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Equilibrium between Carbonates, CO₂ and Brine

By

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**A report submitted in partial fulfilment of the requirements for
the MSc and/or the DIC.**

September 2011

Declaration of own work

I declare that this thesis “**Equilibrium between Carbonates, CO₂ and Brine**” is entirely my own work and that where any material could be construed as the work of others, it is fully cited and referenced, and/or with appropriate acknowledgement given.

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Table of Contents

Declaration of own work	ii
Acknowledgements.....	iii
List of Figures.....	v
List of Figures in Appendices	v
List of Tables	v
List of Tables in Appendices	v
Abstract.....	1
Introduction	1
Experiments	3
Experimental Conditions	3
Experimental Apparatus	4
Experimental Procedure.....	4
Equilibration between Carbonates, CO ₂ and Brine.....	5
Discussion of Results.....	6
Examining the Hydro-phobic Porous Plate against CO ₂ Flow	8
Conclusions and Future Work	9
Conversion factors	9
Nomenclature.....	9
References	10
Appendix A: Critical Literature Review	I
American Journal of Science Vol. 52 (1952).....	II
Poster presented at the 5th Annual Conference on CCS (2005)	III
Geochimica et Cosmochimica Acta Vol. 72 (2008)	IV
SPE 115663 (2008).....	V
International Journal of Greenhouse Gas Control (2009)	VI
Geophysics Research Letters Vol. 38 (2011).....	VII
Appendix B: Core Preparation.....	VIII
Appendix C: CO ₂ -Saturated Brine Experiment 1 Detailed Results	IX
Appendix D: CO ₂ -Saturated Brine Experiment 2 Detailed Results	X
Appendix E: Calcite Solubility in CO ₂ -Saturated Brine (After Duan & Li 2008).....	XI
Appendix F: Time Needed for Equilibrium Calcite Solubility in CO ₂ - Brine System(After Miller 1952)	XII

List of Figures

Figure 1 shows the increasing storage security for CO ₂ with time (Source: IPCC 2005).....	2
Figure 2 shows the Ketton rock sample used in the equilibration between the carbonates and CO ₂ -saturated brine.	3
Figure 3 shows the experimental apparatus used for equilibrating CO ₂ , brine and carbonates.	4
Figure 4 shows the average amount of dissolved carbonates per sample for the 2 nd experiment.	6
Figure 5 shows the average amount of dissolved carbonates per cycle for the 2 nd experiment.	6
Figure 6 shows the average dissolved carbonates in solution (per cycle) for both experiments.	8
Figure 7 shows the experimental apparatus used to examine the oil-wet porous plate.....	8

List of Figures in Appendices

Figure AP- 1 shows the process of core preparation prior to placing it inside an oven.	VIII
Figure AP- 2 shows the Hassler cell installed in the oven.	VIII
Figure AP- 3 shows the predicted calcite solubility using Duan and Li 2008 thermodynamic model.	XI
Figure AP- 4 shows the time needed for calcite solubility to reach equilibrium (source Miller 1952).	XII

List of Tables

Table 1 shows the volumes of CO ₂ -saturated brine injected into the rock sample in each cycle of experiment 2.	5
Table 2 shows differences in experimental errors for the analysed samples in experiment 2.	7

List of Tables in Appendices

Table AP- 1 shows the detailed raw data and calculations for experiment 1.....	IX
Table AP- 2 shows the detailed raw data and calculations for experiment 2.....	X

Equilibrium between carbonates, CO₂ and brine

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Abstract

Since the 1950's, CO₂ injection into geological formations has been used in the petroleum industry to enhance oil recovery. It has been suggested that this major greenhouse gas can be stored safely in geological formations to help mitigate global warming. Deep saline aquifers have the highest capacity to store CO₂ underground. Since the presence or integrity of a sealing cap rock in an aquifer is not certain most of the time, an effective mechanism to store CO₂ safely without leakage is through capillary trapping. In capillary trapping, CO₂, which is usually the non-wetting phase, is trapped by brine. While capillary trapping has been observed in sandstone, there is less direct evidence of this mechanism in carbonates. This is due to the reactivity of carbonate rocks with CO₂ which might result in dissolution or precipitation of carbonate minerals, confusing the experimental results. In this experiment, we inject CO₂-saturated brine into a carbonate rock sample at 9 MPa and 50 °C to produce an equilibrium solution between carbonates, brine and CO₂ which will allow future capillary trapping experiments on carbonate rock without the competing effects of mineral precipitation or dissolution. At these conditions, we obtain an equilibrium solution in the third injection cycle after injecting fifty-five pore volumes of CO₂-saturated brine into the carbonate rock sample. The dissolved quantity of carbonates in the solution was measured at equilibrium to be 0.00224 g/mL. A secondary experiment was conducted to examine the hydrophobic (oil-wet) porous plate against CO₂ flow. It has been found that CO₂ could pass through the hydrophobic porous plate. Therefore, the oil-wet porous plate can be used to conduct waterflood experiments at controlled water saturation for capillary trapping experiments.

Introduction

Fossil fuels supply around 85% of the world's energy and they are likely to remain the major source of energy in the near future. However, burning fossil fuels increases the concentration of greenhouse gases significantly in the atmosphere and therefore it augments global warming. Major greenhouse gases include carbon dioxide, methane and nitrous oxide. Carbon dioxide is the largest produced greenhouse gas when petroleum sources are burnt (Bouzalakos and Maroto-Valer 2010). The average concentration of CO₂ has been increasing from 317 ppm in 1960 to 390 ppm in 2010 based on the mean annual data measured at Mauna Loa Observatory (ESRL Website 2010). If the world use of energy follows current trends, the concentration of CO₂ in the atmosphere will almost double by 2054, very likely resulting in major changes in the climate that will negatively affect life on this planet (Bouzalakos and Maroto-Valer 2010).

In order to meet the world's energy need for energy without having significant harmful effects on the environment, one option is to continue using fossil fuels in combination with carbon capture and storage (Hester and Harrison 2010). Carbon dioxide capture and storage (CCS) includes separating CO₂ from large sources (such as power stations and refineries), transporting it to locations where it can be injected and stored in underground geological formations (Bouzalakos and Maroto-Valer 2010). According to the 2005 IPCC report, CCS could result in considerable reductions of the CO₂ level in the atmosphere (IPCC 2005).

CO₂ can be stored efficiently in depleted oil & gas reservoirs and deep saline aquifers. It can be also injected into a producing oilfield to enhance the oil recovery. In this case, the cost of the CO₂ storage projects can be offset by the additional oil recovered due to CO₂ injection. Deep saline aquifers have the highest capability to store CO₂ due to, in part, their largest volume and, in part, their immediate availability to store CO₂ without awaiting hydrocarbons to be depleted for oil and gas reservoirs. It is noteworthy to mention here that it is also plausible to store CO₂ in un-mineable coal beds but the technology to do so is not fully developed yet (IPCC 2005).

Field applications of CO₂ injection into oilfields indicated that it is a promising technology to enhance oil recovery (IOCC 1983). One advantage of injecting CO₂ rather than hydrocarbon gas or nitrogen is that the minimum miscibility pressure (MMP) is considerably lower with CO₂. Another advantage is that the gravity segregation between CO₂ and reservoir oil is not significant due to the similar densities of both fluids at reservoir conditions (Stalkup 1983). This results in a better contact between the CO₂ and reservoir oil which in turn improves the sweep efficiency of the reservoir. On the other hand, a disadvantage of CO₂ flooding is the low viscosity of carbon dioxide at reservoir conditions which results in unfavorable mobility ratio between CO₂ and oil in the reservoir. To overcome this problem, it has been the practice to displace the injected CO₂ with water (Stalkup 1983). However, some of the injected CO₂ will be trapped by the injected water due to the

immiscibility between the two fluids. Furthermore, some of the CO₂ will dissolve in the injected water at reservoir conditions (Stalkup 1983). Even though trapping and dissolving CO₂ are not desired in enhanced oil recovery processes as the sweep efficiency will be reduced, this concept can be used to store CO₂ in oil reservoirs during enhanced oil recovery operations. In this case, the cost of CO₂ storage, which is a main obstacle in implementing CCS projects at a large scale, can be offset by the incremental oil recovery achieved due to CO₂ injection (IPCC 2005; Vega & Kavscek 2010). One simulation study performed by (Qi *et al.* 2008) suggested that injecting more water than the traditional water gas ratio would co-optimize both enhanced oil recovery and CO₂ storage in oilfields.

