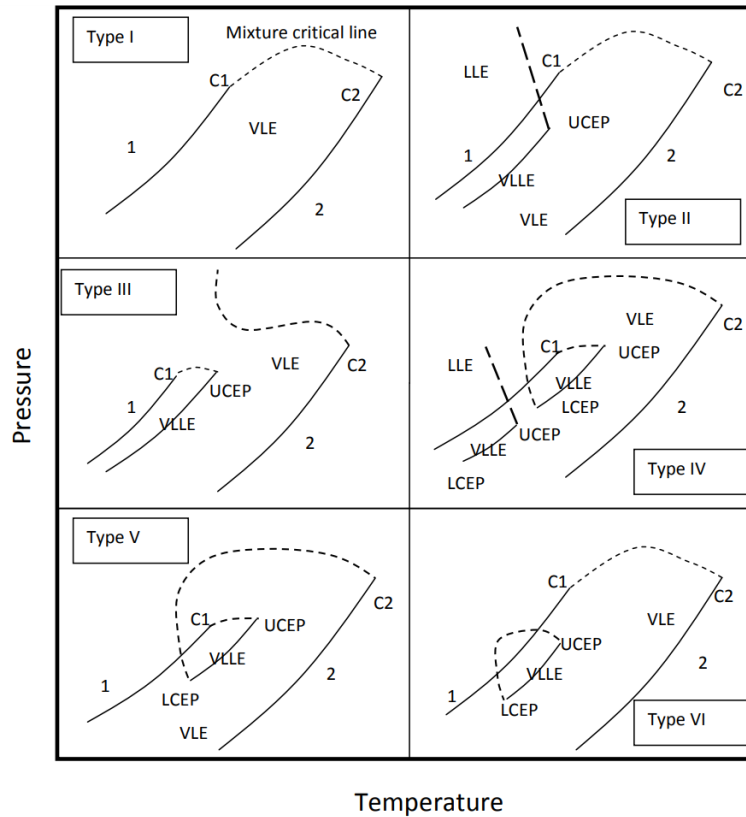


Figure 12 Phase diagram behavior. (Coquelet, 2012)

The type of system showed by the CO_2 - H_2O binary equilibria is type III binary mixture (Scott, 1980) (Muller, 1983) with a discontinuous Vapor-Liquid critical curve, a wide region of liquid-liquid coexistence below the critical temperature of CO_2 and very limited mutual solubility in the region of two and three phase equilibria (Shu-Xin, 2012). (Valtza, 2004) also mention a liquid-liquid equilibria at pressures close to CO_2 vapor pressure below his critical temperature. (Shu-Xin, 2012) confirms the type III behaviour according to the same classification. They also confirmed the existence of a Vapor-Liquid-Liquid (VL_1L_2)

three-phase line equilibria, which lies very close to the saturated vapor pressure of pure CO₂ around 298.15 K. Few liquid-liquid equilibria points were measured at 298.15 K. For higher temperatures, they found no other kind of equilibria (LL or VL₁L₂) of coexisting phases than Vapor-Liquid. Good understanding regarding CO₂+H₂O system is even being used to describe the behavior of water systems in Mars by Longhi J. (2006) (Longhi, 2006) Annex 7.1.

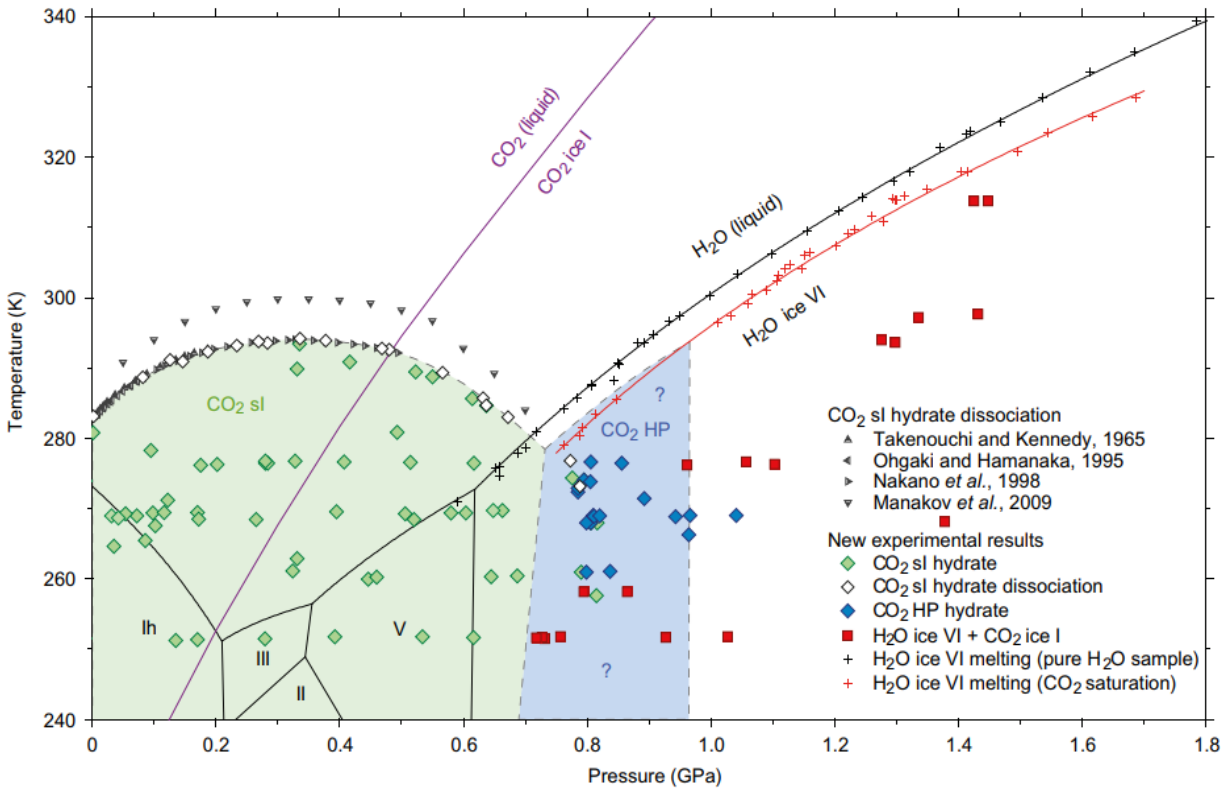


Figure 13 Phase equilibria in the H₂O-CO₂ system between 250–330 K and 0–1.7 GPa: Stability of the CO₂ hydrates and H₂O-ice VI at CO₂ saturation (Bollengier, 2013)

CHAPTER 4

4.1 Hypothesis

Description of the $\text{CO}_2+\text{H}_2\text{O}$ system becomes necessary in order to boost scientific knowledge and technology improvements that allows to move forward in the direction of a more massive and economically sustainable ways to handle CO_2 . The data available regarding transport and thermodynamic properties of systems of interest seems to be scarce and it limits the development of CCUS.

4.1.1 Objectives

4.1.1.1 Main objective

Contribute to the available data regarding transport and thermodynamic behavior of systems containing $\text{H}_2\text{O}+\text{CO}_2$ at conditions relevant to Sequestration and transporting condition to support CCUS technologies development.

4.1.1.2 Secondary objective

- Evaluate current T and p conditions for transport and sequestration stages on a CCUS process chain are suitable for characteristic high- CO_2 sources.
- Evaluate the impact of contaminants over the phase boundaries of characteristic mixtures.
- Estimate according to different models the mutual diffusivity of CO_2 and H_2O .
- Analyze the impact of convection over diffusion process.

4.2 Properties on the CO₂+H₂O system

The increasing human population demands more goods every year to sustain life quality. All the requirements demanded to sustain it needs bigger and faster industrial production. To meet these demands, power must be supply. The cheapest and available in the required amount is mainly coal and other high carbon fuels. As consequence of high carbon fuel burning, CO₂ is produced at a faster rate than the earth's natural carbon cycle can take from the atmosphere. This produce a bottleneck, increasing the atmospheric CO₂ concentration.

Carbon dioxide, as a few other gases in minor quantity, has the property of reflecting infrared radiation as heat, therefore, an increasing concentration of this gases at atmospheric level produce an increase in the global average temperature, causing environmental problems. In order to mitigate global warming, several options have been weighted to handle carbon dioxide emission, were the power sector due to high carbon fuel burning, is the main contributor. Some of the measure to mitigate this emission are:

- Change to alternative fuels
- More green energies
- Reduce power demands
- Carbon capture, utilization and sequestration

Among the alternatives, CCUS seems to be the one most promising and realistic concepts to an effective reduction of atmospheric CO₂. This technology proposes the separation of CO₂ from the main stream, followed by purification of the CO₂ rich mixture, transport and sequestration in reservoirs or use it as raw material. CCUS face the problem of coming from a wide range of processes and it causes that the composition of the CO₂ rich mixture vary. Water and other species may be present, causing corrosion and other undesirable effects. Not only technical and practical matters means difficulties to CCUS technologies, also regarding the available knowledge and experience (*know how*) represents challenges to a proper

implementation. $\text{CO}_2+\text{H}_2\text{O}$ system is of interest among many companies that work with oil, cement, power, etc. Much of the research done about remains as industrial knowledge and it is not share with the community, resulting in the lack of free data to improve and spread CCUS use.

Given the difficult access to data regarding $\text{CO}_2+\text{H}_2\text{O}$ behavior, leading to a successful CCUS implementation, a development of methods and techniques to fill the gap in data available becomes not only desire, but needed. Diffusion coefficient, phase boundaries and interfacial tension are measured, reviewed and compared with the few published data available. Furthermore, different models are applied to calculate diffusion coefficients. A discussion regarding the different diffusional processes and influences on the system are included.

4.2.1 Phase behavior of CO₂ + impurities

Good understanding of phase equilibria is necessary in many industrial and non-industrial fields, it allows to design and optimize chemical processes such as CCUS, hydrate formation, application to ionic liquids, and many separation processes. When pressure change at constant temperature, phase transition may occur, which change the properties of the phases present, it happens regardless if it is a pure compound or a mixture. If it is a mixture, a different chemical composition between phases will occur as consequence of the phase's coexistence. Since the general aim of this work is to evaluate suitable conditions of p and T for transport and Sequestration stages in a CCUS based process and contribute to the data available up to this date, measurement of phase behavior becomes necessary. It is also one specific aim of this work to understand the effects of impurities over the pure CO₂ phase behavior. Three CO₂ rich mixtures phase boundaries were measured between [255-300] K and pressures of [2-8] MPa, being the higher temperature and pressure around the critical point of pure CO₂. Now days, there are many methods and techniques available for experimental measurements of phase equilibria boundaries. The selection of an appropriate method depends on the interest of the researchers and advantages and disadvantages must be considered before selecting one method.

4.2.1.1 Analytical methods

Analytical methods consider the determination of composition of the existing phases at the equilibrium. This can be done by sampling, in situ or extracting from each phase for a later analysis. The main challenge is to accurately estimate the composition of each phase. Analytical methods had the

advantage of giving information on tie lines for binary and multicomponent mixtures and is particularly suitable for systems where the phase boundaries depend strongly on composition. The main disadvantage of this method lies on the method of analysis, since taking samples change the equilibria inside the cell, changing the overall composition of the mixture and stabilization time must be considered. There are many analytical methods, based on the classification done by (Dohn, 2012), they are listed in table 6:

Table 6 Analytical methods classification. Extracted and adapted from Dohn et al (2012)

Method		Advantages	Disadvantages
Analytical Isothermal	Stirring	Effective mixing, fast equilibration	Temperature gradients, dead corners
	Rocking	Simple mixing, good if presence of hydrate is expected	Connecting pipette must be movable, cause vibration that leads to material fatigue/damage
	Vapor or Liquid-phase recirculation	Sampling volume can be filled isobarically, density measurement is possible in recirculation loop	Additional Pumps, partial condensation of recirculated (saturated) phases
	Capillary sampling	Place of sampling within cell can be chosen	Partial condensation due to pressure loss in capillary (Joule-Thompson effect)
	Valve sampling	Small samples possible, direct coupling to analysis	Less flexible concerning analytical methods
	Blocking off a large sampling volume	Large samples possible	Re-equilibration for each sample needed
	In situ sampling	No valve needed	Complicated handling, careful expansion is crucial
	Material loss analysis	Solubilities in very low-volatile substances (ideal for polymers)	Extrapolation of raw data results in poor accuracy, difficult for multicomponent systems
Analytical Isobaric		Recirculation without pumps, ebulliometer-like heat pipe	Useful for low pressure only, almost never used.
Analytical Isobaric-Isothermal method	Continuous-flow	Short residence time in apparatus, thermolabile substances	Short time available for equilibration, large amount of chemicals needed
	Semi-flow	Suitable for solubilities of solids in gases or gases in liquids.	Difficult when used with multicomponent systems
	Chromatographic	Allow measurement of diffusivities and infinite dilution partition coefficient, like in fluid and ionic liquid or polymers	It has limited applicability, interaction with substrate of stationary phase possible
Method without sampling	Spectroscopic	Fast analysis, suitable for reacting systems	Time-consuming calibration and signal evaluation of spectra
	Gravimetric	Low solubilities and diffusivities of volatiles in polymers or ionic liquids measurements are possible	Buoyancy due to swelling of sample needs correction, expensive equipment
	Other	Particular application	No chance to share experience with other researcher

4.2.1.2 Synthetic methods:

Methods based on a mixture of a known and precise composition for a later observation of the phase behavior as function of pressure and temperature are denominated Synthetic methods. For this method no sampling is required, succeeding when analytical methods fail. An example of sampling difficulties is when the densities of the phases are similar, like near critical point or for separation of the same phase *e.g.* L-L equilibria or V-V equilibria. The difficulty of synthetic methods is related to the preparation of the mixture. All the technical equipment needed for the analysis of the samples are not necessary, but all the apparatus related with the preparation of the mixture are needed instead. Another disadvantage is that it gives less information for multicomponent mixtures, since phase composition analysis is not possible. This method is suitable for very high pressure and temperature, being useful at extreme conditions and to simulate geological and astrophysical environment. Examples of this are the diamond-anvil cell, which resist up to 135 GPa (app. $1.35 \cdot 10^4$ atm) described by (Cohen-Adad, 2001). A rapid description of the most used synthetic methods are listed and described in table 7 below, based on (Dohrn, 2012)

Table 7 Synthetic methods with phase transition. Dohrn et al (2012)

Method with phase transition	Advantages	Disadvantages
Synthetic-visual method	Visual observation allows to detect other phenomena, such as other phases and foam formation.	Highly dependant on the experience and ability of the observer
Synthetic non-visual method	Applicable for systems that does not allow direct observation, such porous media, strong foam formation.	Requieres technical equioment for detection of phase transition

In particular, the method used in this work is a synthetic static visual method (no phase composition analysis, no stirring or recirculation with a visual detection of phase transition), since the composition of the phases is known, the interest is on the phase boundaries and how they vary according to the contaminants present. This method is suitable for VLE determination and more complex systems,

such as solid-liquid equilibria, critical curve of mixture, gas hydrate formation, cloud-point determination or phase equilibria in polymer-solvent systems.

