

Measurements of Non-wetting Phase Trapping in Porous Media

Christopher H Pentland

Department of Earth Science and Engineering

Royal School of Mines

Imperial College London

London SW7 2AZ

United Kingdom

A dissertation submitted in fulfilment of the
requirements for the degree of Doctor of Philosophy of

Imperial College London

November, 2010

(Awarded 2011)

Declaration

I declare that this thesis, **Measurements of Non-wetting Phase Trapping in Porous Media**, is entirely my own work under the supervision of Prof. Martin J Blunt and Dr Branko Bijeljic. The work was performed in the Department of Earth Science and Engineering at Imperial College London. All published and unpublished material used in the thesis has been given full acknowledgment. This work has not been previously submitted, in whole or in part, to any other academic institution for a degree, diploma, or any other qualification.

Christopher Holst Pentland

Department of Earth Science and Engineering

Imperial College London

November 27th 2010

Abstract

Saline aquifers have been identified as a preferred storage location for anthropogenic carbon dioxide emissions due to their large capacities and wide geographical spread. The storage of carbon dioxide in such formations must be carefully designed so that the carbon dioxide is trapped securely and will not escape to the surface. Of the various subsurface mechanisms, capillary trapping is a fast and secure means of rendering injected carbon dioxide immobile. The carbon dioxide is trapped on the pore scale as residual phase bubbles surrounded by formation brine. Local capillary forces prevent the movement of the carbon dioxide bubbles and retain them within individual pores or groups of pores.

The trapping of a phase in this manner can be characterised by the relationship between initial and residual saturation, known as the capillary trapping curve. The maximum trapped saturation and the form of the capillary trapping curve are of key importance in characterising the underlying physics of this phenomenon, giving an important indication of system wettability. To date the form of the capillary trapping curve has not been measured for a carbon dioxide-brine-rock system and there is limited technical literature available on maximum trapped carbon dioxide saturations.

The aim of this study is to measure the maximum saturation and the form of the capillary trapping curve in a carbon dioxide-brine-sandstone system at conditions representative of a storage location through coreflood experiments. Similar measurements are required on analogue systems of known wettability in order to infer the wettability of the carbon dioxide-brine-sandstone system. In addition measurements of capillary pressure are sought to better understand the

migration of carbon dioxide after injection, and the influence of petrophysical properties on capillary trapping is investigated.

We initially measure trapping in unconsolidated sand at ambient conditions with analogue fluids: oil-brine and gas-brine. The maximum trapped saturations are relatively low – 12.8% and 14.3% for oil and gas respectively. The form of the capillary trapping curve is shown to be slightly different in each case.

We then measure the capillary trapping curve for Berea sandstone at temperature and pressure representative of a storage location ($T = 343$ K; $P = 9.0$ MPa). The maximum residual carbon dioxide saturation is measured as 35.3% and the form of the trapping curve is accurately predicted by the trapping correlation proposed by Spiteri et al., [1]. The primary drainage capillary pressure curve is also measured and it is shown that the irreducible brine saturation is 14.9% for an applied capillary pressure equivalent to a carbon dioxide column height of 37 m. For comparison oil-brine measurements are also made on the same sandstone. Trapping is shown to be different for each system. More oil than carbon dioxide is trapped in Berea sandstone – 48.3% versus 35.3%. Subtle changes in imbibition contact angle and system wettability are proposed as the cause – with the rock surface being slightly less hydrophilic in the presence of carbon dioxide. Brine remains the wetting phase however, explaining the substantial quantities of carbon dioxide trapped. A simple term to quantify trapping capacities is developed – the capillary trapping capacity – being the product of maximum trapped saturation and porosity. A capillary trapping capacity of up to 7.8% of the gross rock volume for a carbon dioxide-brine-Berea sandstone system is measured.

We also investigate the influence of petrophysical properties on capillary trapping in oil-brine systems. Maximum trapped oil saturations are measured for five consolidated sandstone systems in addition to six unconsolidated sands. Strong relationships exist between trapped saturation and porosity, permeability and a characteristic geometric property (aspect ratio divided by coordination number). These relationships may prove valuable for future predictions of maximum trapped saturations when coreflood data is not available.

The publications as a result of this research are:

Peer Reviewed Journal Articles

Pentland, C. H., R. El-Maghraby, S. Iglauder, and M. J. Blunt (2011), Measurements of the capillary trapping of super-critical carbon dioxide in Berea sandstone, *Geophysical Research Letters* (**in press**).

Gittins, P., S. Iglauder, **C. H. Pentland**, S. Al-Mansoori, S. Al-Sayari, B. Bijeljic, and M. J. Blunt (2010), Nonwetting Phase Residual Saturation in Sandpacks, *J Por Media*, 13(7), 591-599, doi:10.1615/JPorMedia.v13.i7.10.

Al Mansoori, S. K., E. Itsekiri, S. Iglauder, **C. H. Pentland**, B. Bijeljic, and M. J. Blunt (2010), Measurements of non-wetting phase trapping applied to carbon dioxide storage, *International Journal of Greenhouse Gas Control*, 4(2), 283-288, doi:10.1016/j.ijggc.2009.09.013.

Pentland, C. H., E. Itsekiri, S. Al-Mansoori, S. Iglauder, B. Bijeljic, and M. J. Blunt (2010), Measurement of Nonwetting-Phase Trapping in Sandpacks, *SPEJ*, 15(2), 274-281, doi:10.2118/115697-PA.

Al Mansoori, S. K., S. Iglauder, **C. H. Pentland**, and M. J. Blunt (2009), Three-phase measurements of oil and gas trapping in sandpacks, *Advances in Water Resources*, 32(10), 1535-1542, doi:10.1016/j.advwatres.2009.07.006.

Conference Proceeding Papers

Pentland, C. H., R. El-Maghraby, A. Georgiadis, S. Iglauder, and M. J. Blunt (2010), Immiscible Displacements and Capillary Trapping in CO₂ Storage, in *Proceedings of the Greenhouse Gas Controls Technology Conference 2010*, Amsterdam, The Netherlands.

Pentland, C. H., S. Iglauder, R. El-Maghraby, Y. Tsuchiya, H. Okabe, and M. J. Blunt (2010), Measurement of Carbon Dioxide Capillary Trapping in Core Analysis, in *Proceedings of SPE 2nd International Conference on CO₂ Capture, Storage, and Utilization*, Paper SPE 138476, New Orleans, Louisiana, USA.

Okabe, H., Y. Tsuchiya, **C. H. Pentland**, S. Iglauder, and M. J. Blunt (2010), Residual CO₂ saturation distributions in rock samples measured by X-ray CT, in *Proceedings of the 3rd International Workshop on X-Ray CT for Geomaterials*, New Orleans, Louisiana, USA.

Pentland, C. H., Y. Tanino, S. Iglauder, and M. J. Blunt (2010), Capillary Trapping in Water-Wet Sandstones: Coreflooding Experiments and Pore-Network Modeling, in *Proceedings of SPE Annual Technical Conference and Exhibition*, Paper SPE 133798, Florence, Italy.

Lamy, C., S. Iglauder, **C. H. Pentland**, M. J. Blunt, and G. Maitland (2010), Capillary Trapping in Carbonate Rocks, in *Proceedings of SPE EUROPEC/EAGE Annual Conference and Exhibition*, Paper SPE 130720, Barcelona, Spain.

Al Mansoori, S., **C. H. Pentland**, S. Iglauder, and M. J. Blunt (2009), Three Phase Measurements of Nonwetting Phase Trapping in Unconsolidated Sandpacks, in *Proceedings of SPE Annual Technical Conference and Exhibition*, Paper SPE 123994, New Orleans, Louisiana, USA.

Al Mansoori, S. A., S. Iglauder, **C. H. Pentland**, B. Bijeljic, and M. J. Blunt (2009), Measurements of Non-Wetting Phase Trapping Applied to Carbon Dioxide Storage, *Proceedings of the Greenhouse Gas Controls Technology Conference 2009*, Washington D.C., U.S.A.

Iglauder, S., W. Wüling, **C. H. Pentland**, S. Al Mansoori, and M. J. Blunt (2009), Capillary Trapping Capacity of Rocks and Sandpacks, in *Proceedings of SPE EUROPEC/EAGE Conference and Exhibition*, Paper SPE 120960, Barcelona, Spain.

Pentland, C. H., S. Al-Mansoori, S. Iglauder, B. Bijeljic, and M. J. Blunt (2008), Measurement of Non-Wetting Phase Trapping in Sandpacks, in *Proceedings of SPE Annual Technical Conference and Exhibition*, Denver, Colorado, U.S.A.

Acknowledgments

I would like to express my gratitude to my main PhD supervisor Prof. Martin J Blunt. His insightful direction, support and encouragement was integral to this thesis. It has been a pleasure working in his research team throughout the past three years.

I would also like to acknowledge the help and support of Dr Stefan Iglauder. Many of the things I have learnt about scientific research, especially laboratory practices, I have learnt from him.

There are many other colleagues that it has been a great pleasure to work with. A special mention goes to my colleagues in the laboratory, especially Dr Branko Bijeljic, Dr Yukie Tanino, Dr Saleh Al-Mansoori, Dr Eli Leinov, Dr Jan Vinogradov, Amer Syed, Rehab El-Maghraby, Oussama Gharbi, Graham Nash and Alex Toth. Outside the laboratory a special mention must go to the clean fossil fuel community at Imperial College, and not least Prof. Geoffrey Maitland, Dr Tara La Force, Apostolos Georgiadis and Aaron Goater. Outside Imperial College I would like to thank Dr Mohammad Piri and Dr Hiroshi Okabe for their insightful advice.

Last, but by no means least, I would like to thank my family: my parents Stewart and Hillary for their never-ending support and love – I hope I made them proud; my grandma, Ida Holst, without whose love, cups of tea and morale-boosting chats I would undoubtedly have struggled much more than I did; Karin, my partner, for her love and support, but mainly for her patience; and finally my other grandparents Frederick Rasmus Holst, James Pentland and especially Maureen Pentland. I wish they could have seen their grandson finish his PhD. This thesis is dedicated to their memory.