In order for a CCS project to be successful, it is important for CO₂ to be stored for a long time (up to thousands of years) without leaking from the storage formation. There are four main trapping mechanisms for CO₂: structural, dissolution, mineralisation and residual trapping (capillary trapping) (IPCC 2005 and Blunt 2010). Structural trapping occurs when the CO₂ plume is prevented from upward migration by a cap rock which usually has a very low permeability (IPCC 2005). Dissolution trapping occurs when some of the injected CO₂ is dissolved in the formation water. This process is quick at the beginning (Rosenbauer and Koksalan 2002). However, it can take thousands of years for CO₂ to saturate the formation water as dissolution depends on the contact between CO₂ and formation water which eventually becomes less favourable due to the density differences between CO₂ and formation water (Ennis-King and Paterson 2000). Furthermore, the resultant solution (CO₂ dissolved in formation water) is a weak acid and it may react with formation rocks to form immobile carbonate minerals which can be trapped for a very long time. This mechanism is referred to as the mineral trapping mechanism. However, the mineralisation reaction is slow and it can take thousands to millions of years (Gunter *et al.* 1993; Blunt 2010). Capillary trapping occurs when the injected CO₂ is trapped inside the pores by water. This is considered important as trapping can occur during the CO₂ injection time (IPCC 2005; Blunt 2005). Therefore, CO₂ storage security increases with time as different trapping mechanisms become more dominant and hence the issue of storage security is more critical during CO₂ injection time as shown in Figure 1.

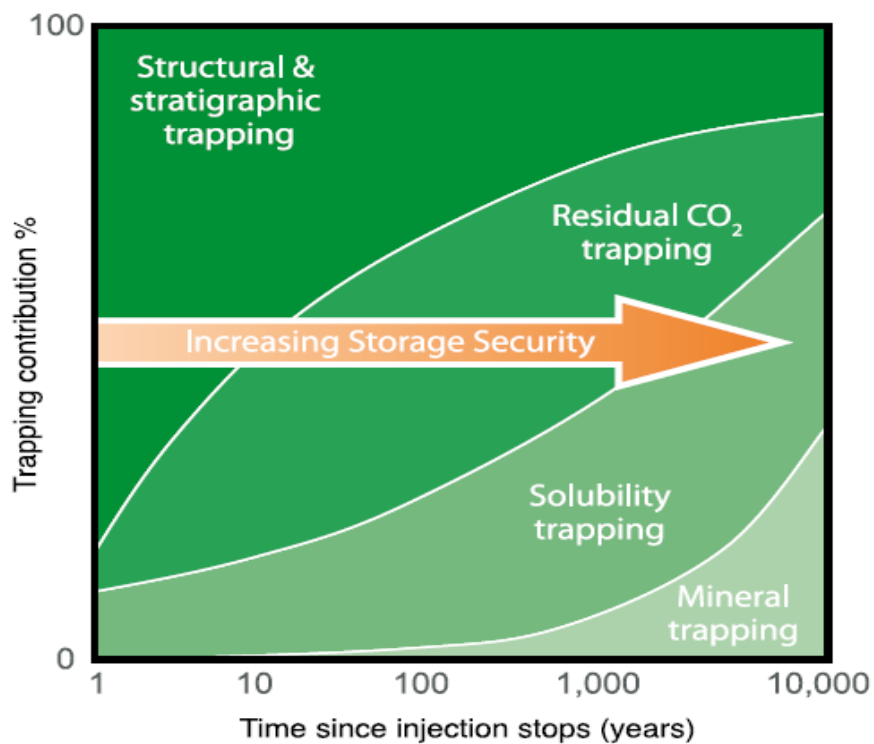


Figure 1 shows the increasing storage security for CO₂ with time (Source: IPCC 2005).

Since solubility and mineral trapping may take hundreds or thousands of years to become efficient trapping mechanisms, carbon dioxide has to be trapped safely without significant leakage by other mechanisms. A quick trapping mechanism could be the presence of a sealing cap rock which is considered a key element to assess the capability of a geological formation to be a potential storage site (IPCC 2005). Whereas the integrity of a cap rock might be known with a good level of confidence in depleted oil and gas reservoirs, this might not be the case in a deep saline aquifer as its geological characterisation is not clearly defined most of the time. In such cases, CO₂ can be rendered immobile by means of capillary

trapping. This mechanism could be used efficiently because CO₂ is the non-wetting phase in the storage locations and hence it can be trapped in the larger pores by the wetting phase (brine). Capillary trapping can be further enhanced if chase brine is injected into the formation. This trapping mechanism has proved its efficiency in many simulation studies (for example, Obi & Blunt 2006; Juanes *et al.*, 2006 and Ide *et al.*, 2007 and Qi *et al.* 2009).

Due to the significance of the capillary trapping particularly in deep saline aquifers, it is important to develop a good level of understanding about it. Capillary trapping has been studied and observed more in sandstone compared to carbonate rocks. The trapping curve (CO₂ residual saturation vs. CO₂ initial saturation) is already available in the literature for water-wet sandstone (see Pentland *et al.* 2011). However, the reactivity between CO₂ and carbonates in the presence of aqueous solution makes it more difficult to perform similar experiments on carbonate rocks as there will be alteration in the rock matrix (refer to Grigg *et al.* 2005). The solubility of limestone minerals (calcite, dolomite and magnesite) in water is significantly enhanced if carbon dioxide is added to the system. Other factors which affect the solubility are pressure and temperature. As pressure increases, the solubility will increase. On the other hand, the effect of increasing temperature is a decline in the limestone solubility in a water-CO₂ system (Boynton 1980).

Since CO₂ is stored underground at high pressures, it is expected to have significant limestone solubility in brine. It is possible that carbonates show insignificant or no capillary trapping for CO₂. Therefore, it is necessary that confounding factors, such as minerals dissolution or precipitation, are eliminated when capillary trapping experiments are conducted on carbonates. The objective of this project is to produce an equilibrium solution between carbonates, carbon dioxide and brine that will allow for capillary trapping experiments without alteration of the rock matrix. In field settings where CO₂ is injected into carbonates, fluids and rock are in equilibrium away from the wellbore as they have been in contact for some time. Therefore, a displacement experiment with equilibrium between fluids could be used to represent realistic conditions.

Experiments

The primary experiment is conducted to produce an equilibrium solution between CO₂, brine and carbonates. The equilibration between the three elements is studied by injecting CO₂-saturated brine at a rate of 3 mL/min into a Ketton carbonate rock sample. Ketton is a Lincolnshire oolitic limestone. It was deposited in warm and shallow seas approximately 165 million years ago under estuarine conditions (Hains 1969). Ketton rock is extracted from a site located in the village of Ketton, Rutland in central England (Natural England Website 2011). Using the x-ray diffraction analysis, the composition of Ketton limestone was found to be 99.1% calcite (CaCO₃) and 0.9% quartz (SiO₂) (Gharbi 2011, Pers. Com.). Therefore, the equilibrated solution in this experiment is to be obtained between carbon dioxide, calcite and brine. Figure 2 shows the picture of a Ketton rock sample.