4.2.2 Material and Methods

Experimental set up

Apparatus:

The apparatus (figure 14) consists on a high-pressure view cell equipped with a sapphire window (model PEVC-100, volume: 50 mL, max. pressure: 180 bar, max. temperature: 120°C) a source of light and an USB monochromatic camera facing one window, design and constructed by *Eurotechnica* GmbH (www.eurotechnica-hd.de), containing cooling fluid (technical degree ethanol) through a coil placed around the view cell, connected to a cooling unit (Julabo®, temperature range: -95°C + 80°C, volume 22 liter). A pressure gauge (max. pressure: 160 bar, accuracy ± 0.16 bar) and a Pt100 (class A: accuracy at 0 °C ± 0.15 °C and at -100 °C ± 0.35 °C) are connected to measure conditions at the view cell.

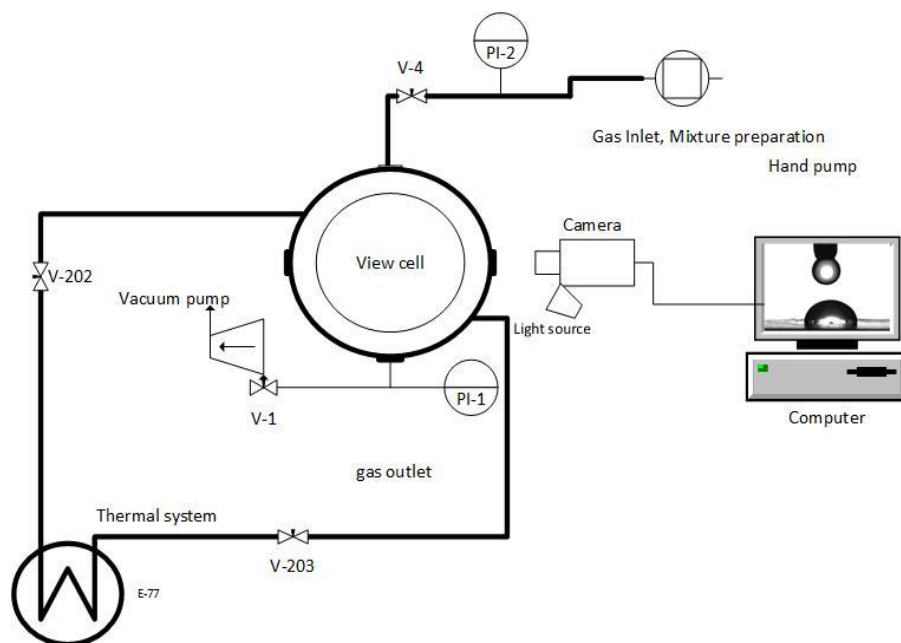


Figure 14 Experimental Set up for Phase boundaries Measurements

Materials

Gas mixtures were prepared by B.A.M. (Bundesanstalt für Materialforschung und -prüfung). Measurement, representing fumes from a power plant in Germany (power plant and the fuel names are under confidentiality agreement) were mixed in order to represent the main composition of the fumes analyzed. The composition of each mixture are listed on tables 8 to 11.

- **Original mixture**

Table 8 Original characteristic fumes samples.

Compounds	Oxidize mixture. mol %	Reduced mixture. mol %
CO ₂	98.56	98.55
N ₂	0.53	0.37
O ₂	0.67	-
Ar	0.22	0.026
NO ₂	0.01	-
SO ₂	0.007	-
CO	0.003	0.04
H ₂	-	1.0
H ₂ S	-	0.005

- **Mixture 1** was prepared as a representation of oxidize mixture:

Table 9 Composition of the oxidize representative mixture fumes

Compound	Mol %
CO ₂	98.797
N ₂	0.5312
O ₂	0.6716

- **Mixture 2** was prepared as a representation of the reduce mixture:

Table 10 Composition of the reduced representative mixture fumes

Compound	Mol %
CO ₂	98.63
N ₂	0.37
H ₂	1.00

- **Mixture 3** was prepared as a better representation of the real mixture. This allows to see the influence of the contaminants as a result of fuel being contaminated or under poor cleaning.

Table 11 Composition of representative of the original mixture.

Compound	Mol %
CO ₂	98.2865
CO	0.00215
H ₂	1.00
H ₂ S	0.005
O ₂	0.67
SO ₂	0.007
NO ₂	0.01

Experimental Procedure

Before pressurizing the equipment with the designated mixture gas, vacuum is pulled out in order to displace air, humidity or any traces of previous measurements. Then, temperature is set as low as possible (measurements were done in a facility at 313 K, low temperatures were difficult to achieve), between 250 K and 270 K. Once the lowest possible temperature is achieved, the gas mixture designated is charged slowly (2-5 bar per minute) to keep temperature constant. T and p were recorded when the first drop is observed (dew point), then, p will be increased slowly until the last bubble is observed, once this happen, p and T will be recorded (bubble point). Then, the process will be performed again to repeat twice the bubble point. T is increased, and the procedure will be repeated up to app. 300 K.

4.2.3 Results and discussion

The operating mode and the functionality of the view-cell were tested by measuring the phase boundaries of the oxidize gas mixture and compared with the phase boundaries calculated by REFPROP NIST V.9.1.. of a mixture consisting on a mixture of 98.797% [$\text{mol} * \text{mol}^{-1}$] CO_2 , 0.53128% [$\text{mol} * \text{mol}^{-1}$] N_2 and 0,67161% [$\text{mol} * \text{mol}^{-1}$] O_2 . Parameters for nitrogen, carbon dioxide and oxygen can be found on (Span R. , 2000), (Span R. , 1996) and (Schmidt, 1985) respectively. Comparison of the oxidize mixture and each measurement can be seeing on figure 16 to 18, all data obtained is provided in Annex 7.2.

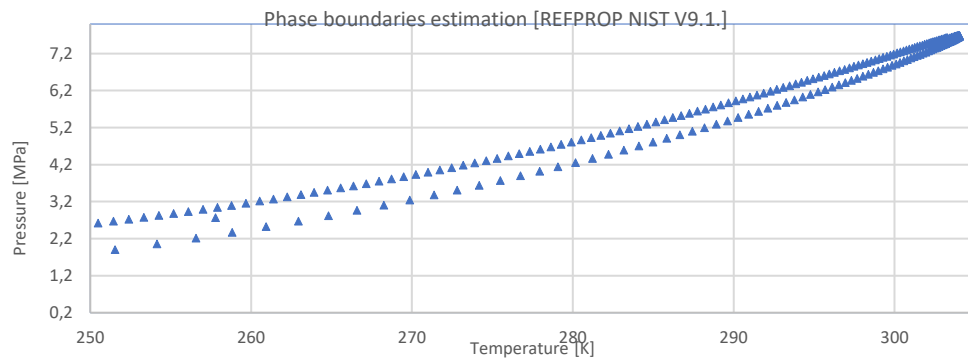


Figure 15 Phase behavior of simulated oxidize mixture, by REFPROP NIST V.9.1.

- **Oxidize mixture**

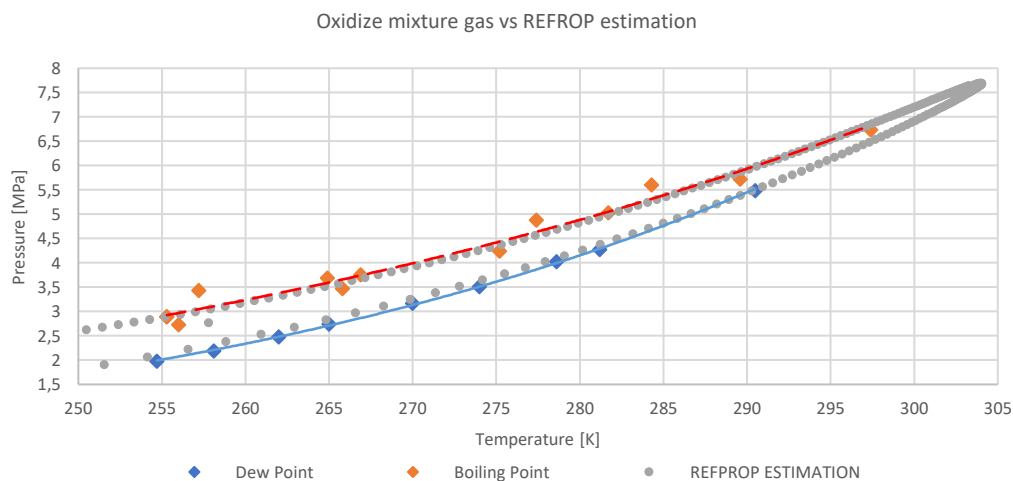


Figure 16 Comparison between simulated oxidize mixture and actual measurements performed

Is possible to appreciate that the simulated oxidize mixture fits the boundaries measured, matching the phase behavior with errors smaller than 5 bars. The expected narrow area between boundaries represent the vapor liquid equilibria, validating that amounts in the order of 1% of contaminants change the behavior of pure CO₂. It is also observed the convergence of the dew and boiling lines to a critical mixture line, that due to the high content of carbon dioxide it looks almost like a point. Discrepancies between simulation and actual data are less than 5 bars at constant T in this system, in consequence, the method used is considered as acceptable, being easy to perform. Regarding transport conditions, oxidize mixture should be at dense condition (supercritical or liquid), being the most used conditions 278 K and pressure over 5 MPa. These values are over the boiling line as it is possible to see in the p-T diagram for the oxidize mixture and it is considered as a safe condition for transport. No combination of p and T on the transportation stage should be under conditions below the boiling line (red line) to avoid condensation. As for Sequestration conditions (313-333 K, and over 8-20 MPa), measurements show a very narrow equilibria over 290 K and 5,5 MPa. This shows that the critical line of the mixture should be near the measurement performed at the highest T and p, and it is supported by the modeling of the mixture that shows a critical mixture point for the given composition at 303 K and 7,6 MPa, very close to the critical point of pure CO₂ (7.39 MPa and 304 K). The critical line estimated for the oxidize mixture gives evidence that the current conditions suggested for sequestration conditions by previous works like (IPPC, working group III, 2015) and (Riaz, 2006) agreed on [313-333] K, and [10-20] MPa. These conditions are over the estimated critical mixture point of the oxidize mixture. This increase in the critical pressure range compared with pure CO₂ is due to the presence of N₂ (126.2 K, 3.4 MPa, REFPROP NIST V9.1.) and O₂ (154 K 4.98 MPa REFPROP NIST V9.1.) with very low critical temperature. Since these compounds are over their critical temperature, they are denominated gases, meaning that they will not condense into a liquid phase for any pressure, so higher pressures are needed to increase their density compared with a vapor. Each data point can be seen in the Annex 7.2.

- **Reduced mixture**

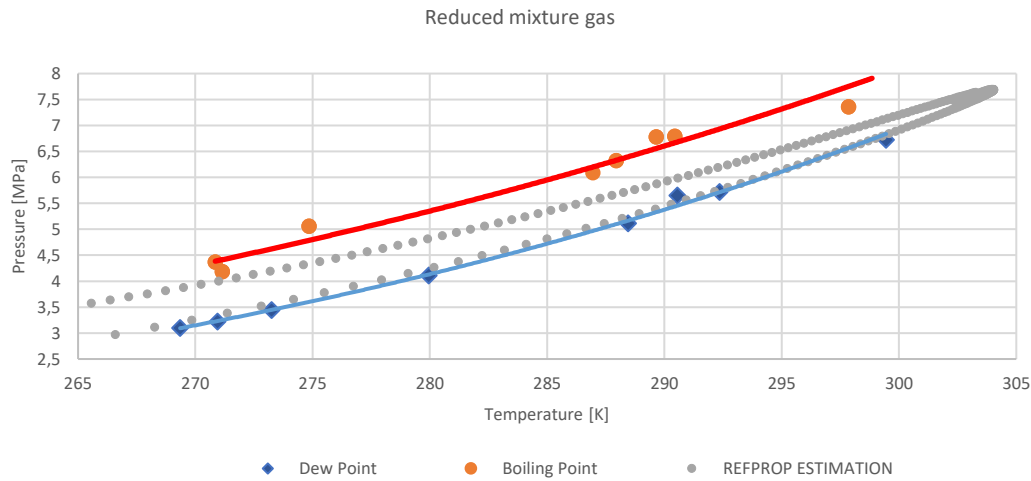


Figure 17 comparison between reduced gas mixture and simulated oxidize mixture.

Reduced mixture contains H_2 instead of O_2 , causing a widening on the area between the phase boundaries due to the critical point of H_2 (33 K and 1.29 MPa). Being at so high temperature compared with its critical one, the pressure necessary to bring H_2 to a denser condition is very high. At experimental conditions H_2 is already over its critical conditions, needing higher p than the other mixtures to become a dense phase, locating the mixture critical line away from the pure CO_2 critical point or the oxidize mixture. This wider VLE must be considered when designing processes because the areas where one would expect dense phase for a oxidize mixture, would result into a VLE for a reduced mixture. To assure a single dense phase, reduced mixtures should be transported at lower temperatures or higher pressures than the oxidize one. Temperatures over 279°C should be achieved during transporting to avoid hydrate formation, therefore pressures over 5.5 MPa should assure an homogeneous dense phase of the mixture.

For Sequestration conditions, it seems difficult to keep the mixture over its critical line due to the influence of H_2 , therefore only in liquid condition sequestration could be performed (313-333 K, and over 10-20 MPa), since the critical line is not founded within the measured p and T . Lower T and higher p are suggested for storing this reduced mixture. Considering that higher p is usually cheaper than increasing T ,

it is suggested to keep a temperature of 293 K, and p should reach a minimum value of 8 MPa to achieve a dense state, which in general terms means to keep CO_2 at its pure component supercritical conditions. Considering that the geothermal gradient of the earth is around 10 K/km and pressure is 45 MPa/km up to 3000 km (Völgyesi, 1982), other authors propose a gradient of 25-35 K/km and 10 MPa/km (Azin, 2012) but agreed on 800 meters depth sequestration (Riaz, 2006). This mixture should be Sequestration at approximately at 800 m depth or bellow, which are practiced today. This depth provides two advantages, both result on suitable p encounter at these depths, which results on a CO_2 density high enough to allow efficient pore filling of the reservoir and to decrease the buoyance compared with in situ fluids (Benson, 2008) .