Contents

Declaration	2
Abstract	3
Acknowledgments.....	7
Contents.....	8
List of Figures	11
List of Tables.....	17
Introduction	19
1.1 Carbon Capture & Storage	21
1.1.1 Anthropogenic Carbon Dioxide Emissions and Climate Change.....	21
1.1.2 Geological Carbon Dioxide Storage as a Mitigation Method.....	22
1.1.3 Carbon Capture & Storage Demonstration Projects	25
1.2 Capillary Trapping	27
1.2.1 Fundamentals of Immiscible Displacement.....	27
1.2.2 Previous Experimental Studies of Capillary Trapping	38
1.2.3 Previous Experimental Studies with Supercritical Carbon Dioxide	47
1.2.4 Summary	52
Experiments	54
2.1 Sandpack Experiments	55
2.1.1 Introduction.....	55
2.1.2 Equipment and Conditions.....	55

2.1.2	Experimental Procedure	57
2.1.3	Results.....	62
2.2	Consolidated Oil/brine Coreflood Experiments	68
2.2.1	Introduction.....	68
2.2.2	Equipment and Conditions.....	68
2.2.3	Experimental Procedure	71
2.2.4	Results.....	74
2.3	Consolidated CO ₂ /brine Coreflood Experiments	79
2.3.1	Introduction.....	79
2.3.2	Equipment and Conditions.....	79
2.3.3	Experimental Procedure	81
2.3.4	Results.....	84
2.3.4	Unsteady State Collaborative Experiments	88
Discussion and Conclusions		92
3.1	Discussion	92
3.1.1	The Influence of Petrophysical Properties on Capillary Trapping	93
3.1.2	Capillary Trapping in CO ₂ -brine-sandstone systems.....	100
3.1.3	Recommendations for Future Work.....	104
3.2	Conclusions	107
Bibliography.....		109
Appendices		117
Appendix 1 – Sandpack Experiments		117
Appendix 2 – Core-plug Characterisation.....		123
Appendix 3 – Mercury Injection Capillary Pressure.....		127
Appendix 4 – ETP Oil-brine Experiments		131
Appendix 5 – CO ₂ -brine Mixing.....		138
Appendix 6 – ETP CO ₂ -brine Coreflood Procedure		141
Appendix 7 – ETP CO ₂ -brine Measurements		146

Appendix 8 – Wettability Indices.....	153
---------------------------------------	-----

List of Figures

Figure 1.1: A segmented 2D slice of a 3D micro-CT image of a sandstone rock (black) containing brine (blue) and oil (red). The oil is trapped in the centre of the pores as it is the non-wetting phase while the wetting phase – brine – is covering most of the rock surface. The oil is rendered immobile by capillary forces [2].	20
Figure 1.2: An illustration of an integrated Carbon Capture and Storage (CCS) project [7].	22
Figure 1.3: Carbon Dioxide phase diagram reproduced from ChemicalLogic (www.chemicallogic.com/co2tab/). In typical subsurface storage formations CO ₂ will be a supercritical phase. The critical pressure and temperature of CO ₂ are 7.40 MPa and 304.25 K respectively [11].	24
Figure 1.4: Carbon Dioxide density and viscosity vary as a function of depth – they increase as the temperature and pressure increase with distance below ground level. Based on a typical geothermal gradient of 30 K per 1000 m (surface temperature of 288 K) and a typical hydrostatic gradient of 10 MPa per 1000 m (surface pressure of 0.1 MPa) [17]. CO ₂ is supercritical below 728 m for these gradients. Density and viscosity are calculated from literature equations [18], [19].	25
Figure 1.5: A map of the world showing the locations of the ten operating CCS projects [23].	26
Figure 1.6: A cross-section through a storage formation illustrating the displacement regions in an injected CO ₂ plume. (1) Near-wellbore region – formation water dissolves into the freshly injected (dry) CO ₂ . (2) CO ₂ and brine are equilibrated – saturation changes in the pore space are due to immiscible phase on phase displacements. (3) Leading edge of the CO ₂ plume – CO ₂ comes into contact with under-saturated formation brine and CO ₂ dissolves into the brine.	28
Figure 1.7: Interfacial tensions and contact angle in a three-phase (CO ₂ ; brine; solid) system. sc stands for supercritical.	28
Figure 1.8: Contact angle hysteresis in a CO ₂ -brine-solid system where brine is the wetting phase, (a) advancing brine contact angle during imbibition, (b) receding brine contact angle during drainage.	30
Figure 1.9: Possible distribution of CO ₂ (black) and brine (white) within an idealised porous media (grey). (a) Initial CO ₂ saturation after primary drainage. (b) Residual CO ₂ saturation after waterflooding.	31
Figure 1.10: Capillary pressure curves for drainage and waterflood displacements. The solid bounding drainage and waterflooding curves represent the maximum saturation changes that occur in a system with the application of the largest possible capillary pressures (positive and negative). The bounding curves define the connate water saturation (S_{wc} , point A) and the maximum residual non wetting phase saturation (point B). If a smaller positive capillary pressure is applied prior to waterflooding then scanning curves (dashed lines; 1a-1b, 2a-2b, 3a-3b) can be plotted in-between the bounding curves.	32
Figure 1.11: A typical trapping curve relating initial to residual non-wetting phase saturations. The end point of the curve is given by the maximum initial non-wetting phase	

saturation (S_{nwmax}) and the maximum residual non-wetting phase saturation (S_{nwrmax}). Note that the points on the trapping curve relate to the end points of the bounding and scanning capillary pressure curves (A-B; 1a-1b; 2a-2b; 3a-3b) in Figure 1.10.....	33
Figure 1.12: Entrapment of a non-wetting phase (black) by a wetting phase (white) by snap-off within a porous medium (grey). (a) The wetting phase is connected through wetting layers across the solid surface. (b) The wetting layers swell as the capillary pressure drops during imbibition. (c) The wetting layers within the throat swell until the throat spontaneously fills with the wetting phase, isolating and trapping the non-wetting phase in the preceding pore.....	35
Figure 1.13: A three-dimensional CT scan image of a sandstone rock (left). This can be used to extract a representative network of pores and throats (right). The extracted network can be used in network modelling simulations to determine rock-fluid properties such as capillary pressure and trapping curves [46].	37
Figure 1.14: Dong and Blunt's [46] maximal ball (MB) predicted primary drainage (a) and water flooding (b) relative permeabilities for water-wet Berea sandstone compared to Oak's experimental data [48] (sample 13) and Valvatne and Blunt's predictions [40]. Figure reproduced from Dong and Blunt, 2009 [46].	37
Figure 1.15: Dong and Blunt's [46] maximal ball (MB) predicted primary drainage (a) and water flooding (b) relative permeabilities for water-wet Berea sandstone compared to Oak's experimental data [48] (sample 14). Figure reproduced from Dong and Blunt, 2009 [46].	37
Figure 1.16: Database of residual non-wetting phase saturation $S_{(nw)r}$ versus initial non-wetting phase saturations $S_{(nw)i}$ in the literature [52-60].	39
Figure 1.17: Database of trapping capacity $\phi S_{(nw)r}$ versus initial non-wetting phase saturations $S_{(nw)i}$ in the literature [52-60].	40
Figure 1.18: Literature data of maximum trapped saturation (S_{rmax}) versus permeability (K) [52], [54], [55], [57-60], [67-76].....	43
Figure 1.19: Literature data of maximum trapped saturation (S_{rmax}) versus porosity (ϕ) [52], [54-60], [67-78].	44
Figure 1.20: Relationship between formation factor (F) and maximum residual non-wetting phase saturation (S_{rmax}). Measurements were performed on clean well sorted sandstone samples with an air-toluene fluid system, from Yuan, [79].	46
Figure 1.21: Schematic diagram of an experimental set up for measuring maximum trapped gas saturations (figure reprinted from Suekane <i>et al.</i> [49]).....	50
Figure 1.22: Cross section of the sampled holder used by Plug: 1. gas inlet; 2. water inlet; 3. stainless steel end piece; 4. stainless steel end piece; 5. stainless steel ring; 6. porous medium; 7. Concentric grooves; 8. perforated plate; 9. perforated plate; 10. hydrophobic filter (pore size = 0.45 μm); 11. SIPERM filter; 12. SIPERM filter; 13. water-wet filter (pore size = 0.1 μm); 14. o-rings; 15. o-rings; 16. nylon filter (pore size = 210 μm); 17. stainless steel bolts. Reprinted from Plug [67].	51
Figure 2.1: Ambient condition oil/brine sandpack experimental apparatus.	57
Figure 2.2: Oil saturation profiles. The lines to the right show the initial conditions, while the lines to the left show the trapped oil saturation. Three S_i replicates and three S_r replicates are shown for each experiment. (a) Experiment 1: vertical 71 ml oil injection. (b) Experiment 2: vertical 118 ml oil Injection. (c) Experiment 3: vertical 189 ml oil injection. (d) Experiment 4: horizontal 930 ml oil injection (see Table 2.3).....	63
Figure 2.3: Experimental oil-brine trapping curve showing results from all four experiments (see Table 2.3).....	64
Figure 2.4: Comparison between the experimental oil-brine data and empirical trapping equations in the literature.	64
Figure 2.5: Gas Saturation profiles from the gas-brine LV60 sandpack experiment. The lines to the right show the initial conditions, while the lines to the left show the trapped	