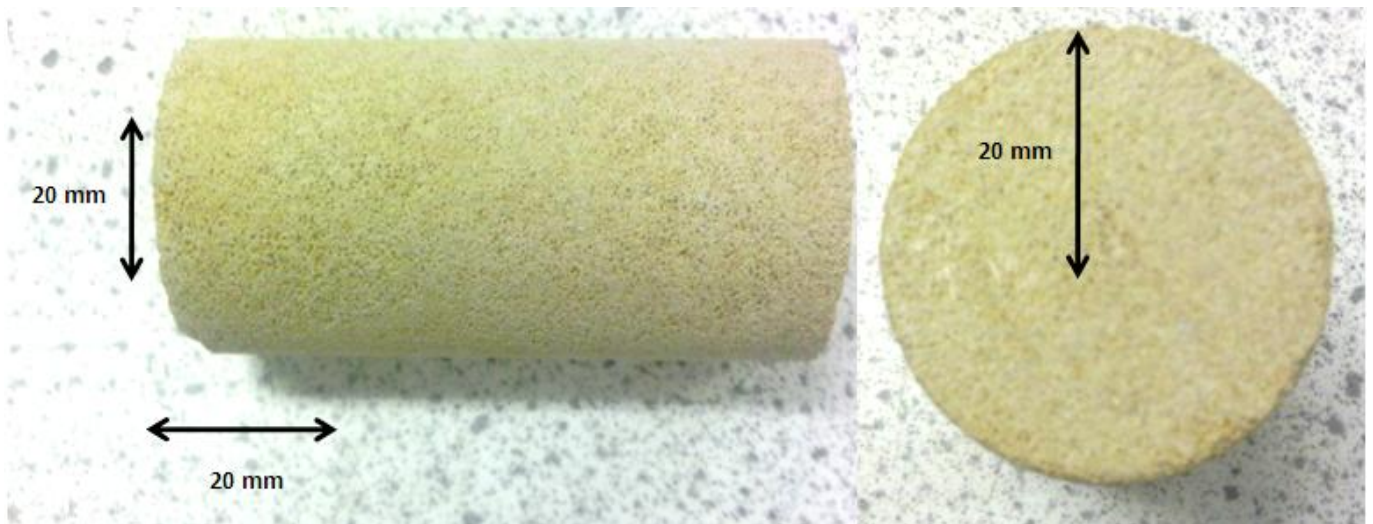


Figure 2 shows the Ketton rock sample used in the equilibration between the carbonates and CO₂-saturated brine.

Also, a secondary experiment was conducted to examine whether the hydro-phobic (oil-wet) would allow CO₂ to pass through it or not. This is done to see if oil-wet porous plates can be used to conduct waterflood experiments to controlled water saturation for capillary trapping experiments.

Experimental Conditions: Experiments were conducted at a pressure of 9 MPa and temperature of 50 °C representative to storage conditions for CO₂. The Ketton rock sample was placed in a Hassler cell which was put inside an oven during the experiments. The pumps used to inject and receive the solution were kept at 50 °C by circulating water from a water bath

system. All tubes outside the oven were isolated by insulators to minimise the heat transfer. The brine used has 5 wt. % sodium chloride and 1 wt. % potassium chloride. The density of this brine is 1.0405 g/mL at 20 °C.

Experimental Apparatus: A Hassler cell was used to house the rock sample inside the oven. The flow rate was adjusted at the experiment pressure using High precision syringe pumps (Teledyne ISCO 500D & 1000D, Lincoln, NE, USA). A radial confining pressure (2.76 MPa higher than the pore pressure) was applied on the rock sample to maintain flow from the inlet to the outlet of the core only. Hastelloy flow lines were used to minimise the corrosion which is augmented by adding CO₂ to the system. Mesh filters were installed to avoid flowing suspended particles to the pumps causing them to erode. Each filter set consists of 7 µm and 0.5 µm installed from the upstream to the downstream flow, respectively. To equilibrate CO₂ with brine at experiment conditions, a stirred reactor (1200 mL C276 autoclave with gas entrainment stirrer- Parr Instruments Co., IL, USA) was used. The experimental apparatus is illustrated in Figure 3.

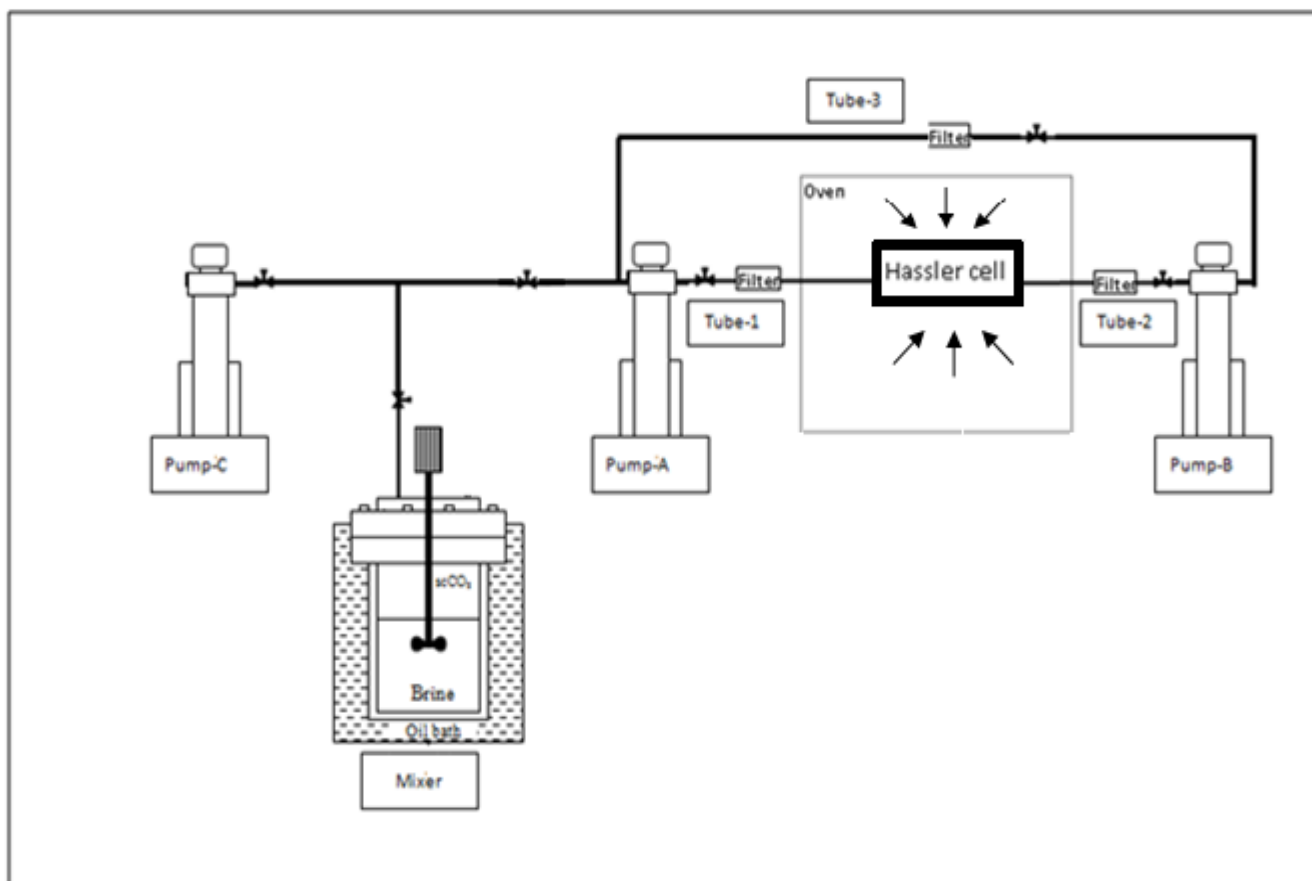


Figure 3 shows the experimental apparatus used for equilibrating CO₂, brine and carbonates.

Experimental Procedure: The core preparation procedure is explained in Appendix B. Before starting the equilibration experiment, brine is equilibrated with supercritical CO₂ using the equilibration reactor as shown in the following procedure:

1. The reactor is filled with 800 ml of de-aerated brine. The reactor is heated in an oil bath.
2. Pump-C is filled with CO₂.
3. CO₂ is then pressurised to 9 MPa. Also, the pump temperature is maintained at 50 °C by circulating water through a water bath system.
4. Supercritical CO₂ is pumped to the reactor and stirred for one hour. The equilibration between brine and CO₂ is confirmed when the volume of CO₂ in the pump remains constant implying no more CO₂ is dissolved in the brine.
5. After equilibrium has been reached between the supercritical CO₂ and brine, the solution is transferred to Pump-A.

After equilibrating brine with supercritical CO₂, the following procedure is followed to produce an equilibrium solution between the CO₂-saturated brine and carbonates:

1. The system temperature (including oven, pumps and the reactor) is maintained at 50 °C.

2. The entire system is vacuumed using a vacuum pump. After that, the system is filled with CO₂-saturated brine.
3. Pump-A is filled with a known volume solution. This pump is adjusted to a constant pressure mode (9 MPa) throughout the experiment.
4. CO₂-saturated brine is injected from Pump-A through the rock sample to Pump B at constant flow rate.
5. Samples are collected from a sampling valve frequently. When all solution has been transferred from Pump-A to Pump B, one cycle is complete. After that, the solution is transferred to Pump-A through Tube-3.
6. We repeat step-1 to step-4 for the subsequent cycles.