- **Real mixture**

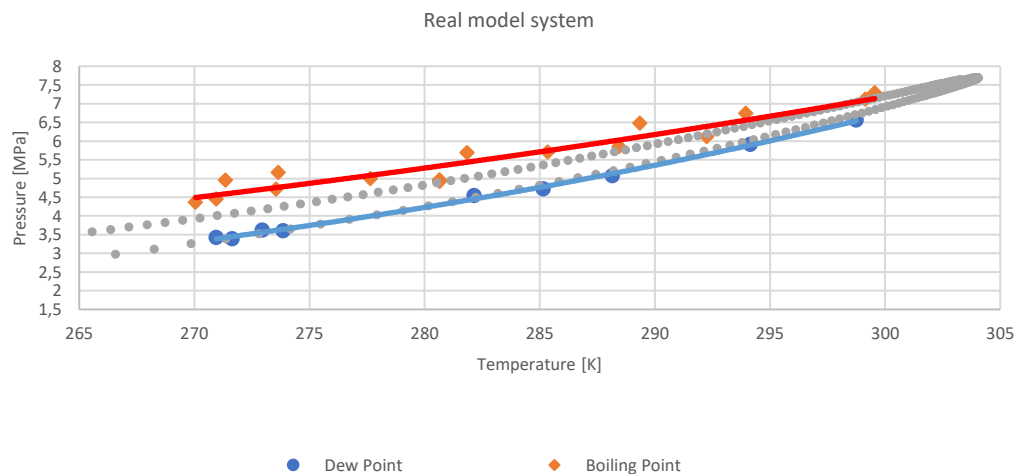


Figure 18 Comparison between real mixture model system and simulated oxidize mixture simulated by REFPROP NIST V.9.1.

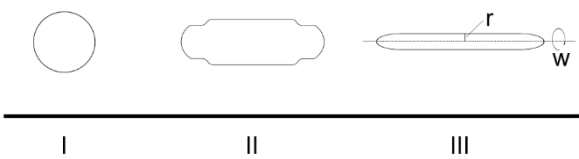
Real mixture shows a phase behavior between the oxidize and the reduced mixture. This kind of mixture could be considered as representation of a poor purification stage. What is important to notice is that at the beginning of the VLE measured, it is wider than the oxidize mixture. As T and p increase, the system converges to the critical line, which means that transport conditions should be at higher p than the oxidize mixture, but regarding Sequestration conditions, same conditions can be applied. This

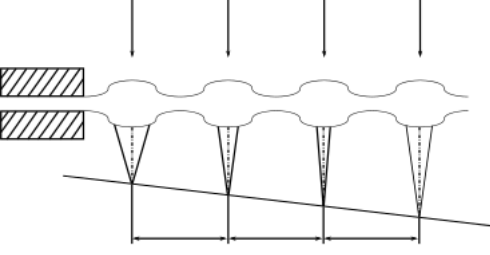
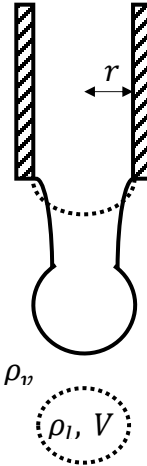
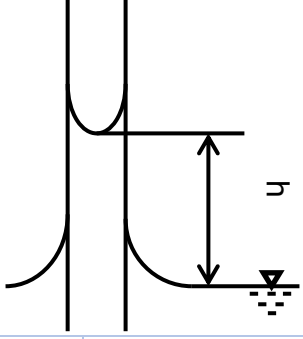
measurement evidences that impurities, even in small quantities (less than 1%), can change/influence the behavior of the mixture. Poor cleaning of the mixture can cause condensation and undesirable behavior if it not kept under control.

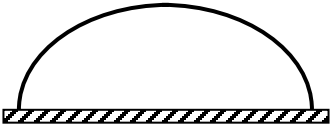
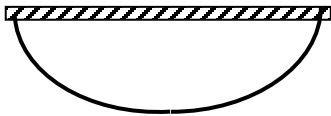
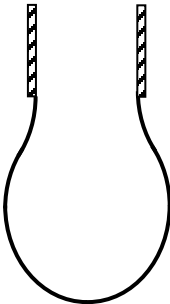
4.3 Interfacial tension equipment and technique.

Interfacial tension (IFT) is a fundamental property which influences the shape fluids boundaries and controls their deformability, in other words, the size and shape of bubbles and drops. The shape of this drops or bubbles influences how they nucleate over surfaces, such is the case at transport stage, when condensation may occur. An understanding of this property and an estimation of its values regarding the CO₂+H₂O system will give information on the effective contact area between a fluid and the walls which contains it can increase or decrease the corrosion rate. Hence the interfacial tension is related to a big field of applications, for example in the oil and natural gas industry, where interfaces occur at elevated pressures and a wide range of temperatures. Several methods have been developed in order to measure IFT under high pressure. The most used methods are listed in table 12.

Table 12 IFT measurement methods adapted from Eurotechnica (2013).

Method		Description
Spinning drop 		A transparent tube, which is loaded with a drop or a bubble surrounded by a denser phase, spins about its longitudinal axis. Due to the pressure caused by the centrifugal forces, the drop or the bubble tends to join the rotational axis and elongate along it until it reaches an equilibrium position. The shape of the drop or the bubble radius r and the interfacial tension σ are correlated with the speed of rotation ω and the density difference of the liquids or the phases $\Delta\rho$ according to the energy balance. (Vonnegut, 1942), (Anatolii, 1996)
Equation	Evaluation	
$\sigma = \frac{\Delta\rho \cdot \omega^2 \cdot r^3}{4}$	Not suitable for high pressure Can be coupled with optical analysis Suitable for low IFT and SFT	
Oscillating Jet		In this special dynamic method, a liquid jet leaves an elliptical orifice, so that it oscillates and adopts the properties of standing waves. The wavelength λ depends only on the interfacial tension σ , the liquid density ρ_l , the liquid flow rate $\dot{V}_l$ as well as the mean cylinder radius r and the oscillation persists until no viscosity nor compressibility occurs. (Anatolii, 1996)

		
Equation	Evaluation	
$\sigma = \frac{2 \cdot \rho_l \cdot \dot{V}_l^2}{3 \cdot r \cdot \lambda^2}$	Suitable for high pressure Can be coupled with optical analysis Suitable for low IFT and SFT	
Drop Weight or Volume 		A drop of density ρ_l and volume V drips in a low flow rate from a capillary of radius r into a surrounding phase of density ρ_v . The gravity force of the falling drop ($F_G = \Delta\rho \cdot g \cdot V$) corresponds ideally to the surface tension force ($\sigma = 2 \cdot \pi \cdot R$). An empirical correction factor f adjusts the deviation to the reality. (Hartland, 2004), (Boucher, 1975), (Boucher E. , 1978), (Tate, 1864)
Equation	Evaluation	
$\sigma = \frac{V \cdot \Delta\rho \cdot g}{2\pi r \cdot f}$	Suitable for high pressure Optical analysis Not recommendable for low IFT and SFT	
Capillary Rise 		The interfacial tension is based on capillary effects of a liquid. Due to wetting of the inner wall of a capillary glass tube by a liquid, the surface of this liquid is bent causing a pressure difference across the surface. One problem especially at high pressures is the lack of knowledge on the contact angle the capillary rise significantly depends on. (Washburn, 1921), (Lucas, 1918).
Equation	Evaluation	
$\sigma = \frac{h \cdot \Delta\rho \cdot g \cdot R}{2 \cdot \cos(\theta)}$	Pressure applicability depends on the material used	

	<p>Very sensitive to angle variation if coupled with optical analysis</p> <p>Not recommendable for low IFT and SFT</p>	
<p style="text-align: center;">Drop Shape</p> <p>Gravity tends to elongate a pendant drop or to flatten a sessile drop while interfacial tension opposes elongation and tends to make a drop spherical. There are three different possibilities to form the drop (Bashforth, 1883), (Young, 1805) (Laplace, 1806):</p>		
Equation	Evaluation	
$\Delta p = \sigma \cdot \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$ <p>Where R_1 and R_2 are two radius of the drop that maximize Δp</p>	<p>Suitable for high pressure</p> <p>Very good when coupled with optical analysis</p> <p>Good accuracy</p>	
<p>Sessile Drop</p> 	<p>The drop is deposited on a solid, where it does not spread spontaneously. The actual drop shape reflects the result of two effects: The gravity increases the drop diameter or flattens the drop, whereas the interfacial tension favors a smaller drop of greater height. Whether or not this method is feasible for determining IFT depends on the contact angle</p>	
<p>Captive Bubble</p> 	<p>If the whole set-up from the sessile drop measurement is turned upside down, it is applicable for drops or bubbles with less dense phase than the surrounding phase.</p>	
<p>Pendant Drop</p> 	<p>A drop is suspended from a capillary and the shape is influenced by gravity and interfacial tension.</p>	

Capillary rise method was the most used method for estimate interfacial tension of liquids in equilibria with its vapor. This method depends strongly on the contact angle between the capillary and the interface, it is unknown how little deviation from a straight angle can influence the results. A pendant drop

apparatus was used for determining the interfacial tension for fluid phases systems (L-L and V-L). This allows measuring IFT between a liquid and a vapor up to 400 bar and a temperature range of 193 to 473 K. The interfacial tension between CO₂ and H₂O was measured in a temperature range of 277 to 313 K and pressures of 5 to 20 MPa and compared with literature. The accuracy of the instrument is estimated to be approximately $\pm 0.7 \text{ mN/m}$.

4.3.1 Theory

The pendant drop method has been developed to determine the interfacial tension from the shapes of drops. *Bashforth & Adams* (1883) (Bashforth, 1883) established a fundamental equation to correlate the IFT and the pressure difference between two phases or two fluids at each point along an interface. This equation is based on the equation of capillarity, which was first introduced in by Young (1805) (Young, 1805) and Laplace (1806) (Laplace, 1806).

$$\Delta p = \sigma \cdot \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad 4.3.1$$

For any point P on the drop surface, the pressure difference (Δp) over a meniscus between two fluids is proportional to the interfacial tension (σ) and the sum of the reciprocal of the principal radius of curvature R_1 as well as R_2 . Relating the classical Young-Laplace equation to the hydrostatic pressure between point P and the apex, one obtains:

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{2}{R_0} - \frac{\Delta \rho \cdot g \cdot z}{\sigma} \quad 4.3.2$$

This equation combines the radius of curvature R_1 and R_2 with the radius at the apex R_0 (see figure 19), the density difference between the phases, the gravity constant (g), the interfacial tension as well as the height difference (z) between the apex and the point P .

Replacing equation 4.3.2 by a set of three first-order differential equations to apply it to a non-steady state for the interfacial loci X as well as Z and turning angle ϕ of the interface as a function of the arc length s , leads to (Sutjiadi-Sia et al. 2007):

$$\frac{d^2 Z}{dX^2} + \frac{1}{X} \cdot \frac{dZ}{dX} \cdot \left[1 + \left(\frac{dZ}{dX} \right)^2 \right] = (2 - B \cdot Z) \cdot \left[1 + \left(\frac{dZ}{dX} \right)^2 \right]^{3/2} \quad 4.3.3$$

Two dimensionless variables are introduced:

- $X = \frac{x}{R_0}$
- $Z = \frac{z}{R_0}$

The capillary constant B is defined by material properties, the gravity constant g and the drop radius R_0 :

$$B = \frac{\Delta\rho \cdot g \cdot R_0^2}{\sigma} \quad 4.3.4$$

The shape of a drop is mathematically fitted and the equation 4.3.3 is solved by using parameters including the location of the apex (X_0, Z_0) , the radius of curvature at the apex R_0 and the capillarity constant B .

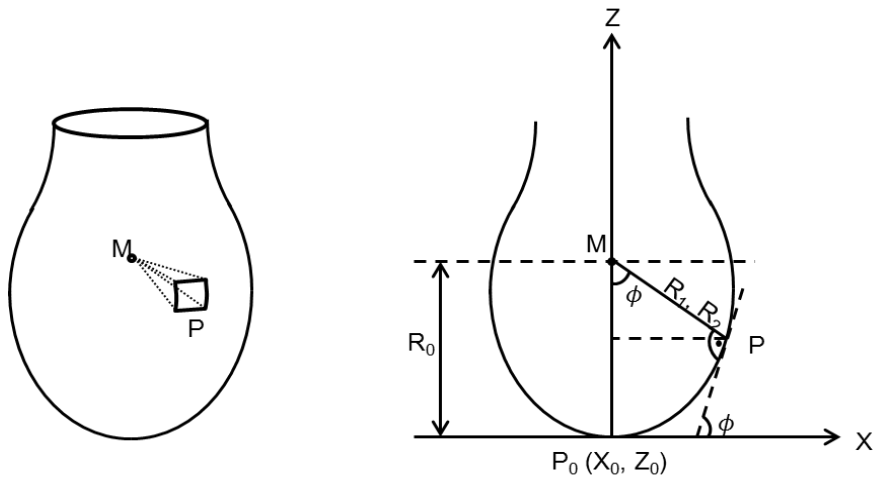


Figure 19: Pendant drop (left) and the geometry of a two dimensionally projected pendant drop (right). Redrawn from (Sutjiadi-Sia et al. 2007)

Commercial software is available, e.g. DSA4 (KRÜSS, Germany), for solving the set of differential equations while adjusting the interfacial tension until the theoretical and experimental drop profile coincide (Song, Springer 1996). Density of H₂O and CO₂ changes as saturation is reached, but since many of the literature reviewed does not correct density changes of the surrounding, to compare at more similar conditions, no density correction due to solubility were applied (Espinoza, 2010).