gas saturation. Three S_i replicates and three S_r replicates are shown for each experiment.	65
Figure 2.6: Gas-brine trapping curve data and best-fit Aissaoui correlation match (Eqn. 14).	65
Figure 2.7: Oil/brine and gas/brine trapping curves.	66
Figure 2.8: The modified porous plate design allowing for faster waterflooding of the core-plug samples. The left hand face features a single port for non-wetting phase injection during primary drainage and production during waterflooding. The right hand face has two ports: the upper port terminates flush with the face of the porous plate and allows brine to be produced during primary drainage; the lower port passes through a hole in the centre of the porous plate terminating flush with the core-plug face – this port is used during brine injection (initial saturation and waterflooding). It is sealed with o-rings to prevent bypassing.....	70
Figure 2.9: Oil/brine ETP coreflood apparatus. The porous plate was situated at the right hand end of the core holder. Valve 4 is connected to the brine production port and valve 5 is connected to the waterflood injection port (Figure 2.8). Pump A was used for oil injection; pump B for brine injection; pump C for back pressure and receiving production from the core; and pump D applied radial confining pressure to the core-plug.	71
Figure 2.10: Brine saturation after primary drainage as a function of $J(S_w)$ (Eqn. 21) for (a) Berea 11 and (b) Clashach JP. Vertical bars depict the standard deviations over sampling time. Horizontal bars depict the disagreement between the different methods of saturation determination for a given run. Where the bars are not visible, they are smaller than the size of the marker. Dashed lines are translated from MICP data. Solid lines depict predictions by Valvatne and Blunt's network model [40]. Tabulated data is included in Appendix 4.	75
Figure 2.11: Comparison of measured (circle) $S_{nwr}(S_{nwi})$ in (a) Berea 11 and (b) Clashach JP, with empirical expressions proposed by Land (1968; Eqn. 9, dashed line) and Spiteri et al. (2008; Eqn. 15, solid line). S_{nwrmax} and S_{wc} in Eqn. 9 were taken as the mean S_{nwr} and S_w of all runs for which initial oil saturation is greater than 0.70. Fitting parameters C in Eqn. 9 and α and β in Eqn. 15 are listed in Table 2.11. Horizontal and vertical bars depict the disagreement between the different methods of saturation estimation for a given run. Where the bars are not visible, they are smaller than the size of the marker or are not available.	76
Figure 2.12: Comparison of measured (circle) and simulated $S_{nwr}(S_{nwi})$ in (a) Berea 11 and (b) Clashach JP core-plugs. Horizontal and vertical bars depict the disagreement between the different methods of saturation estimation for a given run. Where the bars are not visible, they are smaller than the size of the marker or are not available. Predictions by Valvatne and Blunt's pore-network simulator assuming intrinsic contact angles distributed in the range 0° to 30° (dashed line) and 35° to 65° (solid line) are included [40].	77
Figure 2.13: The initial versus residual non-wetting phase data of Kleppe et al., [52] compares well to the end-point saturation measured in this study. Both experiments were performed on Aerolith 10 samples using the porous plate method.	78
Figure 2.14: CO_2 -brine ETP coreflood apparatus. The porous plate was situated at the right hand end of the core holder. Valve 4 is connected to the brine production port and valve 5 is connected to the waterflood injection port (Figure 2.8). Pump A was used for CO_2 pressurisation and injection; pump B for back pressure and receiving production from the core-plug; pump C for measuring S_r by isothermal depressurisation of the core-plug pore space; and pump D applied radial confining pressure to the core-plug.....	81
Figure 2.15: A drop of CO_2 generated from a capillary tube is brought into contact with a porous plate substrate angled at 21° . The bulk phase is de-ionized water ($P = 48.9$ MPa).	85

- Figure 2.16: Primary drainage capillary pressure curve data measured on Berea sandstone. The three sets of data (CO₂-brine; oil-brine; mercury-air) have been normalised using the Leverett-J Function (equation 21) [96].86
- Figure 2.17: Capillary trapping curve data measured on Berea sandstone. Empirical trapping equations (Land, 1968 – Eqn. 9; Spiteri *et al.*, 2008 – Eqn. 15) matched to the CO₂-brine data are shown.87
- Figure 2.18: Comparison of measured (circle) and simulated Sr(Si) in Berea sandstone. Predictions by Valvatne and Blunt's pore-network simulator assuming intrinsic contact angles distributed in the range 0° to 30° (long dashed line), 35° to 65° (solid line) and 75° to 105° (short dashed line). If CO₂ is assumed to wet the surface trapping is over-predicted. If the system is assumed to be intermediate-wet trapping is under-predicted.88
- Figure 2.19: X-ray CT derived saturation distributions during CO₂ injection (upper) and brine waterflooding (lower) on a Berea sandstone sample. Phases are injected from the left hand end of the core-plug. Homogeneous piston-like immiscible displacements of the equilibrated phases are observed. After 5 pore volumes of CO₂ injection (upper right hand image), injection is switched from CO₂ to brine and 0.14PV brine injection is shown in the lower left image. A total of 5 pore volumes of brine are injected (lower right image).90
- Figure 2.20: X-ray CT derived saturation distributions during CO₂ injection (upper) and brine waterflooding (lower) on a Berea sandstone sample. Phases are injected from the left hand end of the core-plug. These images are from an initial experiment when un-equilibrated brine and CO₂ were used. Note the cone-shaped region of 100% brine saturation after 3 pore volumes of brine injection (lower right hand image) indicating that the residual CO₂ has dissolved in the under-saturated brine.90
- Figure 2.21: A comparison of capillary trapping curve data from porous plate and unsteady state CO₂-brine experiments.91
- Figure 3.1: The five capillary trapping curves measured as part of this study (in colour) compared to literature data [52-60] (greyscale).93
- Figure 3.2: A comparison of maximum trapped saturation (S_{rmax}) versus porosity (ϕ) data from this study and literature [52], [54-60], [67-78]. The results of this study clearly match the general inverse relationship between porosity and maximum trapped saturation seen in the literature. Least square fit regressions to the two sets of data (results of this study; literature) are shown. Least square fit equations and correlation coefficients are included in Table 3.1.95
- Figure 3.3: A comparison of maximum trapped saturation (S_{rmax}) versus permeability (K) data from this study and literature [52], [54], [55], [57-60], [67-76]. The results of this study match the inverse relationship between permeability and maximum trapped saturation seen in the literature. Least square fit regressions to the two sets of data (results of this study; literature) are shown. Least square fit equations and correlation coefficients are included in Table 3.1. A significantly better match to the results of this study – as opposed to the literature data – is achieved.96
- Figure 3.4: A comparison of formation factor (F) versus maximum trapped saturation (S_{rmax}) data from this study and Yuan, [79]. Both sets of data describe the same trend. Least square fit regressions to the two sets of data (results of this study; literature) are shown. Least square fit equations and correlation coefficients are included in Table 3.1.96
- Figure 3.5: R_a versus maximum trapped saturation data (●). The least square fit to the experimental data (—) is shown ($S_{rmax} = 0.0228[R_a] + 0.0746$). An excellent match ($R^2 = 0.97$) is achieved. The result of the Aerolith sample ($R_a = 0.39$) was excluded from the analysis as it lies outside the main trend of the data.98
- Figure 3.6: $N_{coord.}$ versus maximum trapped saturation data (●). The least square fit to the experimental data (—) is shown ($S_{rmax} = 0.0586[N_{coord.}]^2 - 0.6537[N_{coord.}] + 1.9441$). A good match ($R^2 = 0.73$) is achieved. The result of the Aerolith sample

($N_{\text{coord.}} = 10.55$) was excluded from the analysis as it lies outside the main trend of the data.	98
Figure 3.7: The proposed characteristic pore scale geometry term ($R_a/N_{\text{coord.}}$) versus maximum trapped saturation ($\bullet$). The least square fit to the experimental data (—) is shown ($S_{\text{rmax}} = 0.0721[R_a/N_{\text{coord.}}] + 0.0944$). An excellent match ($R^2 = 0.97$) is achieved.	99
Figure A. 1: Grain size distributions of the sands investigated in the sandpack experiments. Grain size distributions were determined by sieve analysis.	117
Figure A. 2: Two-dimensional image slices from three-dimensional micro-CT scans performed on: (a) HST-95; (b) F110; (c) Ottawa F-35; (d) Ottawa F-42; (e) Moneystone OMR; (f) LV60.	118
Figure A. 3: Engineering sketch of the Polymethylmethacrylate column and end cap used for the experimental sandpack.	119
Figure A. 4: Mercury injection capillary pressure database of sandstones – including those studied as part of this research (Stainton, Berea 700, Clashach).	129
Figure A. 5: Pore-throat radius distribution for Berea 400 sandstone – from MICP analysis.	130
Figure A. 6: Pore-throat radius distribution for Clashach sandstone – from MICP analysis.	130
Figure A. 7: A two-dimensional section of X-ray microtomography scans of (a) Berea and (b) Clashach samples. Voxel volume (resolution) is $5.789\mu\text{m} \times 5.789\mu\text{m} \times 5.789\mu\text{m}$. The white horizontal bar in each image depicts 1.00mm.	131
Figure A. 8: (a) ETP oil-brine coreflood apparatus. (b) Closed valves ($\circ$) and tubing used for the initial saturation of the sample. Brine is injected from pump C, back pressure and effluent collection is controlled by pump B (tubing used is highlighted in blue) (c) Closed valves and tubing used for the primary drainage of oil (tubing containing oil is highlighted in red) into the sample. Oil injection is controlled by pump A. Brine production from the core-plug is controlled by pump B (tubing containing brine is highlighted in blue). (d) Closed valves and tubing used during waterflooding.	132
Figure A. 9: CO ₂ pump volume versus time. As CO ₂ dissolves into brine within the reactor the pressure is maintained by injecting additional CO ₂ from an attached pump. As the brine becomes saturated with CO ₂ the rate of injection slows and finally stops when the phases are equilibrated.	140
Figure A. 10: (a) ETP CO ₂ -brine coreflood apparatus. Pump A is charged with CO ₂ and controls phase injection, pump B receives production from the core-plug and controls back-pressure, pump C is used for the isothermal expansion saturation measurement and pump D applies confining pressure. (b) Mixing – brine is introduced to the stirred reactor which is then connected to a CO ₂ reservoir at constant pressure (pump A) Closed valves are marked with a red circle. CO ₂ is injected into the reactor from the pump as it dissolves in the brine under agitation. (c) Initial Saturation – the core is initially vacuumed through pump B. Five pore volumes of fresh brine are then injected through V10. CO ₂ from pump A is then used to displace five pore volumes of equilibrated brine through the core-plug (illustrated). (d) Primary Drainage – CO ₂ from pump A is injected directly into the core-plug. Displaced brine passes through the porous plate – exiting the core holder via valve 4 – and is produced into pump B. (e) Waterflooding – Five pore volumes of equilibrated brine are displaced through the core-plug by CO ₂ from pump A. (f) Saturation Measurement – The core-plug pore space is isolated from the remainder of the apparatus by closing valves 2, 4 and 5. Valve 3 is then opened connecting the pore space to the isothermal expansion pump – pump C. In figures b-f tubing highlighted in blue contains brine and tubing highlighted in red contains CO ₂	142
Figure A. 11: The preparation of the core-plug for use in a CO ₂ -brine ETP experiment. (a) The core-plug is initially wrapped with PTFE tape. This protects the aluminium from the rough rock surface. (b) Adhesive aluminium tape is wrapped around the	