The apparatus and procedure of the secondary experiment, which was performed to test the hydro-phobic (oil-wet) porous plate against CO₂ flow, is similar to the apparatus of the primary experiment. This experiment will be explained further in a later chapter of this report.

Equilibration between Carbonates, CO₂ and Brine

Two experiments have been performed on the same Ketton rock sample to establish equilibrium between carbonates and CO₂-saturated brine. The results of the second experiment are more representative because the rock sample was washed efficiently after injecting approximately 100 pore volumes of CO₂-saturated brine in the first experiment. Therefore, the second experimental results will be discussed thoroughly in this chapter. In both experiments, the brine was firstly equilibrated with supercritical CO₂ using the reactor as explained above in the experimental procedure with an average CO₂ solubility of 0.872 moles of CO₂/kg of brine. The Ketton rock sample used in this experiment has a length of 76.40 mm and a diameter of 37.80 mm. The porosity of this sample was measured using helium porosimeter to be 22.42%.

In the second experiment, Pump-A was filled with 361 mL of CO₂ -saturated brine at a pressure of 9 MPa and a temperature of 50 °C. The solution was injected from Pump-A through the Ketton rock sample and received by Pump-B throughout five cycles at a rate of 3 mL/min. At this rate, the solution residence time in the core at our experimental rate is 6.4 minutes every cycle. Almost 78 pore volumes (PV) were injected into the rock sample as shown in Table 1.

Table 1 shows the volumes of CO₂-saturated brine injected into the rock sample in each cycle of experiment 2.

Cycle	Total Volume Injected mL	Pore Volumes Injected Dimensionless
1	361	18.8
2	323	16.8
3	298	15.5
4	274	14.2
5	249	13.0
Total	1505	78.3

During each cycle, samples were collected in an isolated tube at the same system pressure. After that, the isolated tube is disconnected from the system and emptied in a test tube. This was done to avoid a sudden pressure drop which could result in disturbance in the equilibrated CO₂-saturated brine.

The samples were weighed and then dried in an oven at a temperature of (100-105 °C). After evaporating all the water, the precipitated solids were weighed. The weight of carbonates is calculated by subtracting the weight of sodium chloride and potassium chloride originally dissolved in the known volume of brine which is 0.6285 g/mL at 20 °C. The solution volume was found by dividing the weight of the sample by the density of brine after allowing all CO₂ to liberate from the solution. This assures that the sample volume is found accurately and independently from the pump logs which record the volume at elevated pressure and temperature. The concentration of carbonates is then calculated by dividing the weight of carbonates by the volume of solution. To ensure a good precision is attained, all weighting was recorded to the nearest 0.1 mg.

Figure 4 and Figure 5 show the dissolved carbonates in solution of the second experiment.

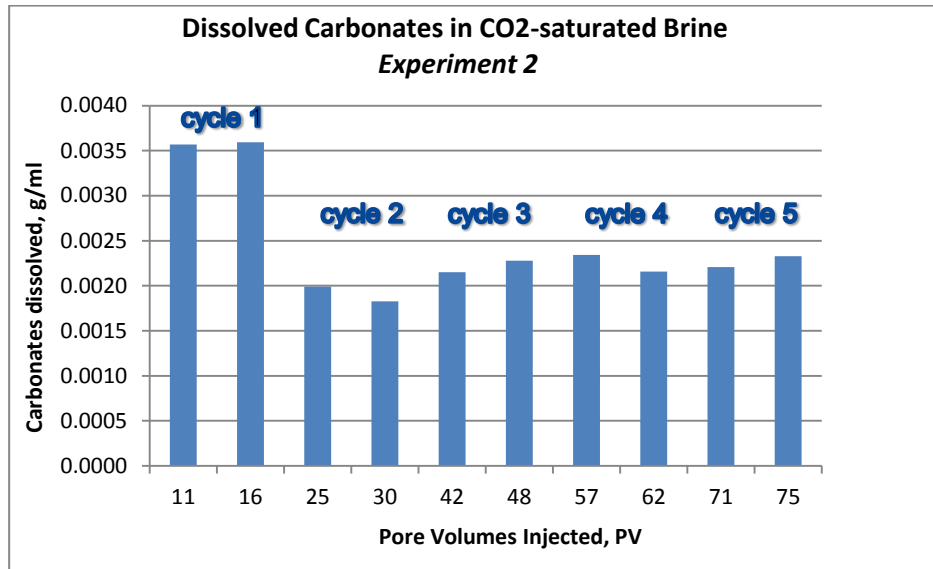


Figure 4 shows the average amount of dissolved carbonates per sample for the 2nd experiment.

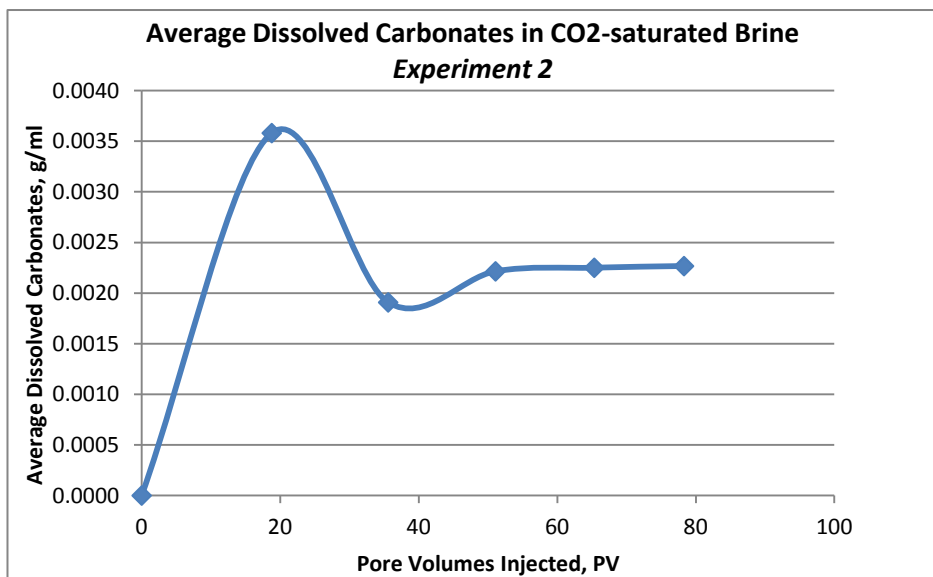
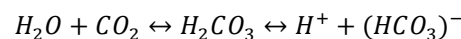


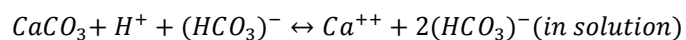
Figure 5 shows the average amount of dissolved carbonates per cycle for the 2nd experiment.

Discussion of Results

As stated previously in the introduction, the solubility of calcite (CaCO₃) in water is improved when there is CO₂ (Grigg *et al.* 2005). CO₂ reacts with water to form carbonic acid (Miller 1952):



This weak acid reacts with CaCO₃ to dissolve bicarbonates in water:



Theoretically, any two samples in the same cycle should have the same concentrations of dissolved carbonates. An error tolerance has been calculated by analysing five samples of the brine used in the experiment and then comparing the results to the amounts of salts originally dissolved in brine. The brine samples were analysed exactly as the samples collected during the experiment. Considering the concentrations of carbonates in our experiment, the error tolerance for dissolved carbonates concentrations is ± 0.0002 g/mL. The results of the two samples in each cycle are within the allowable error

tolerance as shown in Table 2.

Table 2 shows differences in experimental errors for the analysed samples in experiment 2.

Cycle	Concentration of 1st Sample g/mL	Concentration of 2nd Sample g/mL	Difference between results g/mL
1	0.00357	0.00359	0.00002
2	0.00199	0.00183	0.00016
3	0.00215	0.00228	0.00013
4	0.00234	0.00216	0.00018
5	0.00221	0.00233	0.00012

Looking at Figure 4 and Figure 5, there is a relatively high dissolved carbonates in the first cycle compared to the subsequent cycles. Analysis showed an average carbonate concentration of 0.00358 g/mL for the first cycle. This relatively high value can be explained by the deposition of the dissolved carbonates in some components of the system resulting in a lower carbonates concentration in subsequent cycle (Grigg *et al.* 2005). Grigg and his group showed that deposition of carbonates can occur downstream in the rock sample itself. In their CO₂ and brine injection experiments in limestone, they concluded that the deposition is highly augmented by the brine composition. Another explanation is that the lower concentration in subsequent cycles happened because of the deposition of some suspended particles in Pump-B at the end of the first cycle.