4.3.2 Materials and Methods

Experimental Set-up

Apparatus:

The high-pressure equipment PDE – 150 C (volume: 57 ml) was developed and constructed by *Eurotechnica*, Germany (www.eurotechnica-hd.de) containing two windows positioned opposite to each other. Inside the view cell, a capillary is connected to a handpump (max pressure: 350 bar, volume: 66 ml) to make the drops of the denser phase to be captured. The view cell is equipped with a thermosetting jacket for passing cooling fluid (technical degree ethanol) from a cooling circulator (temperature range: -95°C - +70°C, volume 22 liter). A pressure gauge (max. pressure: 300 bar, accuracy ± 0.16 bar), a pressure sensor (ISCO, USA, max. pressure: 250 bar, accuracy: ± 0.25 bar) and a Pt100 (class A: accuracy at 0 °C ± 0.15 °C and at -100 °C ± 0.35 °C) are connected to the cell for monitoring the test conditions. An automatically operated high-pressure syringe pump (max. pressure: 250 bar, volume: 500 ml) supplies the cell with gas for establishing and maintaining the designated test pressure. The view cell can be additionally pressurized with the hand pump. Safety against over-pressure is given by the rupture discs.

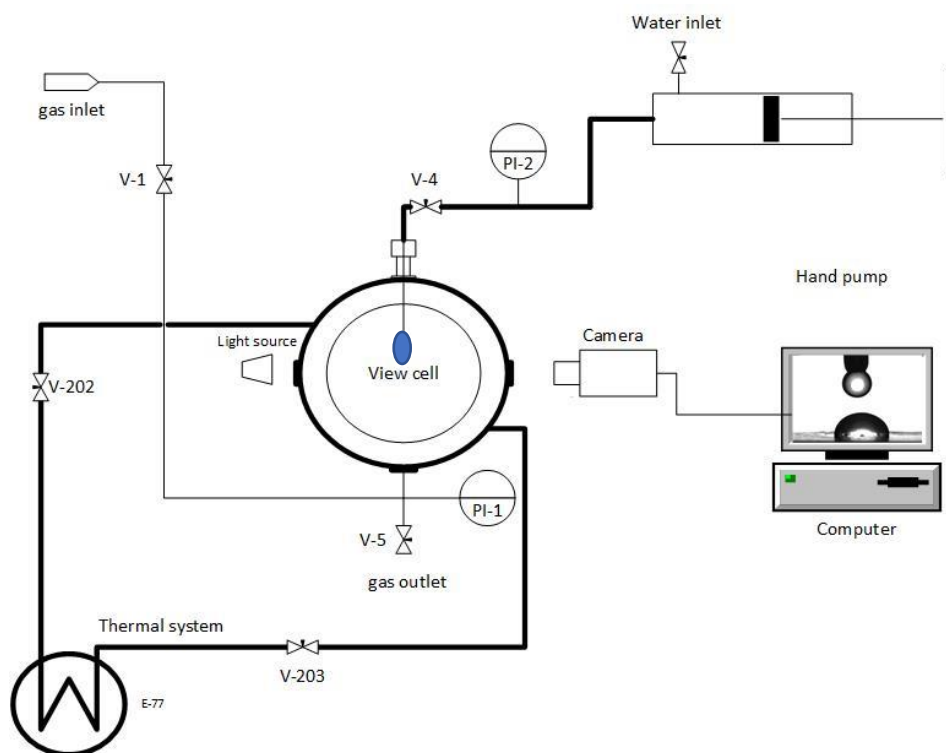


Figure 20 Experimental Set up for Interfacial Tension measurement

Materials

CO₂ (purity: 99,999%), which was provided by Westfalen AG, Germany.

H₂O used corresponded to commercial distillate water.

Experimental procedure

Before pressurizing the equipment with the designated gas, vacuum is pulled in order to displace air and humidity. Subsequently the desired temperature is set. Once temperature is reached, it is pressurized up to the desired pressure, it is done slowly, allowing the gas to reach temperature goal and avoid a later over pressurization. When pressure and temperature is reached and stable, a CCD (charge coupled device)-camera placed in front of the window of the view cell is illuminated with a LED light source from the opposite window will start record. The camera is controlled by the program DSA4 (KRÜSS Germany), which calculate the interfacial tension from the shape and properties of the drop.

By using the handpump, H_2O is pumped manually inside of the view cell. A video is recorded as the drop grow slowly using the handpump until it falls. Knowing that the diffusion of H_2O into the CO_2 rich phase and diffusion of CO_2 into the H_2O rich phase are happening during the experiment, several drops are measured consecutively to observe the effect of phase saturation over the IFT, which would represent in a better way the situation inside the pipping or reservoir.

4.3.3 Results and discussion

IFT values are shown as a function of equilibration time (figure 21) as well as a function of pressure for two defined temperatures 278 to 313 K (figures 22 and 23), specific values can be seen in the Annex 7.3. Is possible to appreciate how the IFT values change along time. As the experiment goes, each drop decreases its IFT value as they equilibrate, after a few drops, IFT decreases strongly to reach certain minimum. This change in IFT is due the diffusion of CO_2 into H_2O and water into CO_2 rich phase. As phase concentration tends to equilibrium, meaning that the dissolution of both compounds into each other decrease the IFT, allowing the drop to grow and stabilize. The arrows show the values that each drop took along time before falling. Each new drop can be identified as an abrupt increase on the IFT value and a soft decrease.

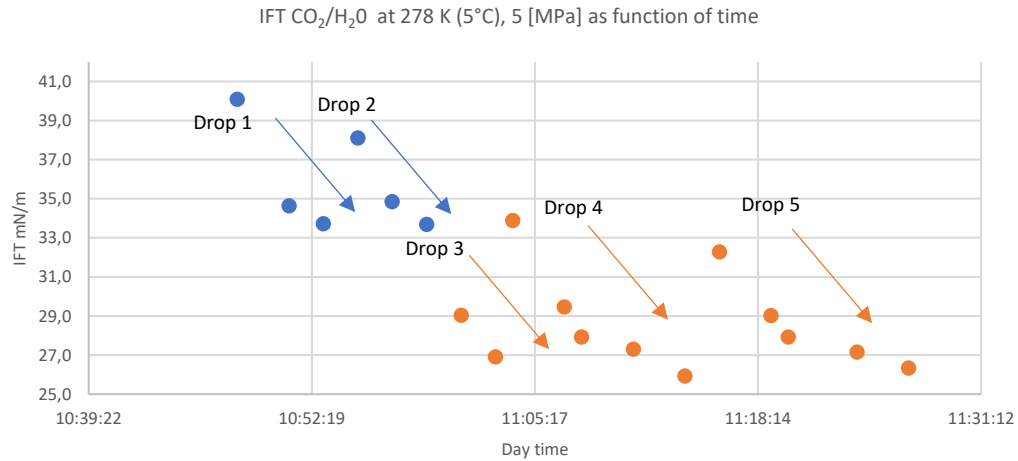


Figure 21 IFT values as function of time

In figure 21 is possible to find 2 data sets, blue and orange. Blue group consist of 2 drops that were consecutively lay into the view cell, allowing the CO₂ rich phase to be saturated with water. The orange group are 3 drops, showing smaller IFT value compared with the blue group. The difference between the orange and the blue group may be due to the saturation degree of the CO₂ rich phase with H₂O after the blue drops comes in contact with CO₂. Each orange drop describes a qualitatively similar behavior, which is a decreasing IFT value as CO₂ goes inside the water drop. Between groups (blue and orange), before and after saturation of the CO₂ rich phase can easily be appreciated, being the diffusion of CO₂ into H₂O the responsible for the decreasing IFT and not the diffusion of H₂O into CO₂.

At 278 K, interfacial tension of CO₂+H₂O system at dense state starts at around 5 MPa with a value of 27 mN/m and remains approximately constant up to 16 MPa, where it decreases down to 12 mN/m at 20 MPa as is possible to appreciate on figure 22, the blue rectangle shows the condensation pressure of CO₂ rich mixture. The data is in good agreement with previous studies (Chun, 1995), (Hebach, 2002).

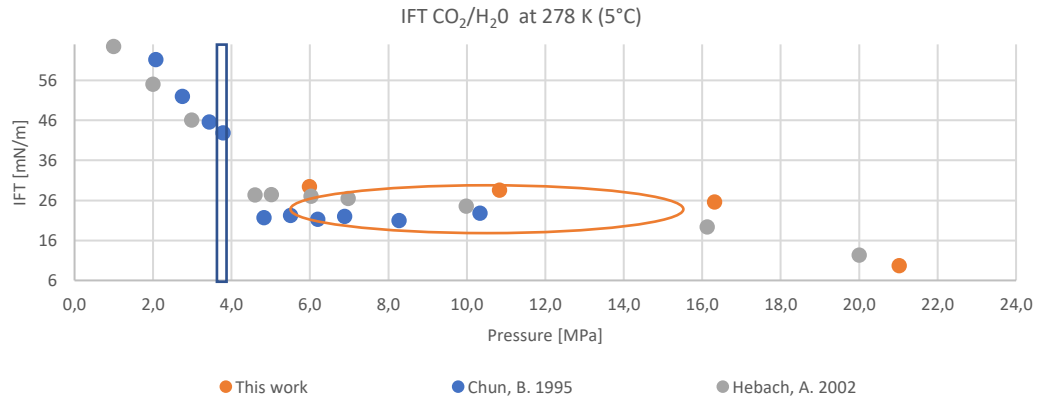


Figure 22 IFT on H_2O+CO_2 system as a function of pressure at 278K. Blue circle shows gas phase for CO_2 and orange circle shows liquid CO_2 phase. Blue line shows CO_2 pure L-V transition at 3,95 MPa

For the IFT values at 313 K, in figure 23, is possible to appreciate a constant decreasing value ($\sim 5 \frac{mN}{m}/MPa$) from 0.1 MPa up to 7.5 MPa, which is close to CO_2 critical pressure (blue rectangle). From 8 MPa, IFT remains approximately constant between 20-32 mN/m up to 20 MPa. Data from other studies shows the same tendency (Chun, 1995), (Bachu, 2009), (Georgiadis, 2010), (Bikkina, 2011).

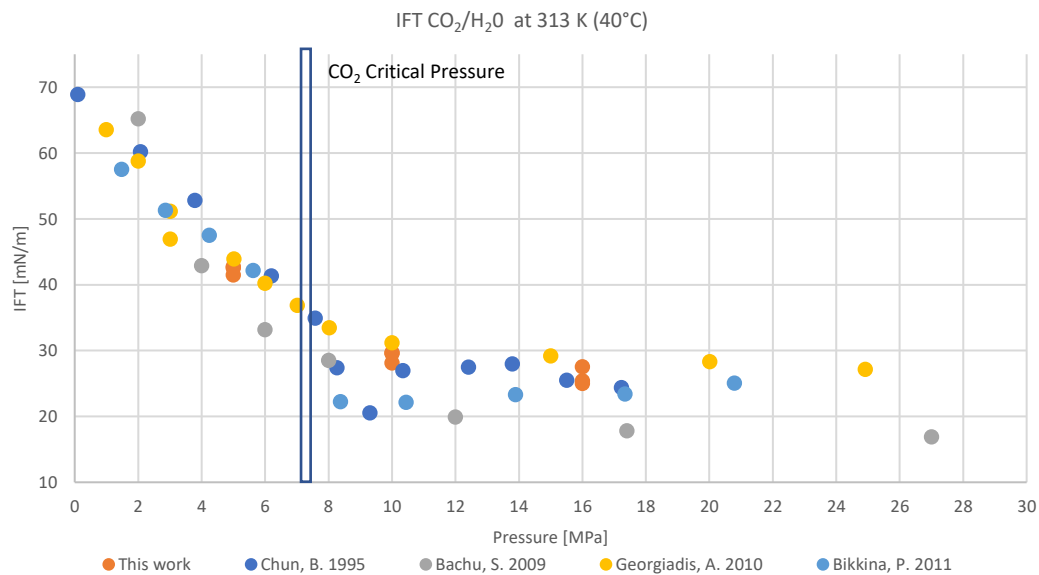


Figure 23 IFT on H_2O+CO_2 system as a function of pressure at 313K.

Measurements of interfacial tension performed for the CO₂-H₂O system are within the values obtained from previous works (Chun, 1995), (Bachu, 2009) (Georgiadis, 2010), (Hebach, 2002), (Bikkina, 2011), showing similar behavior and values, with less than 10 *mN/m* discrepancy for points of different authors at the same pressure and temperature and the accuracy of the instrument is estimated to be approximately $\pm 0.7 \text{ mN/m}$.

Interfacial tension values of the system H₂O+CO₂ slightly decrease as pressure increase and an increasing value as temperature rise. It implies that H₂O rich phase drops will become bigger as pressure increase and smaller as temperature rise. The value of IFT indicate that for the transportation stage, being corrosion a key point, lower temperatures compared with the Sequestration conditions may produce smaller drops if conditions within the pipeline allows for condensation or if there is presence of water in amounts over the saturation value. This is due to the reduction of effective contact area between the H₂O rich phase and the pipeline inner wall as the drop size decrease. Temperatures lower than 278 K are not recommended due to the potential hydrate formation, which could block the pipelines, causing considerable damage. IFT varies strongly if one of the fluids is compressible, once a dense state is reached, pressure dependency decreases. This is observable once CO₂ reach its critical pressure or liquid state, depending on the temperature.

4.4 Mutual diffusivity of the binary system CO₂+H₂O.

4.4.1 Theory

Diffusion is the physical process by which a molecule/particle moves/pass through a media caused by its random motion. This random motion may/can happen for a variety of reasons, being in most of the cases a gradient of some sort the “driving force” or potential. The simplest diffusive process is caused due to stochastic processes, without a quantifiable gradient. This process is known as Brownian Movement, which was observed in particles of a fluid media (liquid, vapor, gas or super critic media) due to the collision of the molecules. This phenomenon was first observed by *Robert Brown* (1773-1857) in 1827 while observing particles of pollen moving on a water container, but it was much later that the process was sufficiently described.

The motion of a single particle can be described in terms of the “random walk” picture, and while is possible to calculate the mean-square distance travelled by a particle in a given interval of time, it is not possible to say in which direction will move in that time, supporting the random nature of this movement. In 1905, Albert Einstein (Einstein, 1905) showed how the postulates of kinetic theory of heat were able to explain how small, but macroscopic particles suspended on a fluid must perform an unceasing motion. He obtained the laws governing this motion, which he identified as Brownian motion. Brownian Movement explained by Einstein had three postulates

- The motion of particles of different species is independent (as is the case of dilute molecules), so that the problem is essentially a one-particle to one
- The movement of a previous time interval will not determine the movement of the next time interval.
- There exists a mean squared displacement of the particle during such interval, or net displacement, independent of the path taken.