	sample. Using adhesive aluminium allows the rubber sleeve (c) to be slid onto the sample without damaging the aluminium. Additional rubber rings are placed over the rubber sleeve to affect a seal between rubber and metal end platens.	143
Figure A. 12:	Brine production data during primary drainage. Graphs a-c correspond to data points 1-3 respectively in Table A. 10.	147
Figure A. 13:	Pressure difference across the core holder versus time. Graphs a-c correspond to data points 4-6 respectively in Table A. 10. Each graph consists of two constant pressure intervals. The higher pressure interval represents the period when brine is being withdrawn from the sample. When flow is stopped the pressure drops to the lower constant pressure interval. This lower pressure interval is taken to represent P_c for the constant rate coreflood experiments.	147
Figure A. 14:	Relationship between expansion volume and pressure during S_r measurement. Graphs a-f correspond to corefloods 1-6 respectively.	150
Figure A. 15:	Relationship between pressure and S_r during isothermal depressurisation.	151
Figure A. 16:	Impact on S_r when the measurement parameters were varied by $\pm 5\%$	151
Figure A. 17:	Impact on S_r when the measurement parameters were varied by realistic ranges based on an understanding of measurement accuracy – Table A. 9.	152
Figure A. 18:	Drainage and imbibition capillary pressure data for a CO_2 -water-sand system [130]. Area A is equivalent to B_1 and A_1 in the HL and USBM indices respectively. Area B is equivalent to area A_2 in the HL and USBM indices. The total CO_2 saturation change caused by waterflooding is equal to the spontaneous saturation change (S_{sp}) and the forced saturation change (S_f) combined. This is equivalent to V_i in the Amott index.	154

List of Tables

Table 1.2: Reservoir wettability distribution based on contact angles. Reproduced from Treiber <i>et al.</i> , [33].	29
Table 1.4: Parameter summary for the literature data correlating maximum trapped saturation versus porosity as displayed in as displayed in Figure 1.17.	45
Table 1.5: Statistical least square fit data to the literature datasets. Permeability units are m^2 .	45
Table 1.6: Summary of brine- CO_2 contact angle measurements on silicate minerals.	48
Table 1.7: Summary of capillary trapping data for CO_2 -brine-silicate systems reported in the literature.	52
Table 2.1: A summary of the range of parameters for the three experiments performed during this study.	54
Table 2.2: Octane and brine properties at ambient conditions of 0.101 MPa and 293.15 K unless stated otherwise ^a .	57
Table 2.3: Table summarising the sandpack experiments performed and their associated parameters. One pore volume (PV) was equal to 111.2 ± 2.7 mL.	58
Table 2.4: Average porosity (ϕ), brine permeability (K_{brine}), formation factor (F), aspect ratio (R_a), coordination number ($N_{\text{coord.}}$), and grain size of the sandpacks investigated.	60
Table 2.5: Flow conditions associated with each experiment.	62
Table 2.6: Best-fit matching parameters, including the correlation R^2 , between experimental data and empirical trapping equations in the literature.	65
Table 2.8: Petrophysical parameters of core-plug samples investigated.	69
Table 2.9: Experimental conditions and associated phase properties. Values are laboratory measurements unless stated.	69
Table 2.10: Petrophysical properties of the networks used in the pore-network simulations. Clay content was set to zero in all three networks. Note that network properties differ from laboratory measurements (Table 2.8).	74
Table 2.12: End-point saturations – and associated primary drainage applied P_c and duration – for one ceramic Aerolith 10 and three sandstone samples. The maximum P_c applied to the sample during drainage is given along with the time averaged P_c over the drainage period.	78
Table 2.13: Petrophysical parameters of the Berea 9 core-plug sample used in the CO_2 -brine porous plate experiments. The properties were considered identical to the Berea 10 and 11 samples used in other experiments.	80
Table 2.14: Estimated phase properties at 343 K and 9 MPa (unless stated) from literature.	80
Table 2.15: Contact angle measurements at 354.5 K between the de-ionized water and CO_2 phase interface on a porous plate (aluminium silicate). Contact angles are reported for the denser brine phase.	85
Table 3.1: Least square fit equations to experimental data from this study and the literature, including the correlation coefficient (R^2). Permeability units are m^2 .	94
Table 3.2: Least square fit equations to experimental data from this study, including the correlation coefficient (R^2). The result of the Aerolith sample ($N_{\text{coord.}} = 10.55$) was	

excluded from the analysis of coordination number as it lies outside the main trend of the data.	99
Table 3.3: Experimental properties and dimensionless numbers for oil-brine and CO ₂ -brine experiments on Berea sandstone. Dimensionless numbers are for waterflooding – brine is the displacing phase.	102
Table 3.4: Approximate relationship between wettability and wettability indices for oil-water systems.	104
Table A. 1: GC measurement parameters.....	119
Table A. 2: Petrophysical characterisation of the samples investigated in this study.....	125
Table A. 3: XRD compositional analysis of dry Clashach sandstone.	126
Table A. 4: XRD compositional analysis of dry Berea sandstone.....	126
Table A. 5: Dead volume components for the oil-brine ETP experiments.....	133
Table A. 6: Calculated saturations based on mass balance and volume balance measurements for the oil-brine ETP experiments.	137
Table A. 7: Capillary pressure data for the ETP oil-brine coreflood experiments.	137
Table A. 8: Measurement error ranges for the parameters contributing to the calculation of S_r	151
Table A. 9: ETP CO ₂ -brine coreflood saturation and capillary pressure results and associated error.	152

Chapter 1

Introduction

Two-phase fluid displacement in geological porous media is a process with wide ranging implications for the fields of energy and the environment. In hydrocarbon reservoirs, water advances through the pore space as oil or gas is produced. This process of water imbibition can result in hydrocarbon trapping on the pore scale due to local capillary forces – a process known as capillary trapping. As a result valuable hydrocarbon reserves may be stranded in the subsurface. In an environmental context geological porous media can be used as a storage location for anthropogenic carbon dioxide (CO₂) emissions. The CO₂ is injected underground where it remains due to a number of trapping mechanisms. One of these mechanisms is capillary trapping where formation water has surrounded the CO₂ and trapped it as a pore scale bubble. Capillary trapping on the pore scale can now be visualised with advances in micro computer tomography (CT) technology (Figure 1.1).

The aim of this study is to quantify capillary trapping for porous media samples representative of CO₂ storage formations by performing coreflood experiments. Several studies have investigated capillary trapping for hydrocarbon-water systems but there is limited data available for CO₂-water systems; the literature on this topic is discussed later.

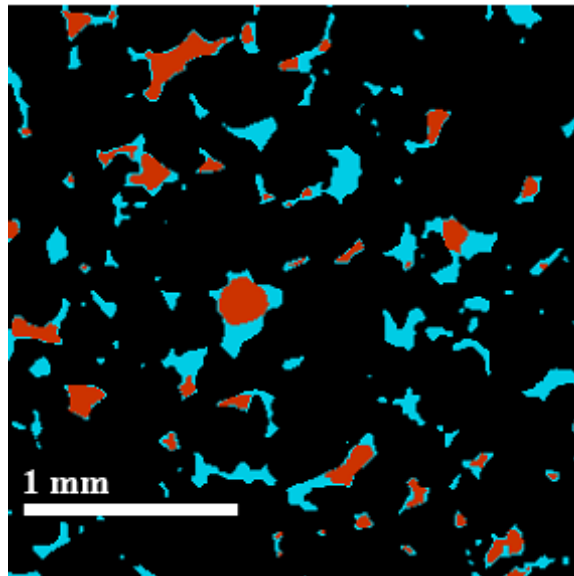


Figure 1.1: A segmented 2D slice of a 3D micro-CT image of a sandstone rock (black) containing brine (blue) and oil (red). The oil is trapped in the centre of the pores as it is the non-wetting phase while the wetting phase – brine – is covering most of the rock surface. The oil is rendered immobile by capillary forces [2].

1.1 Carbon Capture & Storage

1.1.1 Anthropogenic Carbon Dioxide Emissions and Climate Change

Compelling evidence exists to suggest that human activities are impacting upon the natural processes of the earth on a global scale. An example is the impact of anthropogenic carbon dioxide (CO₂) emissions upon the earth's carbon cycle. Consequences include the acidification of the upper oceans and increases in atmospheric CO₂ concentrations [3], [4].

Increasing atmospheric CO₂ concentration is correlated to mean global temperature increases. A number of factors affect global mean temperature. Based on the principle of radiative forcing greenhouse gases are seen as the most influential. Amongst the greenhouse gases CO₂ has the greatest influence [3]. It is predicted that unless the atmospheric CO₂ concentration is stabilised or even reduced the consequences of the associated changes to the earth's climate system could be severe. Aggressive cuts to CO₂ emissions are required to achieve this [5], [6].

The challenge of reducing CO₂ emissions significantly is highlighted when we consider that 85% of primary power demand is met by burning fossil fuels. This energy consumption is the primary source of anthropogenic CO₂ emissions [5]. Stabilising the earth's atmospheric CO₂ concentration at 550 ppm (roughly double the level before the industrial revolution) would require global energy sources in 2050 capable of zero carbon emissions to be equal in magnitude to current global energy supplies in their entirety [5].

A number of different technologies hold the promise of being able to reduce anthropogenic CO₂ emissions. Given the magnitude of the challenge it is likely that all will be required to some extent. One of these technologies is Carbon Capture and Storage (CCS) which relies upon geological carbon dioxide storage [6] (Figure 1.2).