Duan and Li developed a thermodynamic model to predict the solubility of calcite in CO₂ saturated 1M NaCl at 50 °C to be 0.037 mol/kg and 0.051 mol/kg at pressures of 50 bars and 500 bars, respectively (Duan and Li 2008). Results of Duan and Li model are included in Appendix E. By linear interpolation at our experimental pressure, which is 90 bars, the solubility of CaCO₃ is estimated to be 0.0385 mol/kg. Knowing that the molecular weight of CaCO₃ is 100.0869 g/mol and the density of the brine used in the experiment is 1.0405 g/ml, the solubility of CaCO₃ in g/mL is:

$$0.0385 \frac{\text{mol}}{\text{kg}} \times 100.0869 \frac{\text{g}}{\text{mol}} \times 1.0405 \frac{\text{g}}{\text{mL}} \times \frac{1\text{kg}}{1000\text{g}} = 0.00401 \text{ g/mL}$$

In our experiment, all cycles have experimental solubility values that are lower than the value from the Duan and Li model. During our experiment, CO₂ was equilibrated with brine prior to injecting it into the rock sample. However, no additional CO₂ was added to the system at the end of each injection cycle. Therefore, pH of the solution was likely increased after the calcite dissolution in the first cycle affecting the CO₂ saturation in brine. As pH increases, the solubility of calcite in water decreases (Ceyhan *et al.* 2011). We implied that lower solubility values (compared to Duan and Li model) are most likely because the solution is no longer saturated by CO₂ after reacting with the rock. Also, the presence of homogenous impurities which contaminated the rock during deposition (such as quartz) results in a lower solubility value (Miller 1952; Boynton 1980).

During our experiment, the solution was injected into the rock sample through five cycles. Hence, the contact time between the solution and rock sample was 32 minutes (note that the residence time is 6.4 minutes per cycle). We assume that this contact time is sufficient to achieve calcite solubility close to the maximum solubility. At a pressure of 10 bars and 42 °C, the solubility achieved after 30 minutes is less than the maximum solubility, which was achieved after about one hour, by only less than 0.00003 g/mL (Miller 1952). Refer to Appendix F for further details.

Looking at Figure 5, it is clear that equilibrium between carbonates (represented by the stable soluble calcite), CO₂ and brine has been established after the injection of fifty-five pore volumes of the solution in three cycles. This is proved by the approximately equal amounts of dissolved carbonates in cycle-3, cycle-4 and cycle-5. Based on the results of these three cycles, no further dissolution of carbonates was observed despite the additional thirty pore volumes which were injected into the rock sample. As a result, an equilibrated solution between carbonates and CO₂ saturated brine exists at 9 MPa and 50 °C for the Ketton rock sample with an average carbonates concentration of 0.00224 g/mL. This equilibrated solution can be used to study the capillary trapping without the competing effects of dissolving or precipitating more carbonates in the core and hence the properties of the rock sample can be preserved.

However, it is important to mention here that this equilibrated solution between CO₂-saturated brine and carbonates was only achieved after running two experiments on the same rock sample. During the first experiment, a cumulative of one hundred pore volumes of solution was injected into the rock sample. A stabilisation at a concentration of 0.00151 g/mL was observed after injecting approximately eighty pore volumes of solution. The average results of the first experiment are plotted with the second experiment results in Figure 6.

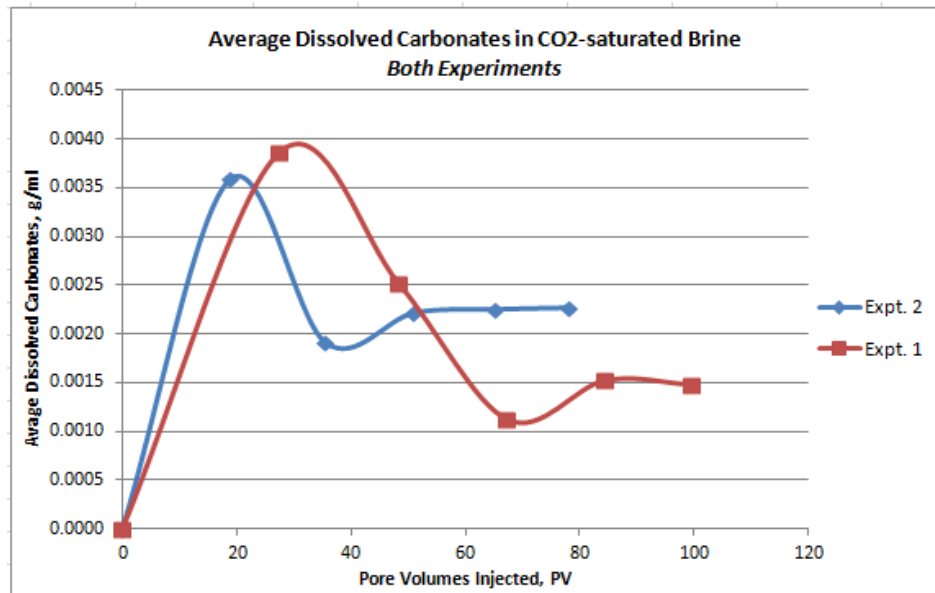


Figure 6 shows the average dissolved carbonates in solution (per cycle) for both experiments.

From the above figure, it is implied that the first experiment stabilisation was achieved at a lower level than second experiment stabilisation (values are 0.00151 and 0.00224 g/mL for 1st experiment and 2nd experiment, respectively). At the end of each experiment, the pump effluent was collected. Experiment 1 effluent was yellow and had coarse grains which were suspended in the effluent. On the other hand, the effluent of experiment 2 had white grains which were initially dissolved in the effluent. We conclude that the second experiment is more representative for equilibration because of the dissolution of pure carbonates (white in colour). Apparently, the higher stabilisation is because the solution was in contact with pure carbonates grains in the second experiment while the contact was with the surface grains of the rock. Even though the x-ray diffraction analysis is almost pure calcite (99.1% calcite), there might have been a change in the properties of the surface grains of the rock due to weathering after rock deposition. This explains the existence of yellow particles, rather than white ones, in the first experiment.

It is noteworthy to mention here that the trends of both experiments were similar. Each experiment starts with a relatively high carbonate concentration and then the concentration becomes lower before stabilising. The delay in the first experiment stabilisation might be due to leaving the solution in the pump overnight together with a free CO₂ phase after the first cycle. We implied that the solution was saturated with CO₂ which resulted in obtaining another high concentration in cycle 2. Because no extra CO₂ was added from cycle 2 onwards, these cycles show similar trend to experiment 2.

For detailed raw data and results for experiment 1 and 2, refer to Appendix C and Appendix D.

Examining the Hydro-phobic Porous Plate against CO₂ Flow

The last part of this experiment was to examine the hydro-phobic (oil-wet) porous plate against CO₂ flow. This porous plate is manufactured to allow the flow of oil and cease the flow of water. The apparatus of this experiment is very similar to the one used in the primary experiment. However, a porous plate was attached to the rock sample before housing it in the Hassler cell. A schematic diagram of the apparatus is shown in Figure 7.

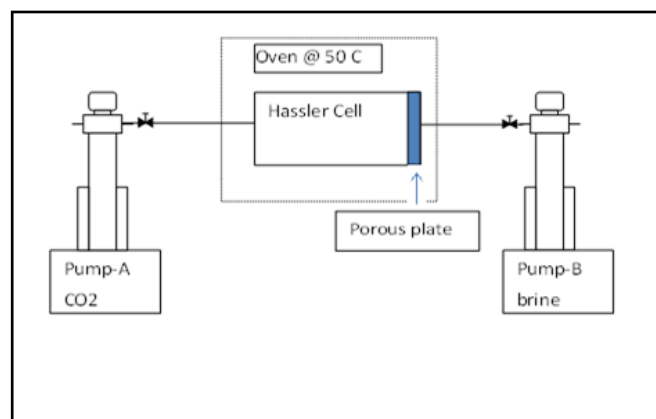


Figure 7 shows the experimental apparatus used to examine the oil-wet porous plate.