“Brownian Movement” is possible to establish that motion in the absence of external forces is of diffusive nature (Sokolov, 2005). Diffusional processes produce spontaneous mass flux through the media, being useful in many engineering applications that requires mass transfer. The application range of diffusional processes is of much importance specially in chemical industry (for example in the field of bioengineering as well as in the processes of environmental protection, conforming the basis of separation and purification processes of fluid mixtures). Therefore, mass transfer by diffusion is a substantial part of the fundamentals of Chemical Engineering. (Burghardt, 2010). Mass transfer is considered as an unitarian operation it self. Example of this is the dissolving of some salts without stirring, caused by the movement through the media, caused by the concentration gradient as a driving force. Concentration gradient driven mass transfer occur, usually, from a high concentration location to a lower concentration one.

Translational velocities of the molecules are very high (hundreds of meters per second), but in contrast the molecular net motion of a species is very low. In gases, the diffusion propagates (at normal conditions) at velocities of about $10^{-3} \frac{m}{s}$, in liquids is around $10^{-5} \frac{m}{s}$ and in solids is $10^{-9} \frac{m}{s}$. The very low rate of diffusion compared with the movement speed of molecules is caused by collisions which occur at a rate of millions per second per cm^3 , producing extremely strong limitations to the molecules movement. Hence, the distance traveled by a molecule in the gaseous phase between two subsequent collisions, called the mean free path, is very low (10^{-8} m). Recognizing that the collision rate increases with temperature, diffusion occurs more intensively at high temperature (higher molecular velocities) and at low pressures (lower molecular density resulting in fewer collisions). The molar mass of the molecule also influences the rate of diffusion as light molecules move faster than heavy ones (effects of gravitational field).

There are some phenomena that can enhance diffusion, such as chemical reaction, force fields and convection. Convection is a macroscopic process in which portion of fluid are moved as a block (same bulk velocity) over much larger distances than in the diffusion process, carrying the transferred component from region of high concentration to region of low concentration (usually aided by change in density due

to mixing). This process is generated by agitation, currents and eddies of the turbulent flow. However, the mass transfer between the newly adjacent stream of the fluid proceeds by mean of diffusion which mixes the portion of the fluids. As Maxwell's mentioned *"Mass transfer is due partly to the motion of translation and partly to that of agitation"* (Domb, 1980). This means that, broadly speaking, all mass transfer process includes diffusion and convection (that can be cause by diffusion and the consequent density change, causing the convective streams to appear).

The mass transfer due to diffusion can, on a simpler way, be described by Fick's law, which states that *"...the rate of transfer of diffusing substance through unit are of a section is proportional to the concentration gradient measured normal to the section"*. (Wilkinson, 2000)

$$\dot{Q} = -D \frac{\partial C}{\partial x} \quad 4.4.1$$

Where $\dot{Q}$ is the rate of transfer per unit area of section, C the concentration of diffusing substance, x the unidimensional space coordinate measured normal to the section, and D is called the diffusion coefficient, known also as diffusivity. In dilute systems, the assumption of a constant D is reasonable, but as concentration increase, D becomes concentration dependant (Crank, 1975). Equation 4.4.1 is valid only for an isotropic medium.

Considering the mass transfer in all directions, is possible to stablished that the change in concertation on a defined differential control volume will be equal to the mass flux in each direction perpendicular to the control volume.

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad 4.4.2$$

This equation is normally simplifying as an unidimensional equation, assuming that diffusion happen equally in all directions (isotropy) and D is not concentration dependent it is known as Fick's second law (Crank, 1975):

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

4.4.3

Experimental set up

In order to characterize the multicomponent gas flow in pipelines, thermophysical properties such as interfacial tensions, phase equilibria and diffusion coefficients must be studied. It is useful to simplify the situation and investigate different influences over the parameters separately, such as diffusion coefficient. Pressure and temperature conditions in this work are the ones used for Sequestration, ranging from 5 to 20 MPa and 40 to 60°C avoiding L-L equilibria.

The apparatus consists of a magnetic microbalance device inside an autoclave with a total volume of 66 mL. A glass container (height = 15 mm, ID = 6.5 mm) filled up with the test liquid (with samples usually of 0.2 gr of water) is connected to a permanent magnet coupling that transmits the magnetic force to an electromagnet on the outside of the autoclave which on its turn is connected to a microbalance. T and p inside the autoclave are measured along with the weight as a function of time. Water is filled into the glass containment and the autoclave is closed, then CO₂ is charged into the autoclave “*as fast as possible*” to keep a short unsteady pressure on the system.

Weight of the glass containment including the sample liquid results from its mass and the buoyancy originating from the surrounding fluid mixture under test conditions. This weight is detected via a magnetic coupling by a microbalance on the outside of the autoclave and recorded by a computer, which also controls the magnetic coupling. This so-called magnetic suspension balance (Rubotherm, Germany, P_{max} = 35 MPa, T_{max} = 120°C) is placed inside a heating air bath for temperature equilibration within ± 0.5K. The change in the volume of the liquid was detected by visual observation through high pressure sapphire windows. The principle setup is depicted in figure 24.

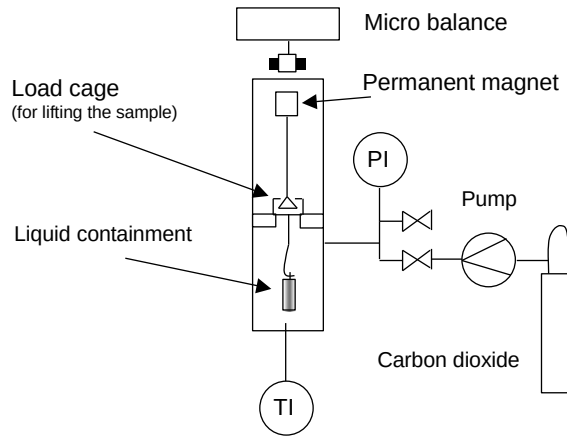


Figure 24 Setup for determining the diffusion coefficients of CO_2 in ionic liquids. Eurotechnica GmbH (2013)

Materials

- Distilled water
- CO_2 (99.8 Mol %) from Westfalen GmbH

Experimental Procedure

Before the sorption experiment the initial weight of the liquid $M_s(t=0)$ is determined. After closing the autoclave, the data acquisition programme is started to record the balance signal $M_b(t)$ at predefined time intervals. The change in weight of the liquid in the compressed gas mixture $M_{s,gas}(t)$ is determined by subtracting the initial balance signal $M_b(t=0)$ from $M_b(t)$ at a given time, i.e.:

$$M_{s,gas}(t) = M_b(t) - M_b(t=0). \quad (4.4.2.1)$$

The weight of the liquid as a function of time $M_s(t)$ is given by:

$$M_s(t) = M_s(t=0) + M_{s,gas}(t) + M_{buo}(t) \quad (4.4.2.2)$$

Where $M_{buo}(t)$ is the buoyancy correction, accounting for the change in volume of the liquid (water) phase during the experiment as a function of time:

$$M_{buo}(t) = \Delta V_s(t) \cdot \rho_{gas} \quad (4.4.2.3)$$

Where ρ_{gas} is the gas density at the given pressure and temperature. The volume swell $\Delta V_s(t)$ is determined by optical determination of the liquid level. At equilibrium the mass change $M_{s,eq}$ of the sample is given by:

$$M_{s,eq} = M_s(t_{eq}) - M_s(t=0) \quad (4.4.2.4)$$

Where t_{eq} is the time after which sorption is in equilibrium (apparent saturation concentration is reached).

The sample holder with distilled water is placed into the autoclave. A small amount of CO₂ is used to purge the autoclave. The CO₂ is charged as fast as possible to avoid initial diffusion of CO₂ into water during the pressurisation stage. In the first period of time the lecture shows a fast increase on the sample mass, followed by a slow and asymptotic decrease (figure 25).

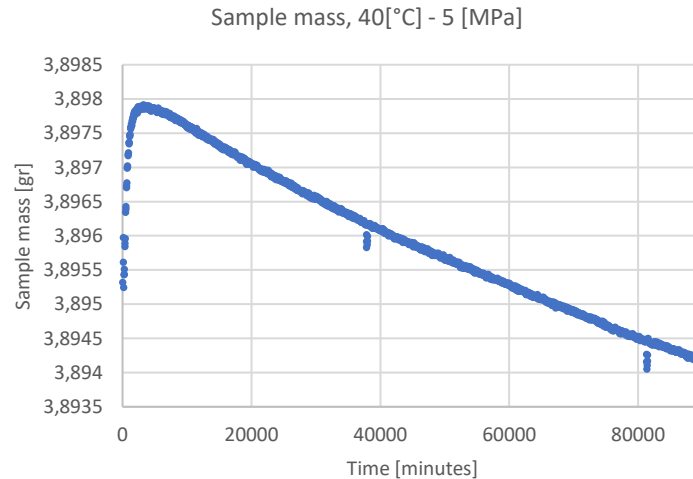


Figure 25 Plot of the corrected data from the sample weight during the experiment at 40°C and 5 MPa

During the entire experiment, two effects overlap to each other. One is that CO₂ is diffusing into the water rich phase and the other is diffusion of water into the CO₂ rich phase. The rate at which these two transport mechanisms occur changes over time. At first the diffusion of CO₂ in water rich phase is

dominating, and subsequently the water dissolving into CO₂ rich phase is the dominating mechanism once the water rich phase is nearly saturated. The corrected weight and time data are used to follow the net mass transfer and define when the period of diffusion of water in CO₂ starts to become the dominant process.

For quantifying the mass transfer of water into CO₂, the distance to diffusion to water is through the empty sampler volume of the containment above the water level. Outside the sampler, it is assumed that water dissolve uniformly through the autoclave, having an homogeneous concentration of water in the CO₂ rich phase. For CO₂ into water, the length use is the water height at the sampler (figure 26).

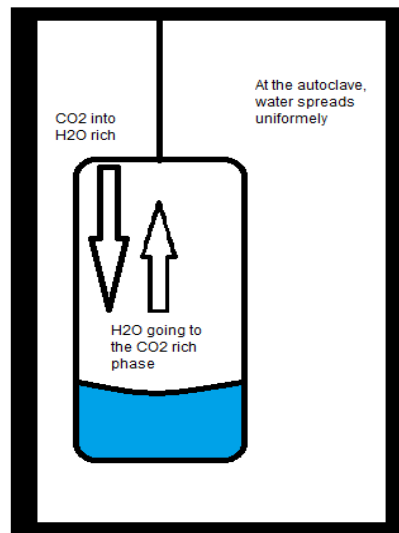


Figure 26 Considerations for mass transfer

4.4.3 Data Analysis

All the data obtained will be compared, as a starting point with the hydrodynamic approach to diffusivity of Stokes-Einstein equation due to the lack of data (Debenedetti, 1985), which take the following form:

$$D = \frac{kT}{c\pi a\eta} \quad 4.4.3.1$$

Where a is the molecular radius of the “solvent” though where the diffusion occur, k is the Boltzmann constant, T is the temperature, η is the viscosity of the solvent (Pa s) and c is an adjustable parameter relating the slip or not slip conditions of the diffusing molecule known as the Stokes-Einstein number, usually it takes values between 4 and 6, but also have been found lower and higher values. In particular, the value of c used for correlating the Stokes-Einstein equation was 4 and the hydrodynamic radius of water, a , was considered as a weak linear temperature function (Shane, 2014).

$$a = a_{298}[1 + \alpha_a(T_k - 298)] \quad 4.4.3.2$$

Cadogan *et al* (2013) published values of 168 picometers for a_{298} , α_a of $2 * 10^{-3} \text{K}^{-1}$.

First mathematical model.

Consider a parallelepiped of known dimension that exchange mass through the length Δh with an area A perpendicular to Δh , and that the concentration at h_o is C and at $(h_o + \Delta h)$ is equal to zero and remain constant, then, based on the first Fick's law, the mass flow per unit of area though Δh is given by:

$$\frac{Q}{A} = -D \frac{\partial C}{\partial x} = -D \left(\frac{\Delta c}{\Delta h} \right) \quad 4.4.3.1$$

To determine the mass flow, it is needed to multiply by the area A :

$$D \left(\frac{A}{\Delta h} \Delta c \right) = Q \quad 4.4.3.2$$

This result is of great importance, because allow to calculate the D from a known Q , concentration at the extremes of the diffusing path and the geometrical characteristic of the magnetic coupling balance technique. This equation is used to simply adjust data from mass over time (mass flow) and the set up geometric characteristic.

The first model is simple and considers just conditions inside the autoclave and diffusion of CO₂ into water only.

$$D_{CO_2 \rightarrow H_2O} = \frac{\dot{Q} \cdot \Delta h}{A \cdot \Delta c} \quad 4.4.3.3$$

Where $D_{CO_2 \rightarrow H_2O}$ is the diffusion coefficient of carbon dioxide into the water rich phase, $\dot{Q}$ is the mean flow of carbon dioxide into water in [gr/s] calculated as the highest sample weight difference and the time to reach that mass. (Wilkinson, 2000)

$$\dot{Q}(t)_i = \frac{M_{t_i} - M_{t_{i-1}}}{t_i - t_{i-1}} \quad 4.4.3.4$$

The term Δh is the height available for diffusion. A is the perpendicular area for the mass transfer. Δc is the CO₂ concentration difference between the apparent solubility and the initial concentration. This model does not take thermodynamic concentration into account and considers that the higher mass readings correspond to the solubility concentration. A few corrections are made in the next model in order to improve this model.

Second mathematical model

Using some ideas from the first mathematical model, new definitions and considerations were chosen to give the model more physical consistency. Two segments of the data were defined, the observed overall diffusion process has two separate effects overlapped, diffusion of CO₂ into the H₂O rich phase sample, and simultaneously, the evaporation of H₂O into the CO₂ rich atmosphere. It will be considered that the first situation is an absorption of CO₂ into the water rich phase, then, H₂O rich phase remains saturated while the evaporation of H₂O into the CO₂ rich phase take place.

Once the highest mass lecture is reached (which is the apparent solubility concentration of CO₂ into H₂O rich phase), the original H₂O amount will be corrected to compensate for H₂O vaporization up to

achieve 99% w/w of the thermodynamic solubility, which is obtained from (Duan, 2005) model for predicting the solubility of CO₂ into H₂O as a function of T, p and dissolved salts (monovalent and bivalent). Then it is assumed that the readings of mass in time are constant. The highest concentration of CO₂ into water is kept constant 10 times what it took to reach that CO₂ concentration, this allows a better calculation of diffusivity. From this consideration it is possible obtain data of the CO₂ absorption and the evaporation of water as shown in figure 27.