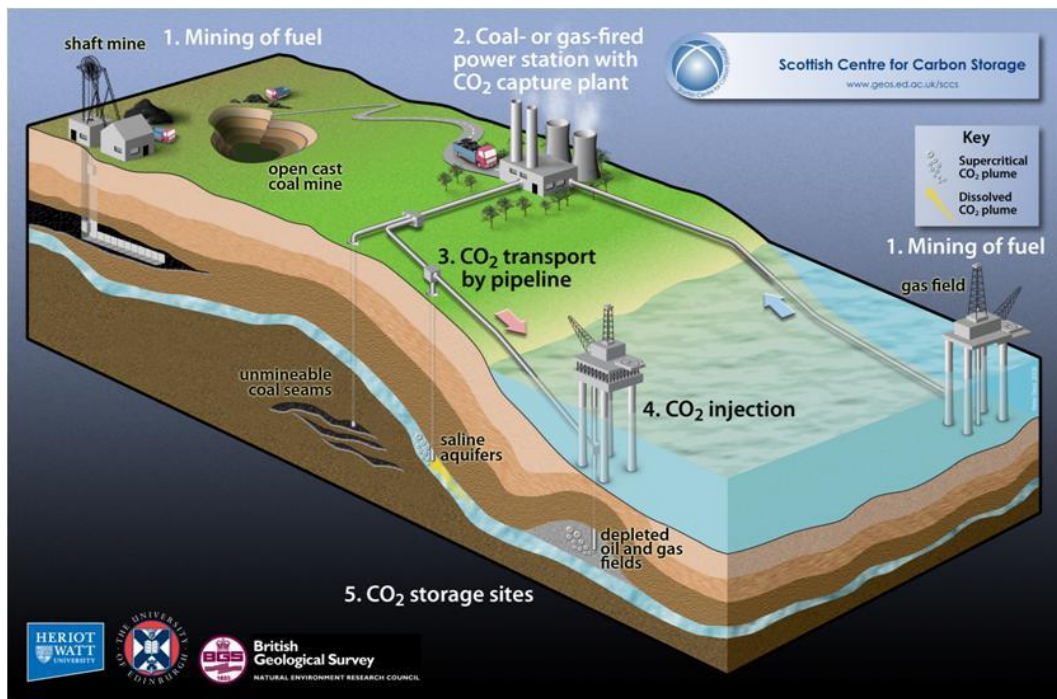


Figure 1.2: An illustration of an integrated Carbon Capture and Storage (CCS) project [7].

1.1.2 Geological Carbon Dioxide Storage as a Mitigation Method

Geological carbon dioxide storage refers to the process whereby CO_2 is stored long term in geological formations such as oil and gas reservoirs, saline aquifers, coal beds and salt deposits [8], [9]. Of these targets deep saline aquifers have the largest potential for storage and the widest geographical spread [10]. If CO_2 injection occurs below depths of approximately 800 m the CO_2 will be in a supercritical state due to the formation pressure and temperature at this depth (critical temperature and pressure of 304.25 K and 7.40 MPa respectively [11]). Supercritical CO_2 has a higher density than gaseous CO_2 and therefore a given volume of rock can hold more mass of CO_2 which is advantageous.

The sequestration of CO_2 in geological formations raises concern over storage effectiveness. Leakage of CO_2 into the atmosphere, even over the space of hundreds of years, would render any sequestration scheme inefficient. Hence CO_2 trapping mechanisms should be understood thoroughly in order to allow the implementation of CO_2 sequestration. The trapping mechanisms can be divided into four groups:

1. Hydrodynamic trapping
2. Dissolution
3. Mineral trapping
4. Capillary trapping

Hydrodynamic trapping is well understood from the oil and gas industry as it is the primary mechanism through which hydrocarbons accumulate in the subsurface. Accumulation occurs below a cap rock due to migration caused by density differences between the hydrocarbons and the host brine. The same mechanism takes place during CO₂ storage, as the less dense CO₂ will rise due to buoyancy forces. Hydrodynamic trapping is a relatively fast trapping mechanism although characterization of the cap rock is a crucial requirement [12].

Carbon dioxide is soluble in water – the CO₂ that dissolves can be safely stored in the geological formation and this is known as solubility trapping. The CO₂ saturated brine is denser than the surrounding brine resulting in convective mixing [13]. The denser CO₂ saturated brine migrates deeper into the formation and slowly dilutes through contact with unsaturated brine at depth. This process is important as it is typically orders of magnitude faster than pure diffusion. It is estimated to begin anywhere between one year and hundreds of years after CO₂ injection, depending upon formation permeability (pure diffusion may take up to tens of thousands of years) [14].

Mineral trapping is also an important mechanism, although it occurs over longer timescales than other trapping methods. As CO₂ dissolves in formation brine carbonic acid forms (H₂CO₃). This acid is unstable and dissociates. The species formed react with the host rock and brine over long periods of time, generally tens of hundreds of years. If the reactions result in carbonate minerals being precipitated then CO₂ is trapped permanently in the subsurface [15], [16].

The final trapping mechanism involves CO₂ being trapped as immobile pore scale bubbles surrounded by brine. This is known as capillary trapping and relies upon displacement hysteresis and the capillary pressure characteristics of the CO₂-brine system. Importantly it can occur over shorter timeframes than the other trapping mechanisms and is proven. In oil fields a considerable quantity of the oil originally in place is not produced as it has been trapped and rendered immobile in

the pore space through the imbibition process of water flooding. The combination of effective well characterised trapping on a short time scale makes capillary trapping important for CCS.

The density and viscosity of CO₂ influence its movement through a storage formation. These CO₂ properties will change with depth. As the formation temperature and pressure change the CO₂ state and properties can change substantially.

Figure 1.3 shows the CO₂ phase diagram and Figure 1.4 shows how CO₂ viscosity and density change as a function of depth.

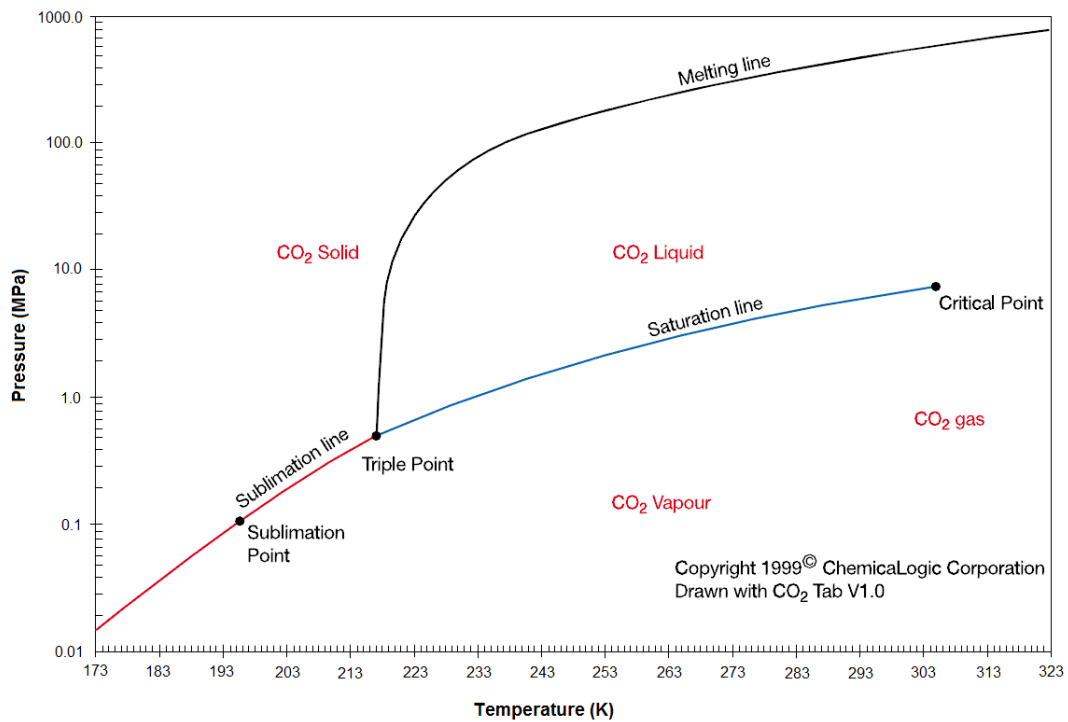


Figure 1.3: Carbon Dioxide phase diagram reproduced from ChemicalLogic (www.chemicallogic.com/co2tab/). In typical subsurface storage formations CO₂ will be a supercritical phase. The critical pressure and temperature of CO₂ are 7.40 MPa and 304.25 K respectively [11].

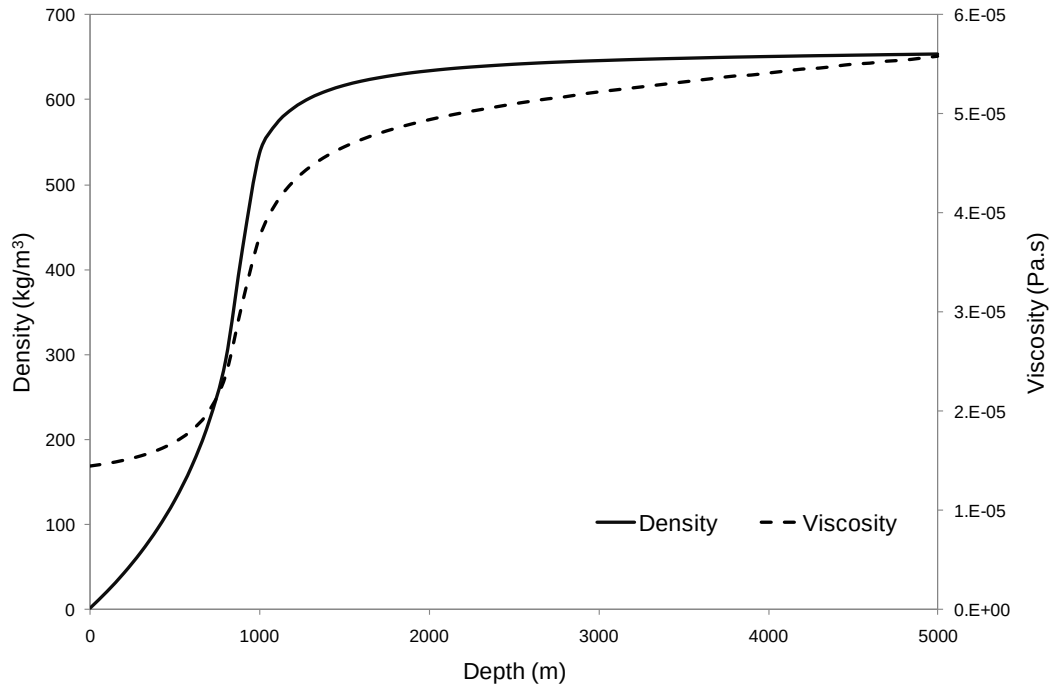


Figure 1.4: Carbon Dioxide density and viscosity vary as a function of depth – they increase as the temperature and pressure increase with distance below ground level. Based on a typical geothermal gradient of 30 K per 1000 m (surface temperature of 288 K) and a typical hydrostatic gradient of 10 MPa per 1000 m (surface pressure of 0.1 MPa) [17]. CO₂ is supercritical below 728 m for these gradients. Density and viscosity are calculated from literature equations [18], [19].