In this experiment, Pump-A was filled with CO₂ while pump-B was filled with brine. Two transducers were installed upstream and downstream from the porous plate to monitor the pressure drop across it. Throughout the experiment, the pressure drop was kept below 1.5 MPa which is the maximum operating limit for this porous plate. Initial pressures at Pump-A and Pump-B were 2.00 MPa and 0.50 MPa, respectively. After opening Pump-A to flow through the core, Pump-A pressure was gradually increased to 5.50 MPa. Simultaneous increase in the downstream pressure had been observed during the experiment maintaining a low pressure drop (less than 0.20 MPa). This proves that the hydro-phobic porous plate could allow CO₂ to flow through it. The quick increase in the downstream pressure (which results in lower pressure drop across the porous plate) is explained by the high mobility of CO₂ due to its low viscosity according to Darcy's law:

$$Q = -\frac{K}{\mu}\nabla P$$

As a result, the hydro-phobic porous plate can be used in experiments where it is desired to allow CO₂ flow through the porous plate and cease water flow. For example, this porous plate could be utilised in waterflood experiments to controlled water saturation for capillary trapping experiments. Water saturation can be controlled as only CO₂, but not water, can be displaced through the porous plate.

Conclusions and Future Work

We conclude that an equilibrium solution exists between Ketton rock sample and CO₂-saturated brine. At pressure of 9 MPa and temperature of 50 °C, the equilibrated solution was reached in the third cycle after injecting about fifty-five pore volumes. It has a calcite concentration of 0.00224 g/ml. We also conclude that it is necessary to wash the core before achieving a representative equilibration. In our case, pure calcite solubility (which has a white colour) appears only after injecting one-hundred pore volumes of CO₂-saturated brine.

Nevertheless, the equilibrium between carbonates and CO₂-saturated brine is expected to change whenever the solubility changes. Solubility depends on pressure, temperature and the concentration of salts dissolved in brine (Miller 1952; Boynton 1980; Duan and Li 2008). Also, the solubility of carbonates in solution will be slightly different if the carbonate rocks contain other minerals like magnesite and dolomite (Boynton 1980). In these cases, the equilibrium solution between carbonates and CO₂-saturated brine should be produced at the desired experimental conditions.

One area of improvement to this experiment is to use a reactor instead of Pump-A to refresh the solution with CO₂ at the end of each cycle (refer to Figure 3). This is done to keep the brine fully saturated with CO₂ after having reacted with calcite in each cycle. This will help achieve higher solubility values which are more reliable as pH will be maintained the same throughout the experiment.

CO₂ capillary trapping with water in carbonate rocks is not well understood in laboratory experiments due to the pronounced reactivity between CO₂ and rock minerals. Having produced an equilibrated solution, capillary trapping experiments on carbonate rocks will be conducted in the future without alteration of the rock fabrics as no further minerals dissolution or precipitation is expected to take place in the rock sample. Prior to conducting a trapping experiment on the carbonate rocks, the CO₂-saturated brine will be equilibrated with a rock sample which is similar to the one at which the trapping experiment will be performed. In addition to trapping experiments, the equilibrated solution can also be used to conduct CO₂-saturated brine and carbon dioxide relative permeability experiments on the carbonate rocks.

The oil-wet porous plate was examined against CO₂ flow. We concluded that this porous plate could pass CO₂. As a result, it can be used to run waterflood experiments at controlled water saturation during capillary trapping experiments.

Conversion factors

<i>MPa</i>	<i>X</i>	1.450 377	<i>E + 02</i>	<i>= psi</i>
<i>bar</i>	<i>X</i>	1.450 377	<i>E + 01</i>	<i>= psi</i>
<i>C</i>	<i>X</i>	1.8 + 32		<i>= F</i>
<i>Pa.s</i>	<i>X</i>	1.0 *	<i>E + 03</i>	<i>= cp</i>

*Conversion factor is exact

Nomenclature

CCS= carbon capture and storage

MMP= minimum miscibility pressure

Q= flow rate

μ= viscosity

P= pressure

K= permeability

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APPENDICES

Appendix A: Critical Literature Review

Paper	Year	Title	Authors	Contribution
AJS Vol. 52	1952	“A portion of the system calcium carbonate-carbon dioxide-water, with geological implications”	Miller J. P	Solubility measurements at wide range of temperature and pressure.
5 th annual conference on CCS	2005	CO ₂ /brine/carbonate rock interactions: dissolution and precipitation	Grigg R. B., Svec R. K., Lichtner P. C., Carey W. and Lesher C. E.	More understanding about dissolution and precipitation when injecting CO ₂ in core floods.
Geochimica et Cosmochimica Acta Vol. 72	2008	Coupled phase and aqueous species equilibrium of the H ₂ O–CO ₂ –NaCl–CaCO ₃ system from 0 to 250 C, 1 to 1000 bar with NaCl concentrations up to saturation of halite	Duan, Zhenhao and Li, Dedong	Introduce a model to predict solubility values for calcite in CO ₂ -water system.
SPE 115663	2008	Design of carbon dioxide storage in Oilfields	Qi R, LaForce T. C. and Blunt M. J.	Introduce a simulation strategy to maximise CO ₂ storage in oilfields.
International Journal of Greenhouse Gas Control	2009	Design of carbon dioxide storage in aquifers	Qi R, LaForce T. C. and Blunt M. J.	Introduce a simulation strategy to maximise CO ₂ storage in aquifers.
Geophysics Research Letters Vol. 38	2011	Measurements of the capillary trapping of super-critical carbon dioxide in Berea sandstone	Pentland C. H., El-Maghrby R., Iglauer S. And Blunt M. J.	First to produce trapping CO ₂ curve for water-wet sandstone.

American Journal of Science Vol. 52 (1952)

A portion of the system calcium carbonate-carbon dioxide-water, with geological implications

Author: Miller J. P.

Contribution to the understanding of calcite solubility in CO₂-brine mixture:

As of time of publication, it is considered the most extensive data measured.

Objective of the paper:

To study the solubility of calcite using different rock samples and the factors affecting it.

Methodology used:

Laboratory experiment

Conclusion reached:

1. Wide range of data is available.
2. Purity and particle size of calcite affect is solubility.

Comments:

Different water compositions were used in the experiments.

Poster presented at the 5th Annual Conference on CCS (2005)

CO₂/brine/carbonate rock interactions: dissolution and precipitation

Authors: Grigg R. B., Svec R. K., Lichtner P. C., Carey W. and Lesher C. E.

Contribution to the CO₂ storage in geologic formations:

More understanding of the complicated minerals dissolution and precipitation process experienced when CO₂ is injected into carbonates reservoirs.

Objective of the paper:

To study the interactions between carbonate rocks and fluids

Methodology used:

Laboratory experiment

Conclusion reached:

1. Minerals dissolution and precipitation were noticed in close proximity.
2. Brine composition affects rock dissolution and precipitation greatly.

Comments:

Porosity and permeability were used to indicate dissolution and deposition. Cores were imaged back-scattered electron imaging.

Geochimica et Cosmochimica Acta Vol. 72 (2008)

Coupled phase and aqueous species equilibrium of the H₂O–CO₂–NaCl–CaCO₃ system from 0 to 250 C, 1 to 1000 bar with NaCl concentrations up to saturation of halite

Authors: Duan, Zhenhao and Li, Dedong

Contribution to the understanding of calcite solubility in CO₂-brine mixture:

A thermodynamic model was developed to estimate solubility values at different pressures (1 to 1000 bar) and different temperatures (0 to 250 C).

Objective of the paper:

To predict calcite solubility of calcite in H₂O-CO₂-NaCl

Methodology used:

Developing a model and then check it against literature data

Conclusion reached:

1. Availability of accurate solubility at high pressure and temperature in aqueous systems that have different salts and CO₂ concentrations.
2. Dissolved CO₂ increases calcite solubility significantly.

Comments:

The model was not developed by fitting experimental data and hence it was able to predict calcite solubility at high pressures and temperatures conditions. The model predictions are comparable to the literature values.