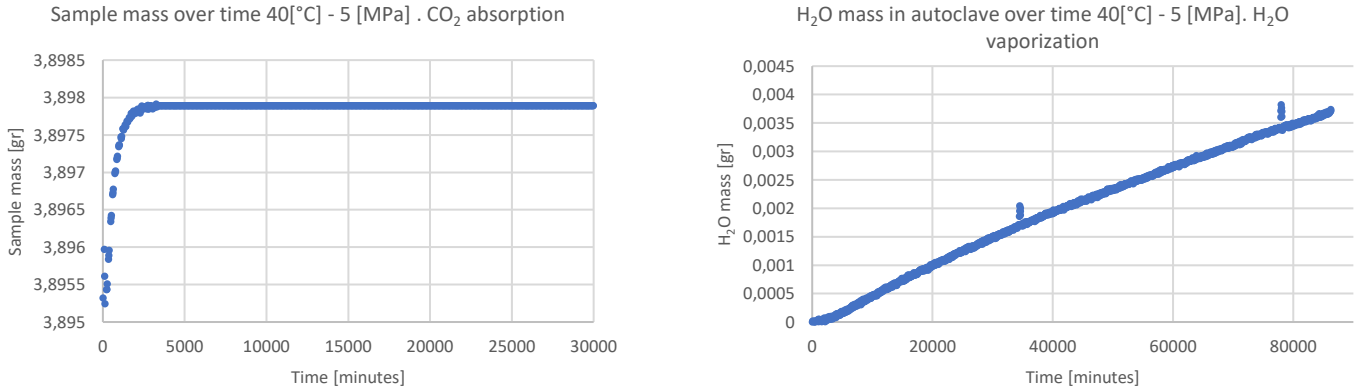


Figure 27 Effect separation at 40°C and 5 MPa. A: CO₂ absorption into H₂O rich phase. B: H₂O vaporization into CO₂ rich phase.

Statistical model

In the statistical model, for every time step of mass reading, a discrete Fick's law solution is fitted, obtaining a value of diffusivity for each period. Then all the diffusion coefficients are weighted with the time step and divided by the total time, obtaining one diffusivity. The instantaneous mass flux of CO₂ into the sample is defined as follows:

$$\dot{Q}(t)_i = \frac{M_{t_i} - M_{t_{i-1}}}{t_i - t_{i-1}} \quad 4.4.3.4$$

Concentration of CO₂ as $\left[\frac{CO_2 kg}{H_2O kg}\right]$ into the sample is defined as the mass increase up to time i over the initial H₂O mass amount.

$$[CO_2]_{t_i} = \frac{M_{t_i} - M_{t_0}}{M_{t_0} - M_{tare}} \quad 4.4.3.5$$

The diffusion coefficient of CO₂ into the H₂O rich phase is calculated as a contribution of discrete diffusivities along the experiment as follows:

$$D_i(t_i) = \frac{\dot{Q}(t)_i}{[CO_2]_{eq} - [CO_2]_{t_i}} \cdot \frac{\dot{\Delta}h}{A} \quad 4.4.3.6$$

Again, equilibrium concentration of CO₂ ($[CO_2]_{eq}$) into the water rich phase is given by Duan's *et al* (2006) solubility model.

Then every diffusivity is weighted with the time step:

$$D_{CO_2 \rightarrow H_2O} = \frac{1}{\sum_i \Delta t_i} \sum_i D(t_i) \Delta t_i \quad 4.4.3.7$$

This model is extended to the diffusion of water into the CO₂ rich phase. In order to do it, the thermodynamic concentration of H₂O into CO₂ was estimated by fitting experimental data available approximately at the same pressure and temperature of the experiments. The concentration is calculated considering the volume of CO₂ inside the autoclave and not for the sampler.

Continuous model

Another way to calculate the diffusivity is to fit a continuous model according to the nature of the system analysed. A good descriptor of the nature of the system (set-up and the properties of the compounds) is the nominal length, based on the penetration theory. Nominal length is defined as the square root of the "measurement time" times diffusivity, which understanding about how close to equilibrium conditions can the diffusing substance reach compared with the length of the set-up available for diffusion.

$$\sqrt{Dt}$$

4.4.3.8

When nominal length exceeds 20% the value of the effective distance involved for diffusion (length of the experimental set-up), the solution methods for Fickian second law at longer time or near equilibrium can be use (Wilkinson, 2000).

$$\frac{\sqrt{Dt}}{L} \geq 0.02$$

4.4.3.9

The solutions for long times to quantify the total mass of solute absorbed by the “solvent” is given by (Wilkinson, 2000):

$$m(t) = m_0 * \frac{8}{\pi^2} \left(1 - e^{\left(\frac{D(t-t_{lag})}{L^2} \right)} \right) \quad 4.4.3.10$$

From this equation, and from the corrected data used for the statistical model, is possible to fit the parameters associated with equation 4.4.3.10. The parameters used in the equation are: apparent interfacial concentration m_0 , delaying time t_{lag} and the diffusion coefficient D . To have an initial nominal length, the results obtained by the statistical model will be used to evaluate the condition for long times on the continuous model.

4.4.4 Results and discussion

The experimental method used allows to have a better understanding by estimating an “effective” diffusivity, which is affected by convection as it is by diffusion. Since available data is very scarce at high pressures, temperature will be chosen as comparison criteria between literature due to the stronger dependency of diffusivity on temperature than on pressure. All results are showed in Annex 7.4

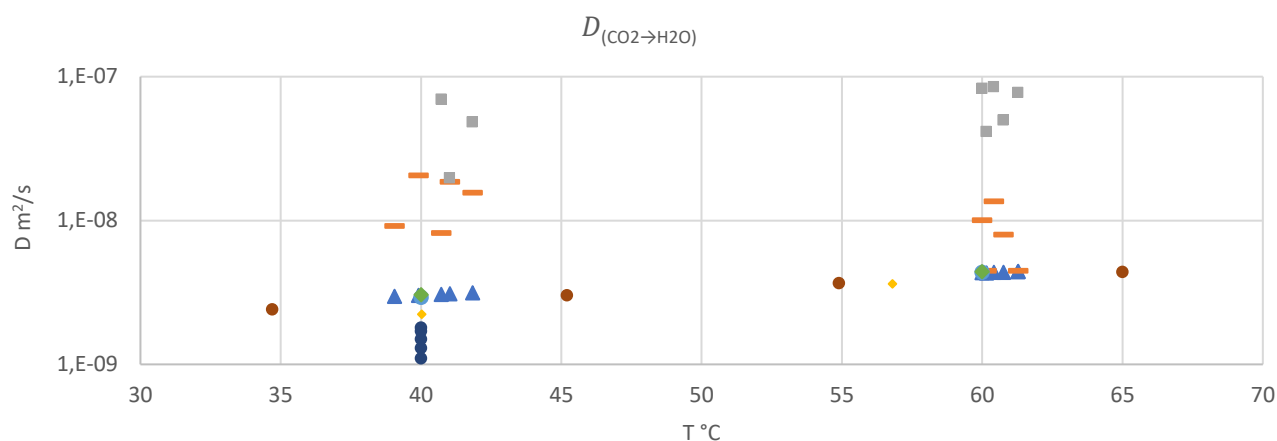


Figure 28 Diffusion coefficient of CO_2 into H_2O as a temperature function. Stoke-Einstein equation (Δ), Statistical model ($-$), Continuous model ($\blacksquare$), Unver, A. & Hummelblau (1964) ($\blacklozenge$), A. Tamimi et al (1994) ($\bullet$)

Values obtained from the experimental methods proposed in this work suggest higher diffusivities than the ones predicted by the Stoke-Einstein equation (figure 27), whom uses the viscosity of the solvent as the main property to estimate diffusivities without any other mixing mechanism. Higher diffusivity values indicate the presence of other phenomena in parallel to diffusion that enhance mass transfer. Since temperature is the main condition affecting diffusivity, to compare the values, T was chosen as comparing criteria instead of p. Note that the data presented at the same temperature may differs in pressure causing some disagreements between data beyond experimental error. Pressures range from 0.1 to 30 [MPa] for diffusivities reviewed.

Comparing to data from other researchers, these results seems to be within one order of magnitude higher, which supports the idea of an enhancement mechanism occurring. Enhanced absorption of CO_2 into the aqueous phase could be attributed to the chemical reaction of CO_2 and H_2O to produce carbonic acid, which decrease the net concentration of CO_2 in water and may increase the rate of mass transfer. It is also known that convective streams produced by density variation due to the solubilization of CO_2 into the aqueous phase enhance diffusion. As CO_2 diffuse into the aqueous phase, it

increases the density of the mixture (Garcia, 2010) (Crovetto R. , 1992) (McBride-Wright, 2015) producing convection, which increase the effective diffusion.

Several authors mentioned convection occurring in the CO₂+H₂O system, mentioning that in the reservoir convection is the main sequestration mechanism for short and medium times. For longer times, diffusion is the main mechanism affecting CO₂ sequestration (Soroush, 2012). (Khosrokhavar, 2011).

Convection is related to the stability of the interface between the phases with different density as they mix, density changes. In the case of this system, the mixture has higher density than the pure H₂O, which happen to be the denser pure compound, causing a very unstable interphase. In order to analyze the stability of the interphase and at the same time infer the presence of convective streams, the Rayleigh number is calculated at experimental conditions. The Rayleigh number is a non-dimensional number that relates the convective and diffusive forces of the system according to the geometry and properties. It is defined a critical value depending on the conditions of the set-up. Rayleigh number is defined as follows:

$$Ra = \frac{\Delta\rho g L^3}{D\mu} \quad 4.4.4.2$$

Where $\Delta\rho$ is the density difference between the solute and the solvent, g is the gravitational acceleration, L is the characteristic length of the set-up, D is the diffusivity and μ is the dynamic viscosity of the solvent. The convection conditions on the set-up are “free-rigid boundary”, where one surface is exposed to the diffusing substance and free to circulate, while the opposing surface is static (not available for convection, similar to the slip and no-slip condition for streams near limit layer). For the free-rigid condition the critical Rayleigh number is agreed around 1100 [-] (Azin, 2012). The values of Ra calculated with densities and viscosities calculated by REFPROP V 9.1., diffusivities calculated from the statistical model and characteristic length was calculated dividing the volume of each containment by its perpendicular mass flux area. Results are in table 13.

Table 13 Rayleigh numbers of each measurement. The result of diffusivity using the statistical method was used to calculate Ra .

Pressure [MPa]	Temperature [°C]	Ra [-] for $D_{CO_2 \rightarrow H_2O}$	Ra [-] for $D_{H_2O \rightarrow CO_2}$
5.4	41.8	3.3860.E+07	6.14.E+12
5.8	41.0	3.7755.E+07	7.78.E+12
15.8	39.9	7.8609.E+06	6.23.E+10
14.5	39.1	1.8987.E+07	9.73.E+10
15.4	40.7	2.8817.E+06	4.96.E+10
5.3	61.3	2.8113.E+07	2.17.E+12
10.8	60.4	1.9621.E+07	9.78.E+11
11.7	60.0	3.6006.E+07	6.77.E+11
17.5	60.8	1.5591.E+07	1.50.E+11
16.8	61.3	3.2268.E+05	1.40.E+11
19.3	60.2	1.6469.E+07	7.04.E+10

Ra number are orders of magnitude higher than the critical Ra value for free-rigid condition, which strongly suggest the presence of convection in the system as a mechanism that enhances diffusion.

Considering that the amount of carbonic acid is around 1% of the total CO_2 dissolved (Harned, 1943), it is reasonable to consider convection as the main diffusion enhancer mechanism.

Diffusivity of Carbon dioxide into Water

The presence of convection in these experiments are a very interesting source of enhancement due to the nature inside the reservoir where convection most likely occurs (Fang, 2017). Convection inside the reservoir results in considerable improvement regarding the Sequestration due to a faster mixing. To compare how faster diffusion occurs, a drop is modelled using the equation to describe the total amount of diffusing substance entering a sphere (Wilkinson, 2000):

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{Dn^2\pi^2 t}{r^2}\right) \quad 4.4.4.3$$

Where M_t is the absorbed mass, M_∞ is the mass absorbed at equilibrium, r is the drop radius, t is the time and D is the diffusivity. With this equation the percentage of saturation into an hypothetical drop ($M_t/M_\infty\%$) will be calculated with the diffusivities obtained by the models proposed. It is considered that saturation is reached when the concentration reach 90% of the maximum solubility.

Each saturation simulation are shown in figure 30 and are performed using the same drop diameter (0.21 cm) and considering the diffusivity obtained by each of the models (figure 29) to compare the influence of pressure, temperature and model over the saturation time.