1.1.3 Carbon Capture & Storage Demonstration Projects

There is a long history of CO₂ being injected underground for enhanced oil recovery purposes. As early as the 1970's CO₂ was produced from natural geological accumulations, transported via pipeline, and re-injected into oil reservoirs [20], [21]. As a supercritical phase in the reservoir, the CO₂ acts as a highly efficient solvent dissolving and mobilising trapped oil.

Geological storage of CO₂ to prevent atmospheric anthropogenic emissions is a more recent activity. The first industrial scale project was the Sleipner Project in the Norwegian North Sea which began in 1996. The Sleipner Project involves removing CO₂ from produced natural gas and then re-injecting it into a saline aquifer. The driver is Norway's tax on atmospheric CO₂ emissions which was introduced in 1991 [22].

To date there are ten operating CO₂ storage projects worldwide storing a total of 7.25 Mt of CO₂ per annum [23] (Figure 1.5 and Table 1.1). These include projects where the primary purpose is enhanced oil recovery.



Figure 1.5: A map of the world showing the locations of the ten operating CCS projects [23].

Table 1.1: CCS project statistics [23].

Project Name	Country	In Operation	CO ₂ stored/year
Sleipner	Norway	1996	1.01 Mt
Fenn Big Valley	Canada	1998	17.34 Kt
Weyburn	Canada	2000	1.80 Mt
Spectra	Canada	2003	190.00 Kt
In-Salah	Algeria	2004	1.21 Mt
Salt Creek	USA	2006	2.09 Mt
Otway	Australia	2008	104.72 Kt
Schwarze Pumpe	Germany	2008	100.00 Kt
Snøhvit	Norway	2008	665.00 Kt
Lacq	France	2010	60.00 Kt

1.2 Capillary Trapping

1.2.1 Fundamentals of Immiscible Displacement

Miscible or immiscible displacement takes place when two or more fluids occupy the void space of a porous medium. Miscible displacement occurs when the two fluids are completely soluble in one another and the interfacial tension between them is zero. In immiscible displacements a distinct phase interface exists and there is no mass transfer across it. In this overview only immiscible displacements will be considered. Immiscible displacements include oil-brine systems and supercritical CO₂-brine systems under certain conditions.

Supercritical CO₂ and brine are mutually soluble. Mass transfer will occur between the phases when CO₂ is injected into an aquifer. However where the resident brine has become saturated with CO₂ – and the CO₂ is saturated with water – there will be a region within the aquifer where immiscible displacement occurs. This will be in-between the near wellbore region and the leading edge of the CO₂ plume (Figure 1.6). In the near wellbore region recently injected CO₂ will be under-saturated with water. At the leading edge of the CO₂ plume there will be contact with under-saturated aquifer brine and CO₂ will dissolve into the brine. The extent of these mass transfer zones will be dependent upon the aquifer geology (e.g. geometry, porosity, permeability), the rate of solubility between the phases, and the quantity and rate of CO₂ injected. The important immiscible displacement region will be substantially larger in terms of aquifer volume than the wellbore or leading edge regions for most CO₂ storage projects. It is therefore the critical region for assessing CO₂ storage potential. This conceptual picture has been confirmed by simulation studies of storage [24].

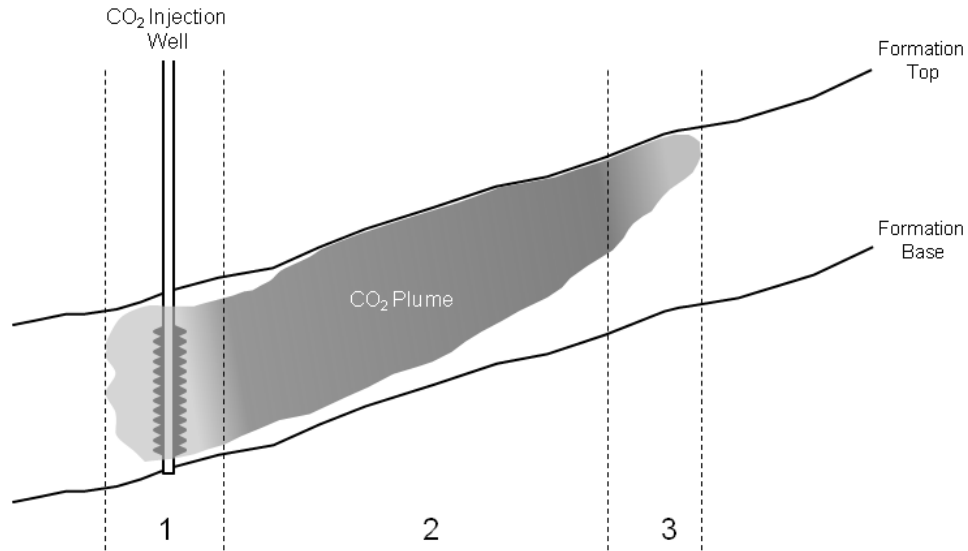


Figure 1.6: A cross-section through a storage formation illustrating the displacement regions in an injected CO₂ plume. (1) Near-wellbore region – formation water dissolves into the freshly injected (dry) CO₂. (2) CO₂ and brine are equilibrated – saturation changes in the pore space are due to immiscible phase on phase displacements. (3) Leading edge of the CO₂ plume – CO₂ comes into contact with under-saturated formation brine and CO₂ dissolves into the brine.

Two immiscible fluids such as equilibrated supercritical CO₂ and brine in contact with a solid surface are shown in Figure 1.7. The interface between phases arises due to the difference in cohesive forces between the molecules at the surface of each phase and the molecules in the bulk of each phase. This results in interfacial tension between the phases. In Figure 1.7 θ is the contact angle between the CO₂-brine interface and the solid surface ($0 < \theta < 180^\circ$). The contact angle is measured through the denser phase, in this case brine. The interfacial tension is denoted by σ .

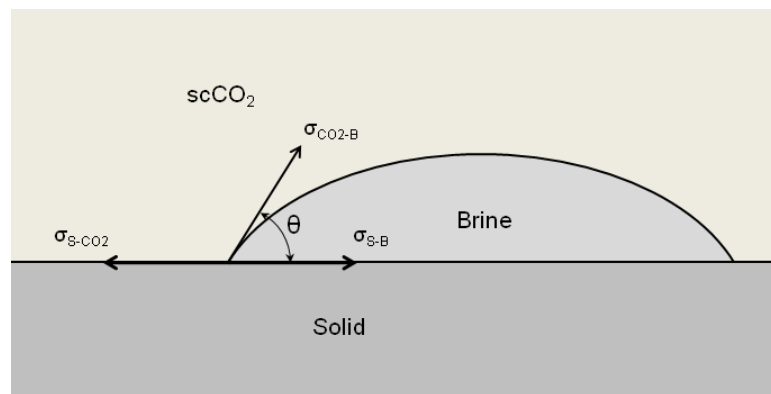


Figure 1.7: Interfacial tensions and contact angle in a three-phase (CO₂; brine; solid) system. sc stands for supercritical.

Young's Equation (Eqn. 1) defines equilibrium for the system shown in Figure 1.7:

$$\begin{aligned}\sigma_{\text{CO}_2-\text{B}} \cos \theta &= \sigma_{\text{S}-\text{CO}_2} - \sigma_{\text{S}-\text{B}} ; \\ \cos \theta &= (\sigma_{\text{S}-\text{CO}_2} - \sigma_{\text{S}-\text{B}}) / \sigma_{\text{CO}_2-\text{B}}\end{aligned}\tag{1}$$

where subscripts CO₂, B and S denote the three phases: supercritical carbon dioxide; brine; and solid respectively. Equation 1 tells us that if $(\sigma_{\text{S}-\text{CO}_2} - \sigma_{\text{S}-\text{B}}) / \sigma_{\text{CO}_2-\text{B}} > 1$ equilibrium is impossible and brine spreads over the solid surface; this is complete wetting with an effective contact angle of zero [25].

In a porous system with two or more fluids present the term *wettability* defines the preference of one fluid over another to be in contact with the rock surface. Most reservoir minerals are originally strongly water-wet [26-28]. Water will preferentially spread on the rock surface in the presence of a second immiscible phase. In oil-water systems the wettability of the rock minerals can be changed over time by the adsorption of polar compounds and/or by the deposition of organic matter originally in the crude oil [26-28]. It is possible to alter the wettability such that oil will preferentially spread over the rock surface in the presence of water. It has been shown that water is the wetting phase in CO₂-water siliclastic systems [29-31].

Contact angle is one measure of system wettability. If $\theta < 90^\circ$ the system is water-wet and if $\theta > 90^\circ$ the system is wet by the second phase (oil or CO₂) [32]. Alternatively Treiber *et al.*, [33] proposed the definition of wettability in an oil-water system shown in Table 1.2.

Table 1.2: Reservoir wettability distribution based on contact angles. Reproduced from Treiber *et al.*, [33].

Wettability State	θ (degrees)
Water-wet	0 to 75
Intermediate-wet	75 to 105
Oil-wet	105 to 180

When CO₂ (the non-wetting phase) displaces brine (the wetting phase) in an aquifer the contact angle will be smaller than the scenario whereby brine displaces

CO₂. The first case (wetting phase saturation decreasing) is known as drainage and the second case (wetting phase saturation increasing) is known as imbibition. The difference in contact angle between these two displacement sequences is an indication of the *hysteresis* of the system. The term hysteresis refers to the fact that the state of a system – in this case a contact angle – is dependent upon its history. i.e. the contact angle is dependent upon the current and previous flow sequences. Figure 1.8 illustrates the difference between imbibition and drainage contact angles.