SPE 115663 (2008)

Design of Carbon Dioxide Storage in Oilfields

Authors: Qi R., LaForce T. C. And Blunt M. J.

Contribution to the CO₂ storage in geologic formations:

A strategy that co-optimises oil recovery and CO₂ storage in oilfields using WAG injection was developed.

Objective of the paper:

To design a reservoir model that maximises oil recovery and trap CO₂ in oilfields.

Methodology used:

Streamline-based simulation was utilised in this study.

Conclusion reached:

1. WAG injection with more water than the optimum value used traditionally followed by a period of a chase brine injection proved to be the optimum design.
2. More than 90% of CO₂ was trapped or dissolved with storage efficiency of 17%.
3. Oil production was almost double the recovery obtained with waterflooding only.

Comments:

This reservoir model used was heterogeneous. More water injection led to avoid early breakthrough of CO₂.

International Journal of Greenhouse Gas Control (2009)

Design of carbon dioxide storage in aquifers

Authors: Qi R, LaForce T. C. and Blunt M. J.

Contribution to CO₂ storage in geologic formations:

A design to maximise CO₂ storage in aquifers is developed

Objective of the paper:

To maximise CO₂ storage in aquifers safely by means of capillary trapping

Methodology used:

Streamline-based simulator

Conclusion reached:

A design to maximise CO₂ is to follow the injection of CO₂ and brine by a chase brine injection.

Comments:

90 to 95% of CO₂ can be rendered immobile in the pore space by means of capillary trapping.

Geophysics Research Letters Vol. 38 (2011)

Measurements of the capillary trapping of super-critical carbon dioxide in Berea sandstone

Authors: Pentland C. H., El-Maghrby R., Iglauer S. And Blunt M. J.

Contribution to CO₂ storage in geologic formations:

First trapping curves (residual CO₂ saturation vs. Initial CO₂ saturation) developed for CO₂ storage in sandstone.

Objective of the paper:

To study the CO₂ capillary trapping by brine in sandstone

Methodology used:

Laboratory experiment

Conclusion reached:

CO₂ can be trapped efficiently (up to 35% of pore space) after injection water.

Comments:

Using equilibrated solution between CO₂ and brine, it was possible to assess the capillary trapping in sandstone. However, in carbonate rocks, where reactivity between CO₂ and minerals is more pronounced, the solution should be equilibrated with CO₂ as well as carbonates to avoid the competing effects of dissolution and precipitation during capillary trapping experiments.

Appendix B: Core Preparation

1. The rock sample is first covered with polytetrafluoroethylene (PTFE) tape. This is done to avoid reaction between CO₂ and the aluminium foil tape that will be installed subsequently.
2. After that, the core is covered with a layer of aluminium foil tape. This is done to ensure that the fluid will only flow from the core inlet to its outlet as shown in the figure:
3. To support the aluminium foil later, a viton sleeve is installed on the core. Both ends of the viton sleeve are supported with smaller pieces of viton sleeve to ensure no leak path develops during the experiment.

Figure AP- 1 shows the core preparation process for the three steps shown above:



Figure AP- 1 shows the process of core preparation prior to placing it inside an oven.

4. The core is then placed in the Hassler cell (see Figure AP- 2) and a leak test is conducted by applying a radial pressure. If no leaks are detected, the core is ready for use in the experiment.

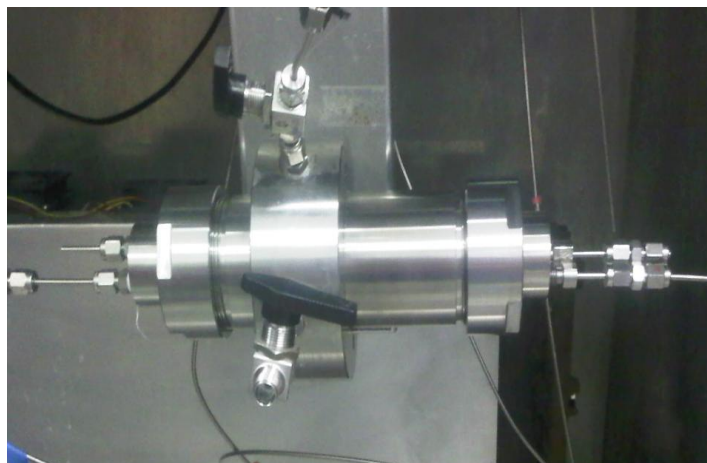


Figure AP- 2 shows the Hassler cell installed in the oven.

Appendix C: CO₂-Saturated Brine Experiment 1 Detailed Results

Table AP- 1 shows the detailed raw data and calculations for experiment 1.

A	B	C	D	E	F	G	H	I	J	K
Cycle Num.	Sample Num.	Weight of empty tube g	Weight of tube after sampling g	Weight of tube and salts after sampling g	Weight of solution (No CO ₂) g	Weight of fresh water g	Weight of NaCl & KCl in sample g	Weight of all salts (NaCl+KCl+CaCO ₃) g	Volume of Solution ml	Calcite concentration g/ml
1	1	12.2556	23.3561	12.9648	11.1005	10.3913	0.6680	0.7092	10.6684	0.00386
2	1	12.2659	23.4144	12.9645	11.1485	10.4499	0.6717	0.6986	10.7146	0.00251
	2	12.2802	23.4587	12.9808	11.1785	10.4779	0.6735	0.7006	10.7434	0.00252
3	1	12.2528	23.5426	12.9454	11.2898	10.5972	0.6812	0.6926	10.8504	0.00105
	2	12.2706	23.4631	12.9586	11.1925	10.5045	0.6753	0.6880	10.7568	0.00118
4	1	12.1733	23.1228	12.8496	10.9495	10.2732	0.6604	0.6763	10.5233	0.00151
	2	12.2668	23.3231	12.9502	11.0563	10.3729	0.6668	0.6834	10.6259	0.00156
5	1	12.0054	22.9700	12.6823	10.9646	10.2877	0.6613	0.6769	10.5378	0.00148
	2	12.0850	23.3031	12.7775	11.2181	10.5256	0.6766	0.6925	10.7815	0.00147

Calculations:

$$F = D - C$$

$$G = D - E$$

$$H = \frac{G * 0.06040}{1 - 0.06040} \text{ NOTE: (0.06040) is the percentage by weight of NaCl and KCl.}$$

$$I = E - C$$

$$J = \frac{F}{1.0405} \text{ NOTE: } 1.0405 \frac{g}{mL} \text{ is the density of brine.}$$

$$K = \frac{I - H}{J}$$

Appendix D: CO₂-Saturated Brine Experiment 2 Detailed Results

Table AP- 2 shows the detailed raw data and calculations for experiment 2.

A	B	C	D	E	F	G	H	I	J	K
Cycle	Sample	Weight of empty tube	Weight of tube after sampling	Weight of tube and salts after drying	Weight of solution (No CO ₂)	Weight of fresh water	Weight of NaCl & KCl in sample	Weight of all salts (NaCl+KCl+CaCO ₃)	Volume of Solution	Calcite concentration
Num.	Num.	g	g	g	g	g	g	g	ml	g/ml
1	1	12.2428	23.4684	12.9570	11.2256	10.5114	0.6757	0.7142	10.7887	0.00357
	2	12.2940	23.4573	13.0045	11.1633	10.4528	0.6719	0.7105	10.7288	0.00359
2	1	12.2959	23.6309	13.0009	11.3350	10.6300	0.6833	0.7050	10.8938	0.00199
	2	12.1682	23.3043	12.8592	11.1361	10.4451	0.6714	0.6910	10.7026	0.00183
3	1	12.2167	23.4547	12.9173	11.2380	10.5374	0.6774	0.7006	10.8006	0.00215
	2	12.2949	23.6255	13.0026	11.3306	10.6229	0.6829	0.7077	10.8896	0.00228
4	1	12.2259	23.5637	12.9347	11.3378	10.6290	0.6833	0.7088	10.8965	0.00234
	2	12.2405	23.4982	12.9424	11.2577	10.5558	0.6786	0.7019	10.8195	0.00216
5	1	12.2506	23.6110	12.9594	11.3604	10.6516	0.6847	0.7088	10.9182	0.00221
	2	12.3038	23.7769	13.0209	11.4731	10.7560	0.6914	0.7171	11.0265	0.00233