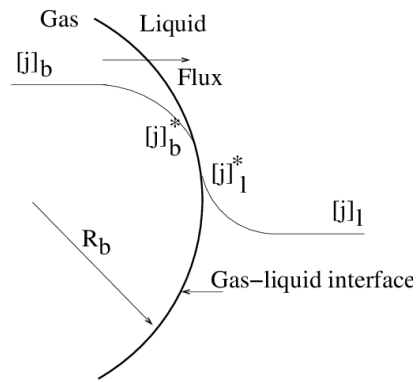


Figure 29 Gas-Liquid diffusion scheme for a drop. (Deen, 2004)

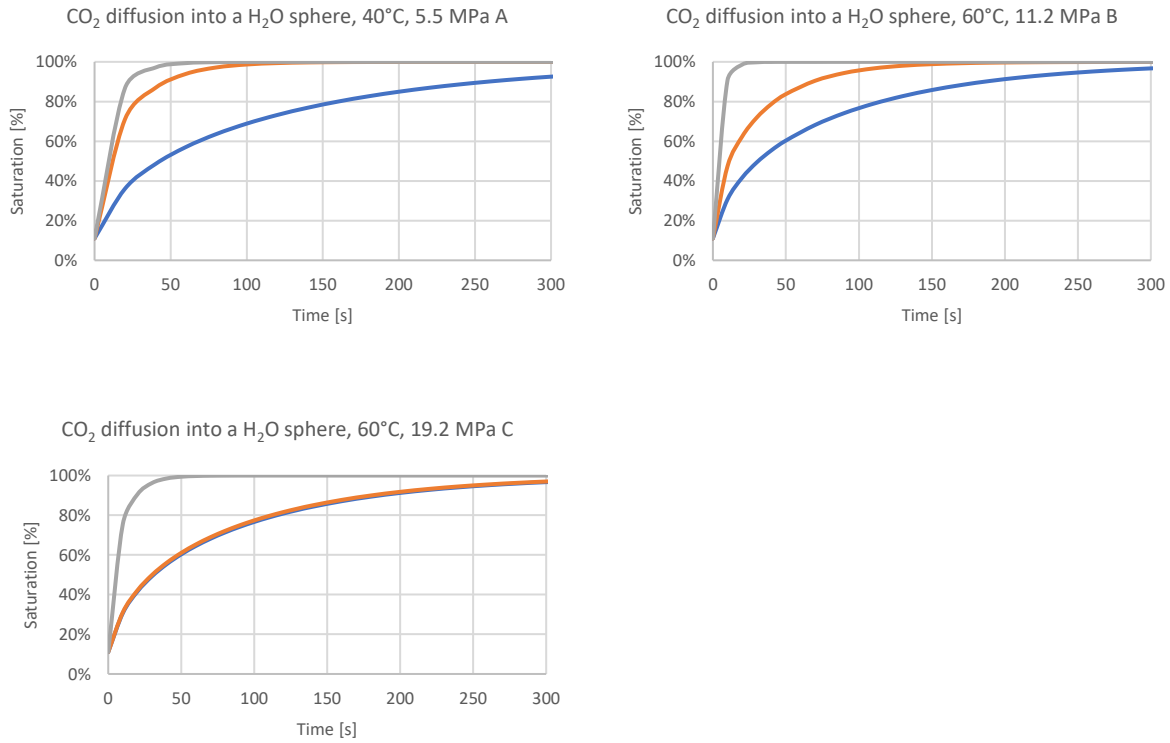


Figure 30 CO₂ diffusion into a H₂O sphere at different pressures and temperature. A [40°C-5.5 MPa], B [60°C-11.2 MPa], C [60°C-19.2 MPa]. Comparison of saturation times for different models obtained from Stoke-Einstein model (Blue). Statistic model (Orange) and Continuous model (Grey)

Comparing saturation times for CO₂ diffusing into H₂O, continuous model results in all the measured conditions to estimate higher diffusivities, followed by the statistic model and Stoke-Einstein prediction at the smaller diffusivities values and highest saturation time, representing the values when only molecular diffusion take place. The statistic model is affected by pressure more than the other models. For all models higher pressure produce a resistance in the system, slowing the diffusion. Temperature on the other hand, produce an increase in diffusivity of the species.

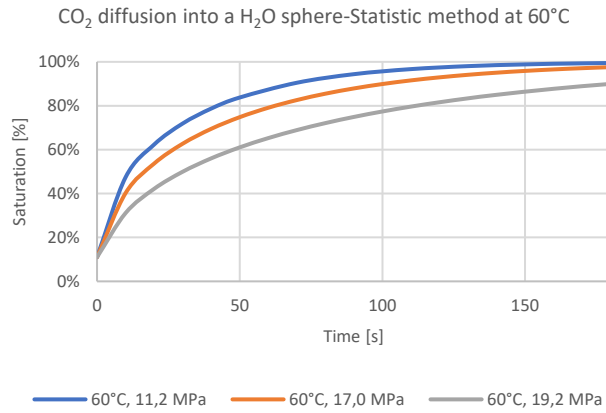


Figure 31 Effect of pressure over saturation times with statistic model

The behavior of the models is consistent along the experiments, showing that pure diffusion (Stoke-Einstein model) predict the biggest saturation times. Statistic model is the most affected by pressure, showing a behavior that is more similar to the continuous model at low pressure and temperature, to end up in a pure-diffusion behavior at the highest pressure and temperature (Stokes-Einstein like behavior). In average, saturation times are one order of magnitude smaller in the presence of convection, compared to pure diffusion.

The effect on saturation times on a reservoir where the characteristic lengths are bigger than drop sizes, the enhancement is noticeable. If the scale of the reservoir consists in spherical spaces of 1 meter diameter, saturation times vary between less than 1 month and 4 months for 60°C and 17 MPa and up to 7 months between methods at 40°C and 5.5 MPa (figure 32)

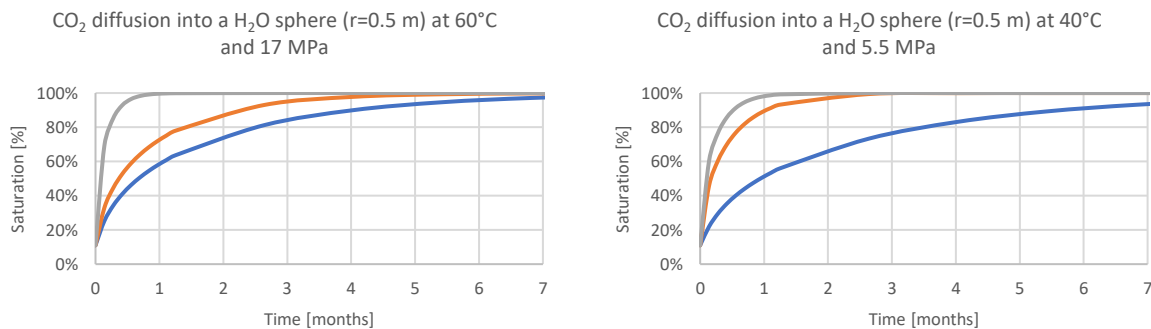


Figure 32 Carbon dioxide diffusion into a reservoir at different conditions and the impact on saturation times regarding each model. Stoke-Einstein (Blue), Statistic (Orange) and Continuous (Grey)

Diffusivity of Water into Carbon dioxide

$D_{H_2O \rightarrow CO_2}$ has similar behavior as $D_{CO_2 \rightarrow H_2O}$ concerning the effects of pressure and temperature. Values vary one order of magnitude compared with literature, supporting the idea that diffusion enhancement is taking place as convection. The main difference compared to $D_{CO_2 \rightarrow H_2O}$ values/behavior is that in this case the statistical model predicts smaller values of diffusivity than the ones predicted by the Stoke-Einstein equation. This can be caused by the large space for free diffusion for H_2O compared to the CO_2 diffusion space. meaning that saturation is very difficult to achieve in the CO_2 rich phase, resulting on a very flat slope in the mass readings of mass readings versus time.

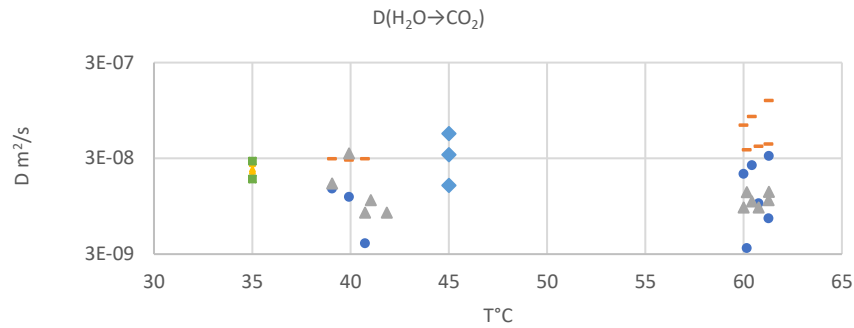


Figure 33 $D_{H_2O \rightarrow CO_2}$ values as a temperature function. Statistical model (●), Continuous model (-), Stoke-Einstein (▲), Bin Xu, et al (2002) (▲), Gregor Kravanja et al (2018) (◆), J.Wambui Moturi et al (2010) (■)

When a CO_2 sphere is simulated on a water media using the diffusivities calculated by our methods, it is possible to see how saturation times increase from continuous to Stoke Einstein to Statistic model at constant T and p and keep the same tendence at higher T and p. As T and p increase. saturation times also increase with them. There is a presence of a buffering effect over diffusion of water into CO_2 as conditions goes up, probably due to the increasing CO_2 density and viscosity.

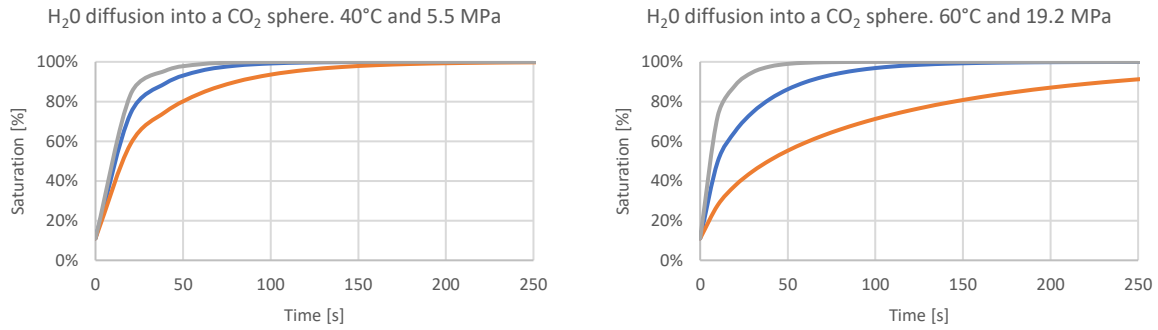


Figure 34 Comparison of saturation times for different p and T , using our diffusivities. Stoke-Einstein (Blue), Statistic (Orange) and Continuous (Grey)

Noticing the way how T and p affect diffusion, it is possible that another particularity of the system is affecting the system. The mutual diffusion of H_2O and CO_2 might be dependant on the $\Delta\rho$, which can be noticed in figure 32, diffusion of both species is faster for low T and p , where the $\Delta\rho$ is higher and slower for higher p and T , when $\Delta\rho$ approach to zero (almost the same density for both fluids). As $\Delta\rho$ is higher, diffusion enhancement take place due to density-driven natural convection. Higher density of the fluids at higher pressures make the less dense phase to compress, increasing its density, approach to the one of the liquid phase.

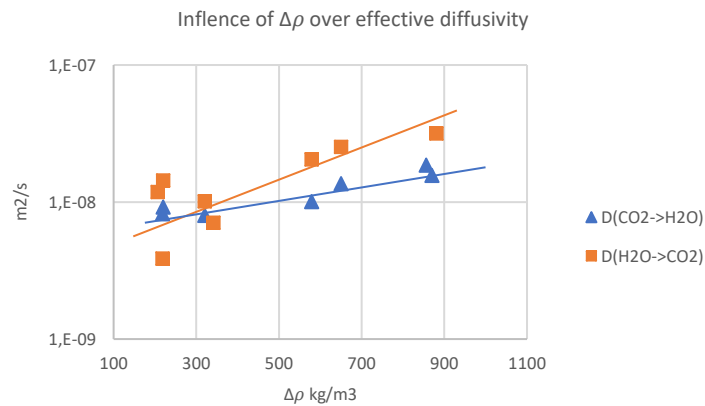


Figure 35 Effect of density difference between phases over diffusivity

Statistical model seems to be the one who represents better the nature of the experiments, since is not bounded by an specific phenomenology as it is with the Continuous model and the Stoke-Einstein equation (Fick's law solution for long times and pure diffusion respectively), rather it weights every interval of the experiment and gives a result that represents a contribution of each stage to the final value. Statistical model has the disadvantage of being more sensible to experimental errors.

Once mutual diffusivities are estimated it is then possible to have an idea about the saturation times at different Sequestration conditions for both phases using only one experiment for both values, which constitute an easy and fast method.

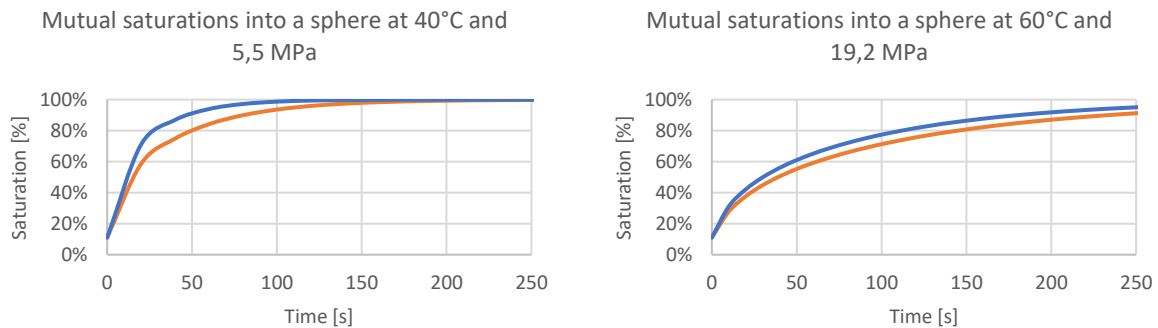


Figure 36 Mutual saturation times into a sphere at two different conditions, diffusivities estimated by Statistical model. $D_{CO_2 \rightarrow H_2O}$ (Blue), $D_{H_2O \rightarrow CO_2}$ (Orange)

5. Conclusion

The properties necessary to describe the $\text{CO}_2+\text{H}_2\text{O}$ system regarding sequestration and transportation conditions relevant to a Carbon dioxide Capture, Utilization and Sequestration facility where measured and compared with the available data. Experimental measurements conditions prioritised low cost and fast results while achieving values close to the previous reported. IFT, mutual diffusivities and phase boundaries of characteristic gas mixtures with high CO_2 content where measured and compared, moreover, diffusion was correlated with three different models in order to roughly describe equilibration times at the reservoir.

Transport conditions for the three mixtures must assure a single dense phase in order to slow the corrosion process. Oxidize and Real mixtures should be at 5°C (278K) and over 5 MPa for the transport stage, these values are over the boiling line as it is possible to see in the p-T diagram (figure 16 and 18). Critical line estimated for the oxidize mixture support current conditions suggested by previous research (313-333 K, and 10-20 MPa) and are over the estimated critical line of the oxidize mixture. Reduced mixtures should be transported at lower temperatures or higher pressures than the Oxidize and Real one. For Sequestration conditions, seems difficult to keep Reduced mixture over its critical line due to the influence of H_2 , therefore only in liquid condition sequestration could be performed if dense phase wants to be reached. This mixture should be Sequestration at approx. 800 m depth or bellow. Measurements validates that impurities, even in small quantities (less than 1%), can change the behavior of the mixture. Poor cleaning of the mixture can cause condensation and undesirable behavior if it not kept under control.

IFT results are within data from previous which shows a weak p dependence and a strong T dependence. For transportation stage, lower T compared with the sequestration conditions may produce smaller drops if conditions within the pipeline allows for condensation or if there is presence of water over the saturation values. It was found that at current transportation p and T (5 – 8 MPa & 0 – 5°C), the IFT of $\text{H}_2\text{O}+\text{CO}_2$

mixture at conditions of transport and sequestration are 12.4 and 26 mN/m respectably, which are close to the lower IFT value measured for this system and suggest drops of bigger size than at lower pressures. This means that contact area, if an aqueous separate phase is formed, on the pipping walls will produce corrosion faster, therefore, these results supports the importance of a good phase behavior control.