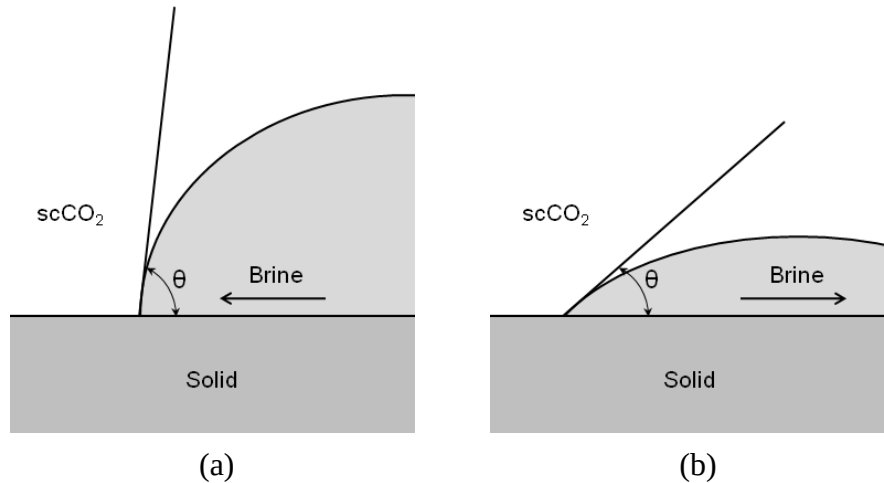


Figure 1.8: Contact angle hysteresis in a CO₂-brine-solid system where brine is the wetting phase, (a) advancing brine contact angle during imbibition, (b) receding brine contact angle during drainage.

Let us now consider the distribution of CO₂ and brine within the pore space of an immiscible displacement system. Figure 1.9 illustrates the CO₂ saturation before and after waterflooding. As CO₂ is the non-wetting phase it occupies the centre of the pore space and a thin layer of brine is retained on the rock surface after primary drainage (Figure 1.9a). As the CO₂ saturation increases it enters progressively smaller and smaller pores. Figure 1.9b shows how the system would look if waterflooded. The term waterflooding is used here interchangeably with the term imbibition to denote an increase in the brine saturation. The CO₂ is retained as isolated droplets in the centre of the pore space, surrounded by brine. The droplets are not extensively inter-connected and are held in place by local capillary forces. The location of the trapped droplets depends on the extent of the initial CO₂ invasion of the pore space. In some cases no CO₂ may be trapped in a pore space initially occupied by some CO₂. The manner in which the non-wetting phase invades progressively smaller pores – and the degree of trapping – is controlled by local capillary forces.

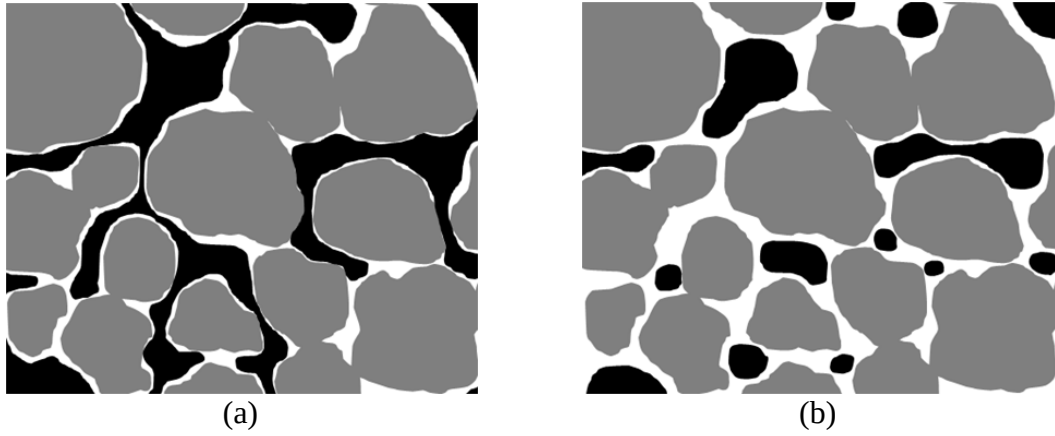


Figure 1.9: Possible distribution of CO₂ (black) and brine (white) within an idealised porous media (grey). (a) Initial CO₂ saturation after primary drainage. (b) Residual CO₂ saturation after waterflooding.

The Laplace equation (Eqn. 2) allows the capillary pressure across an interface between two immiscible phases to be calculated:

$$P_c = P_{nw} - P_w = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (2)$$

where P_c is the capillary pressure, P_{nw} the non wetting phase pressure, P_w the wetting phase pressure, σ the interfacial tension, and r_1 and r_2 the principal radii of curvature of the interface.

There is an inverse relationship between capillary pressure and wetting phase saturation which is characterised by the capillary pressure curves. In Figure 1.10 an immiscible system is shown where water is the wetting phase and CO₂ the non wetting phase. The curves shown represent different displacement events. Initially the system is 100% water saturated. The wetting phase saturation decreases as CO₂ enters the system with the application of a positive capillary pressure. This is represented by the drainage curve. As the water saturation decreases it starts to approach the connate or irreducible water saturation. At connate water saturation the application of a larger capillary pressure will not result in any more water being displaced from the system. This is also the maximum initial CO₂ saturation possible. If waterflooded at this state CO₂ will be produced from the system and the water saturation increases as the capillary pressure decreases. This is represented by the waterflooding curve. This curve terminates when no more CO₂ can be produced for the capillary pressure applied during the displacement. This capillary pressure

may be negative indicating that the water phase pressure is greater than the CO₂ phase pressure during waterflooding. The resulting saturation will be the maximum residual CO₂ saturation – in other terms the maximum amount of CO₂ that can be trapped (stored) in a system as residual disconnected pore scale bubbles, held in place by capillary forces.

In reality drainage may not occur under the maximum positive capillary pressure condition. Imbibition can begin at any point on the bounding drainage curve. The initial CO₂ saturation is proportional to the applied primary drainage capillary pressure, so if a smaller drainage capillary pressure is applied the initial CO₂ saturation will be lower. A new waterflooding curve could then be plotted commencing from the bounding drainage curve. This curve is known as a scanning capillary pressure curve and it lies in-between the bounding drainage and waterflood capillary pressure curves [25].

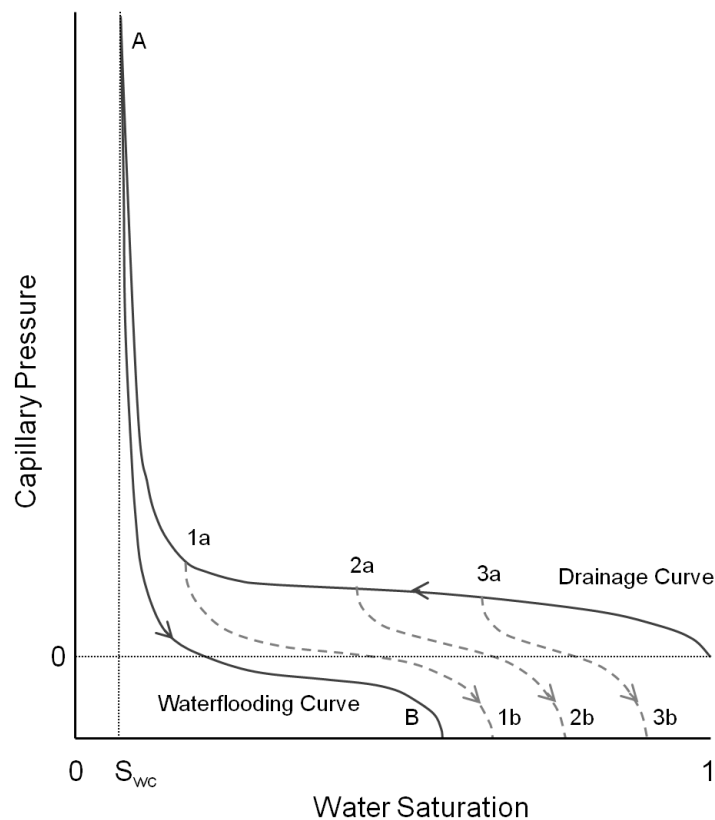


Figure 1.10: Capillary pressure curves for drainage and waterflood displacements. The solid bounding drainage and waterflooding curves represent the maximum saturation changes that occur in a system with the application of the largest possible capillary pressures (positive and negative). The bounding curves define the connate water saturation (S_{wc} , point A) and the maximum residual non wetting phase saturation (point B). If a smaller positive capillary pressure is applied prior to waterflooding then scanning curves (dashed lines; 1a-1b, 2a-2b, 3a-3b) can be plotted in-between the bounding curves.

The hysteresis of a system can be described by the saturations resulting from bounding and scanning curve displacements. Each set of drainage-waterflood displacements yields an initial CO_2 saturation and a residual CO_2 saturation. If a number of these displacements are performed on a system the resulting initial-residual saturation data can be plotted (Figure 1.11). This is known as the *capillary trapping curve* which terminates at the *end point*.

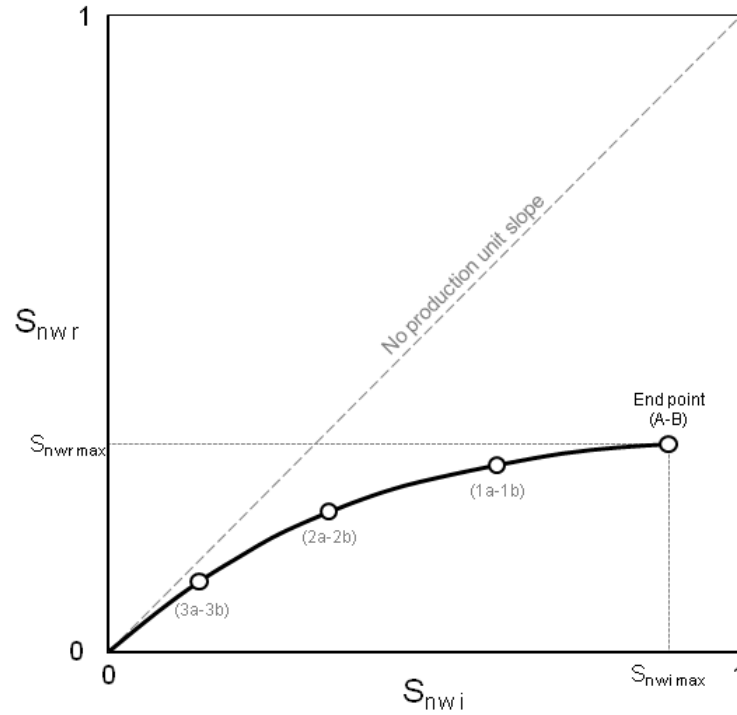


Figure 1.11: A typical trapping curve relating initial to residual non-wetting phase saturations. The end point of the curve is given by the maximum initial non-wetting phase saturation ($S_{(nw)i}^{\max}$) and the maximum residual non-wetting phase saturation ($S_{(nw)r}^{\max}$). Note that the points on the trapping curve relate to the end points of the bounding and scanning capillary pressure curves (A-B; 1a-1b; 2a-2b; 3a-3b) in Figure 1.10.