Calculations:

$$F = D - C$$

$$G = D - E$$

$$H = \frac{G * 0.0604}{1 - 0.0604} \text{ NOTE: (0.0604) is the percentage by weight of NaCl and KCl.}$$

$$I = E - C$$

$$J = \frac{F}{1.0405} \text{ NOTE: } 1.0405 \frac{g}{mL} \text{ is the density of brine.}$$

$$K = \frac{I - H}{J}$$

Appendix E: Calcite Solubility in CO₂-Saturated Brine (After Duan & Li 2008)

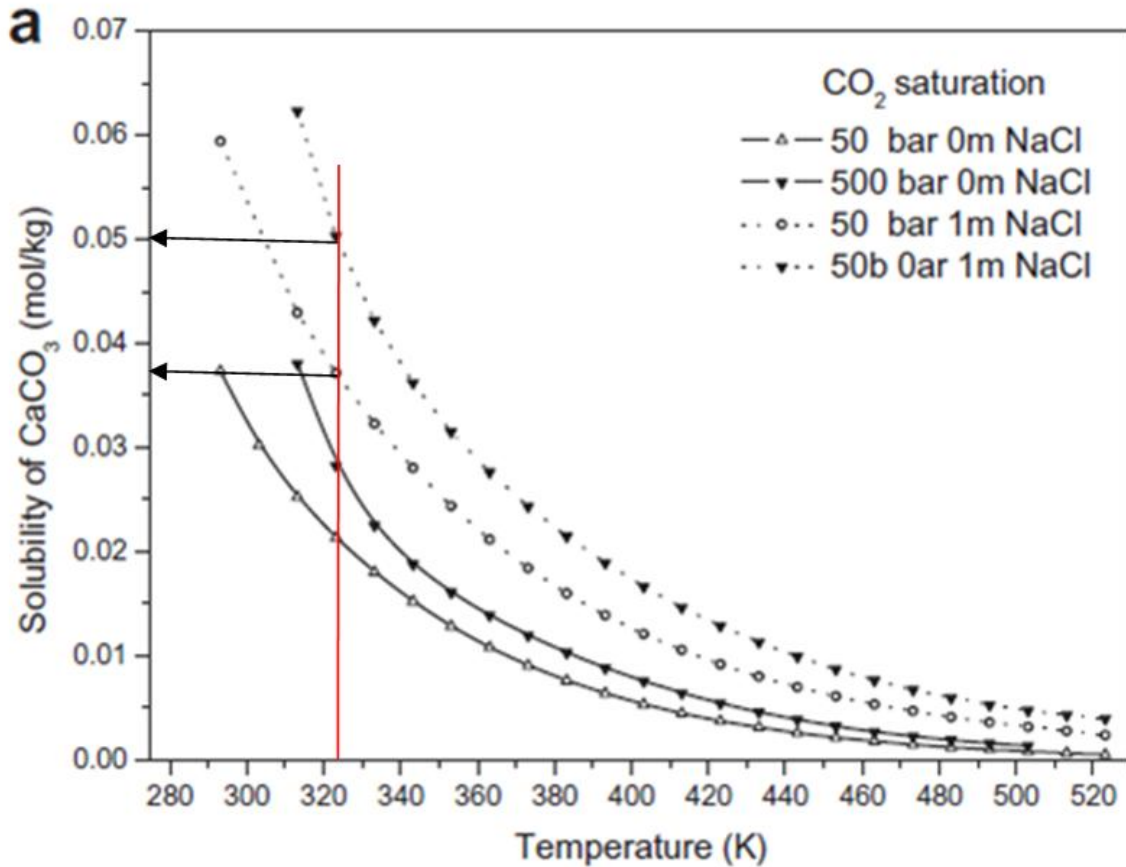


Figure AP- 3 shows the predicted calcite solubility using Duan and Li 2008 thermodynamic model.

Note: to get the values at our experimental conditions, we read the solubility values at 50 C (323 K) which were 0.0373 mol/kg and 0.0510 mol/kg at pressures of 50 bar and 500 bar, respectively. After that, the reference value was calculated by linear interpolation at our experimental pressure of 90 bars to be 0.0385 mol/kg. Linear interpolation can be used as the solubility is linearly increasing with pressure.

Appendix F: Time Needed for Equilibrium Calcite Solubility in CO₂- Brine System(After Miller 1952)

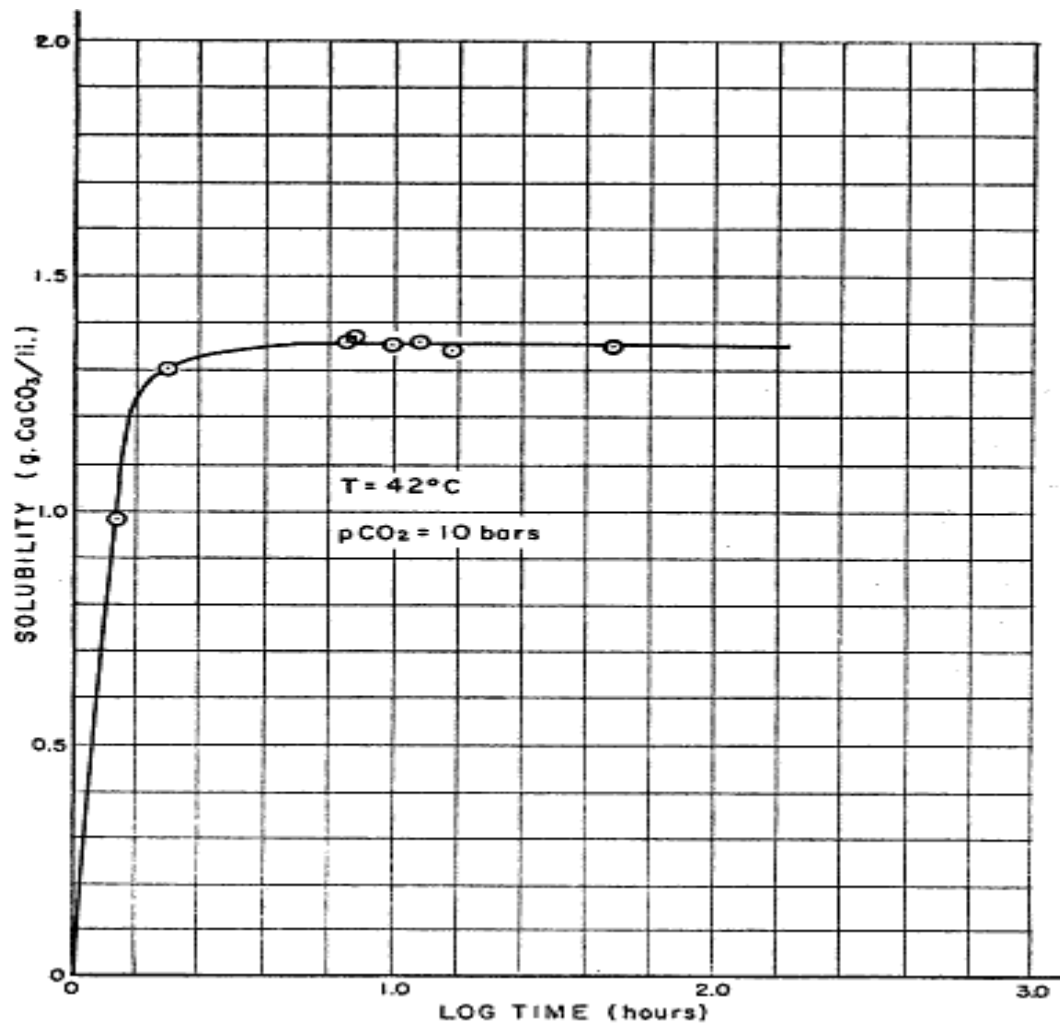


Figure AP- 4 shows the time needed for calcite solubility to reach equilibrium (source Miller 1952).

Note: It is observed from the plot that equilibrium in calcite solubility was reached after less than one hour at a temperature of 42 C and P(CO₂) of 10 bars. From the plot, most of the solubility occurs at the beginning of contact between calcite and solution. This indicates that the contact between carbonates and solution in our experiment (32 minutes at end of cycle 5) is enough to obtain representative value of solubility.