Mutual diffusivity of the system CO_2+H_2O shows agreement with the data published. Values vary one order of magnitude compared with literature, supporting the idea that diffusion enhancement is taking place as convection. The presence of convection on the system, which is validated with the Ra number for each measurement is proven and it becomes useful for real sequestration conditions, allowing estimation of equilibration times. Continuous model results in all the measured conditions to estimate higher diffusivities, followed by the statistic model and Stoke-Einstein with smaller diffusivities, representing the values when only molecular diffusion take place. Statistic model is p sensitive more than the other models. Diffusion showed to be density dependant (when $\Delta\rho$ approach to cero, D is smaller and as $\Delta\rho$ increase, diffusion does), this is related to the natural convection. Statistical model represents better the nature of the experiments, since is not bounded by an specific phenomenology as it is with the Continuous model and the Stoke-Einstein equation (Fick's law solution for long times and pure diffusion respectively).

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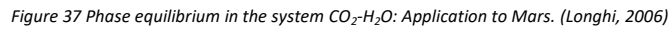
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7.2 Phase boundary data

Table 14 Oxidize mixture phase boundaries data

T [K]	P [MPa]	Point
255.3	2.89	Boiling
255.3	2.89	Boiling
256.0	2.73	Boiling
257.2	3.43	Boiling
264.9	3.69	Boiling
265.8	3.47	Boiling
266.9	3.75	Boiling
275.2	4.24	Boiling
277.4	4.88	Boiling
281.7	5.03	Boiling
284.3	5.6	Boiling
289.6	5.72	Boiling
297.4	6.73	Boiling
254.7	1.98	Dew
258.1	2.19	Dew
262	2.48	Dew
265	2.74	Dew
270	3.17	Dew
274	3.51	Dew
278.6	4.02	Dew
281.2	4.27	Dew
290.5	5.48	Dew

Table 15 Reduced gas mixture phase boundary data

T [K]	P [MPa]	Point
269.35	3.1	Dew
270.95	3.22	Dew
273.25	3.44	Dew
279.95	4.11	Dew
288.45	5.11	Dew
290.55	5.65	Dew
292.35	5.72	Dew
299.45	6.72	Dew
270.85	4.37	Boiling
271.15	4.18	Boiling
274.85	5.06	Boiling
287.95	6.32	Boiling
290.45	6.79	Boiling
289.65	6.78	Boiling
298.85	8.01	Boiling
297.85	7.36	Boiling
270.85	4.37	Boiling
271.15	4.18	Boiling
274.85	5.06	Boiling
286.95	6.09	Boiling
287.95	6.32	Boiling
290.45	6.79	Boiling
289.65	6.78	Boiling
298.85	8.01	Boiling
297.85	7.36	Boiling

Table 16 Real mixture gas system data

T [K]	P [Mpa]	Point
271.35	4.95	Boiling
270.95	4.45	Boiling
270.05	4.36	Boiling
277.65	5.00	Boiling
273.65	5.16	Boiling
273.55	4.71	Boiling
285.35	5.71	Boiling
280.65	4.92	Boiling
289.35	6.48	Boiling
288.45	5.85	Boiling
299.55	7.29	Boiling
299.15	7.12	Boiling
293.95	6.74	Boiling
292.25	6.12	Boiling
281.85	5.69	Boiling
280.65	4.96	Boiling
270.95	3.42	Dew
272.95	3.62	Dew
271.65	3.39	Dew
273.85	3.60	Dew
285.15	4.72	Dew
288.15	5.07	Dew
298.75	6.56	Dew
294.15	5.91	Dew
282.15	4.54	Dew

7.3 IFT Data Values

Table 17 Interfacial tension data. IFT* is the corrected by density IFT values from DSA.

T	p	Density kg/m ³		IFT mN/m	
K	MPa	H ₂ O	CO ₂	DSA	IFT*
277.75	6.03	1002.9	920.05	410	33.9685
277.65	5.97	1002.8	920.16	355	29.3372
277.65	5.95	1002.8	919.98	345	28.5729
277.55	6.00	1002.9	921.08	394	32.23708
277.45	5.97	1002.9	921.46	362	29.48128
277.55	5.95	1002.8	920.63	347	28.51299
277.55	5.94	1002.8	920.54	353	29.03778
277.45	5.92	1002.8	921.01	329	26.90891
277.35	5.98	1002.9	922.2	420	33.894
277.35	5.94	1002.8	921.84	364	29.46944
277.35	5.94	1002.8	921.84	345	27.9312
277.35	5.93	1002.8	921.75	337	27.31385
277.35	5.93	1002.8	921.75	320	25.936
277.35	6.00	1002.9	922.38	401	32.28852
277.35	5.95	1002.81	921.93	359	29.03233
277.35	5.94	1002.8	921.84	345	27.9312
277.35	5.90	1002.8	921.49	334	27.15754
277.45	5.92	1002.8	921.01	322	26.33638
278.65	6.70	1003.2	920.22	420	34.8516
277.55	10.59	1005.1	955.24	636	31.71096
277.55	10.55	1005.1	954.99	509	25.50599
277.55	10.57	1005.1	955.11	516	25.79484
277.65	10.85	1005.2	956.36	636	31.06224
277.55	10.80	1005.2	956.56	549	26.70336
277.55	10.79	1005.2	956.49	523	25.47533
277.65	11.07	1005.3	957.72	700	33.306
277.65	11.05	1005.3	957.6	580	27.666
277.75	11.03	1005.3	956.96	530	25.6202
277.75	10.99	1005.3	956.71	500	24.295
277.75	11.23	1005.4	958.2	700	33.04

277.95	11.20	1005.4	956.99	570	27.5937
277.75	11.20	1005.4	958.01	520	24.6428
277.75	11.18	1005.4	957.89	500	23.755
277.95	11.15	1005.3	956.69	417	20.27037
278.65	10.22	1004.9	947.05	600	34.71
278.75	10.19	1004.8	946.33	640	37.4208
278.85	10.33	1004.9	946.72	620	36.0716
277.95	17.09	1008.2	988.52	1785	35.1288
278.05	16.93	1008.1	987.34	738	15.32088
277.65	15.80	1007.6	983.63	1450	34.7565
277.65	15.67	1007.5	982.99	930	22.7943
277.75	16.20	1007.8	985.14	1200	27.192
277.75	16.12	1007.7	984.76	950	21.793
277.85	16.09	1007.7	984.17	830	19.5299
277.75	16.05	1007.7	984.42	770	17.9256
277.95	16.60	1007.9	986.2	1500	32.55
277.95	16.43	1007.9	985.38	750	16.89
277.75	16.13	1007.7	984.81	1300	29.757
278.85	16.12	1007.7	979.91	1200	33.348
278.85	16.12	1007.7	979.91	1400	38.906
278.85	16.66	1007.9	982.57	830	21.0239
278.95	16.74	1007.9	982.52	720	18.2736
278.95	20.70	1009.8	1000.4	1400	13.16
278.95	20.79	1009.8	1000.8	1200	10.8
278.95	20.80	1009.8	1000.8	1100	9.9
278.95	20.82	1009.9	1000.9	1080	9.72
278.95	20.79	1009.8	1000.8	1060	9.54
278.95	21.57	1010.2	1004.0	1700	10.54
279.05	21.33	1010.1	1002.6	1200	9
278.95	21.27	1010.1	1002.8	1160	8.468
278.95	21.27	1010.1	1002.8	1050	7.665
278.95	20.92	1009.9	1001.3	1010	8.686
313.15	5.00	994.36	113.05	48.3	42.567273
313.15	5.00	994.36	113.05	47.1	41.509701
313.15	5.00	994.36	113.05	48.5	42.743535
313.15	10.00	996.52	628.61	80.6	29.653546

313.15	10.00	996.52	628.61	80.4	29.579964
313.15	10.00	996.52	628.61	76.4	28.108324
313.15	16.00	999.08	794.9	124.4	25.399992
313.15	16.00	999.08	794.9	134.8	27.523464
313.15	16.00	999.08	794.9	122.6	25.032468

7.4 Models for diffusivity

First model results:

- Assuming that at maximum mass reading is the saturation conditions reached.
- Constant flow of CO₂ into water, in other words calculating Q as:

$$Q = \frac{m_{\max} - m_0}{t_{m_{\max}} - t_0} \quad 4.4.4.1$$

Table 18 Diffusivity results for the first model and the respective pressure and temperature of each measurement

Pressure Mpa	Temperature °C	File Name	$D_{CO_2 \rightarrow H_2O}$ m ² /s
5.386E+00	4.184E+01	T40p50_1	3.623E-08
5.754E+00	4.103E+01	T40p50_2	2.414E-08
1.580E+01	3.991E+01	T40p160_1	9.163E-09
1.449E+01	3.905E+01	T40p160_2	1.112E-08
1.536E+01	4.073E+01	T40p160_3	4.318E-09
5.251E+00	6.128E+01	T60p50_2	5.392E-08
1.076E+01	6.041E+01	T60p100_1	1.245E-07
1.167E+01	4.093E+01	T60p160_1	1.245E-07
1.749E+01	6.076E+01	T60p160_2	9.694E-09
1.678E+01	6.127E+01	T60p160_3	6.723E-09
1.926E+01	6.015E+01	T60p200_1	7.292E-09

Statistical model:

- The amount of water in the sample is corrected to achieve thermodynamically consistent conditions
- Fick's law is fitted to each time step to obtain one diffusivity
- Diffusion of CO₂ is considered up to the maximum mass reading, later the sample mass values are kept constant and the vaporization of water begins.
- The mass readings corresponding to vaporization of H₂O are used to estimate H₂O diffusivity into the CO₂ rich phase.

Table 19 Diffusivity results for the statistical model and the respective pressure and temperature of each measurement

Pressure Mpa	Temperature °C	File Name	$D_{CO_2 \rightarrow H_2O}$ m ² /s	$D_{H_2O \rightarrow CO_2}$ m ² /s
5.386E+00	4.184E+01	T40p50_1	1.57E-08	2.4E-07
5.754E+00	4.103E+01	T40p50_2	1.86E-08	4.8E-07
1.580E+01	3.991E+01	T40p160_1	2.07E-08	1.2E-08
1.449E+01	3.905E+01	T40p160_2	9.21E-09	1.4E-08
1.536E+01	4.073E+01	T40p160_3	8.22E-09	3.9E-09
5.251E+00	6.128E+01	T60p50_2	4.49E-09	3.2E-08
1.076E+01	6.041E+01	T60p100_1	1.36E-08	2.5E-08
1.167E+01	4.093E+01	T60p160_1	1.01E-08	2.1E-08
1.749E+01	6.076E+01	T60p160_2	8.02E-09	1.0E-08
1.678E+01	6.127E+01	T60p160_3	1.09E-07	7.1E-09
1.926E+01	6.015E+01	T60p200_1	4.48E-09	3.5E-09

Continuous model:

- Same considerations as statistical model but using long time solution to the second Fick's law to fit parameters instead of a punctual contribution.

Table 20 Diffusivity results for the continuous model and the respective pressure and temperature of each measurement and their nominal length

Pressure Mpa	Temperature °C	File Name	Nominal Length over legth	$D_{CO_2 \rightarrow H_2O}$ m ² /s	$D_{H_2O \rightarrow CO_2}$ m ² /s
5.386E+00	4.184E+01	T40p50_1	1.46923085	4.8404E-08	2.4E-07
5.754E+00	4.103E+01	T40p50_2	2.05905283	1.9804E-08	4.8E-07
1.580E+01	3.991E+01	T40p160_1	0.60242894	4.801E-07	2.9E-08
1.449E+01	3.905E+01	T40p160_2	0.51640969	2.0839E-07	3.0E-08
1.536E+01	4.073E+01	T40p160_3	1.32755154	6.9804E-08	3.0E-08
5.251E+00	6.128E+01	T60p50_2	0.79171835	7.7431E-08	1.2E-07
1.076E+01	6.041E+01	T60p100_1	1.3512332	8.5213E-08	8.1E-08
1.167E+01	4.093E+01	T60p160_1	0.92048451	8.2995E-08	6.6E-08
1.749E+01	6.076E+01	T60p160_2	1.05776712	5.0055E-08	4.0E-08
1.678E+01	6.127E+01	T60p160_3	4.02622258	2.3665E-06	4.2E-08
1.926E+01	6.015E+01	T60p200_1	0.78834585	4.1463E-08	3.7E-08

Stoke Einstein Equation + Cadogan hydrodynamic Radios

- In order to have comparison, the Stoke Einstein equation will be used, with the correction to the hydrodynamic radios of water as function of temperature (Shane, 2014):

Table 21 Mutual diffusivities for CO₂+H₂O system calculated by Stoke-Einstein Equation, with Cadogan's hydrodynamic radio correlation.

H ₂ O viscosity Pa s	CO ₂ viscosity Pa s	Pressure MPa	Temperature °C	File Name	$D_{CO_2 \rightarrow H_2O}$ m ² /s	$D_{H_2O \rightarrow CO_2}$ m ² /s
6.316E-04	1.735.E-05	5.386E+00	4.184E+01	T40p50_1	3.153E-09	8.1E-09
6.411E-04	1.763.E-05	5.754E+00	4.103E+01	T40p50_2	3.103E-09	1.1E-08
6.559E-04	6.974.E-05	1.580E+01	3.991E+01	T40p160_1	3.029E-09	3.4E-08
6.663E-04	6.748.E-05	1.449E+01	3.905E+01	T40p160_2	2.978E-09	1.6E-08
6.461E-04	6.776.E-05	1.536E+01	4.073E+01	T40p160_3	3.078E-09	8.1E-09
4.584E-04	1.786.E-05	5.251E+00	6.128E+01	T60p50_2	4.445E-09	1.3E-08
4.657E-04	2.618.E-05	1.076E+01	6.041E+01	T60p100_1	4.371E-09	1.1E-08
6.431E-04	3.035.E-05	1.167E+01	4.093E+01	T60p160_1	3.093E-09	9.2E-09
4.650E-04	5.330.E-05	1.749E+01	6.076E+01	T60p160_2	4.380E-09	9.2E-09
4.613E-04	5.084.E-05	1.678E+01	6.127E+01	T60p160_3	4.417E-09	1.1E-08
4.696E-04	5.823.E-05	1.926E+01	6.015E+01	T60p200_1	4.333E-09	1.3E-08