The shape of the trapping curve and the magnitude of the end point saturations give important information about capillary trapping in a system. The area in-between the trapping curve and the no production unit slope line indicates the quantity of non-wetting phase produced during waterflooding. The area below the trapping curve indicates the quantity of non-wetting phase which is trapped in the system by capillary forces after waterflooding.

Understanding the pore scale controls on capillary trapping is imperative. Our conceptual model of a porous medium is to imagine it as an irregular lattice of pore spaces – the wider gaps between grains – connected by narrower restrictions, called throats. This conceptual model is illustrated in two dimensions in Figure 1.1 and Figure 1.9. Imbibition is a competition between pore and throat filling and it is this competition – and the manner in which it occurs – that controls the amount of trapping [34]. Piston-like advance occurs when water moving from a water-filled pore or throat displaces the non-wetting phase from a neighbouring pore or throat. The threshold capillary pressure for this process is approximately:

$$P_c = \frac{2\sigma\cos\theta}{r} \quad (3)$$

where r is the radius of the pore or throat being filled. If the pores are much larger than the throats, then a much lower capillary pressure is required to fill a pore than a throat. This ratio of pore diameter to throat diameter is known as the aspect ratio (R_a). In imbibition, the water fills elements (pores or throats) in decreasing order of capillary pressure – it fills the narrowest parts of the rock, with the highest capillary pressures, first. Hence water wants to fill throats. However, it cannot invade a throat by piston-like advance unless the neighbouring pore or throat is water-filled.

The second filling process is snap-off. Water also flows along wetting layers in the corners of the pore space and these layers swell as the capillary pressure drops during imbibition. Essentially, the water is impeded when it reaches a pore, but water can flow around the corners and rough surfaces and enter a nearby throat. This is illustrated in Figure 1.12. The water will swell the wetting layer until the non-wetting phase no longer contacts the wall – at this stage it becomes unstable and the throat spontaneously fills with water. For a throat of square cross-section and inscribed radius r_t , the threshold capillary pressure is:

$$P_c = \frac{\sigma(\cos\theta - \sin\theta)}{r_t} \quad (4)$$

The ratio of capillary pressures of snap-off to pore-filling is therefore:

$$\text{Ratio} = \frac{r_p}{r_t}(1 - \tan\theta) \quad (5)$$

where r_p is the pore radius. This equation demonstrates that for large aspect ratios and small contact angles (strongly water-wet) the ratio of capillary pressures is higher favouring snap-off. Snap-off fills narrow throats, leaving non-wetting phase in the larger pores. If all the surrounding throats are filled, then the non-wetting phase is trapped. In contrast, if piston-like advance in pores has a higher capillary pressure, there is a tendency for the water to advance in a connected front – filling of pores with more surrounding throats filled with water is favoured – with little trapping [34], [35].

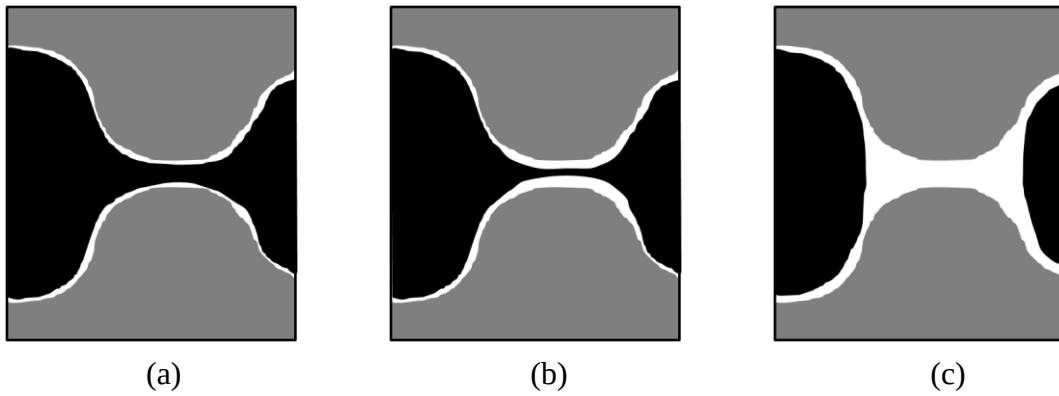


Figure 1.12: Entrapment of a non-wetting phase (black) by a wetting phase (white) by snap-off within a porous medium (grey). (a) The wetting phase is connected through wetting layers across the solid surface. (b) The wetting layers swell as the capillary pressure drops during imbibition. (c) The wetting layers within the throat swell until the throat spontaneously fills with the wetting phase, isolating and trapping the non-wetting phase in the preceding pore.

The number of throats connected to a pore is known as the coordination number ($N_{\text{coord.}}$). Both R_a and $N_{\text{coord.}}$ are used as parameters to characterise porous media. In both cases the parameters are averaged over a statistically representative number of pores and throats. This is done through micro-CT imaging of the pore space.

This analysis shows three effects. First, that as aspect ratio increases, there is more snap-off and trapping. Second large coordination numbers tend to lead to less trapping, since there is more opportunity for the oil to be displaced through a pore before all the surrounding throats are filled. Third, an increase in contact angle suppresses snap-off compared to piston-like advance, leading to less trapping.

When capillary trapping experiments are performed in the laboratory care must be taken to ensure that laboratory flow conditions are representative of

subsurface conditions. The ratio of capillary to viscous forces is quantified by a dimensionless number - the capillary number ($N_{cap.}$) [36-38]:

$$N_{cap.} = \frac{v\mu}{\sigma} \quad (6)$$

where v is the Darcy flow velocity, μ is the displacing phase viscosity and σ is the interfacial tension between the phases. In vertical floods the Bond number (N_b) quantifies the ratio of gravity to capillary forces:

$$N_b = \frac{\Delta\rho gr^2}{\sigma} \quad (7)$$

where ρ is the phase density, g is acceleration due to gravity and r is the average pore radius [39].

It is possible to simulate single phase flow directly on images of a pore space. However for capillary controlled multi-phase flow applications the best results to date have been achieved with network modelling. The conceptual model of a porous medium outlined above is the basis of network modelling. In network modelling an image of the pore space is produced non-destructively by micro computer tomography (micro-CT) scanning a small sample of the media. The resulting three-dimensional images can be used to extract a network of equivalent pores and throats in three dimensions (Figure 1.13) [40-45]. The latest advances in network extraction allow the process to be applied to any 3D image of interest with the application of a modified maximal ball algorithm [46], extending previous work [47]. Primary drainage and imbibition displacements can be simulated on the extracted network with a two-phase simulation code [40]. The simulated displacement sequences produce capillary pressure and relative permeability data which can be compared to experimental data and other modelling or network extraction methods. This approach was taken by Dong and Blunt, 2009 [46] when successfully matching the Berea sandstone experimental results of Oak *et al.*, 1990 [48] – Figure 1.14 and Figure 1.15.

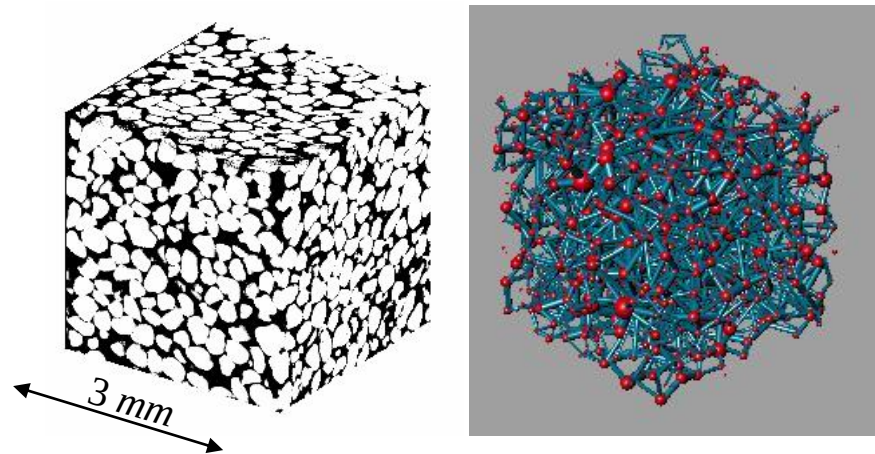


Figure 1.13: A three-dimensional CT scan image of a sandstone rock (left). This can be used to extract a representative network of pores and throats (right). The extracted network can be used in network modelling simulations to determine rock-fluid properties such as capillary pressure and trapping curves [46].

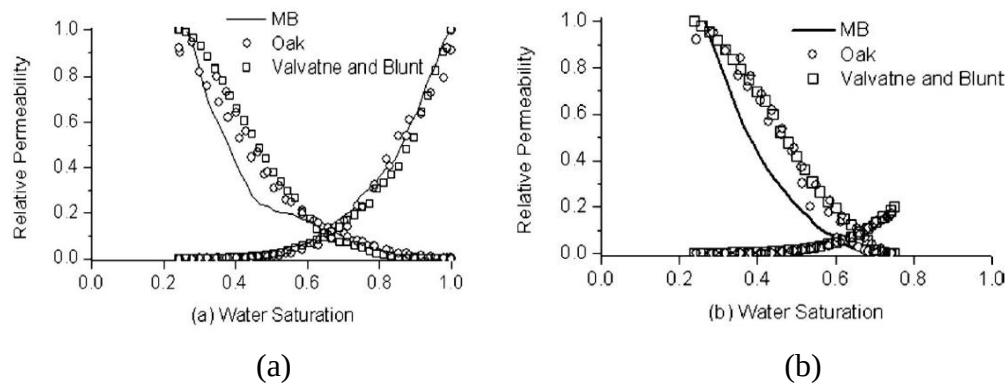


Figure 1.14: Dong and Blunt's [46] maximal ball (MB) predicted primary drainage (a) and water flooding (b) relative permeabilities for water-wet Berea sandstone compared to Oak's experimental data [48] (sample 13) and Valvatne and Blunt's predictions [40]. Figure reproduced from Dong and Blunt, 2009 [46].

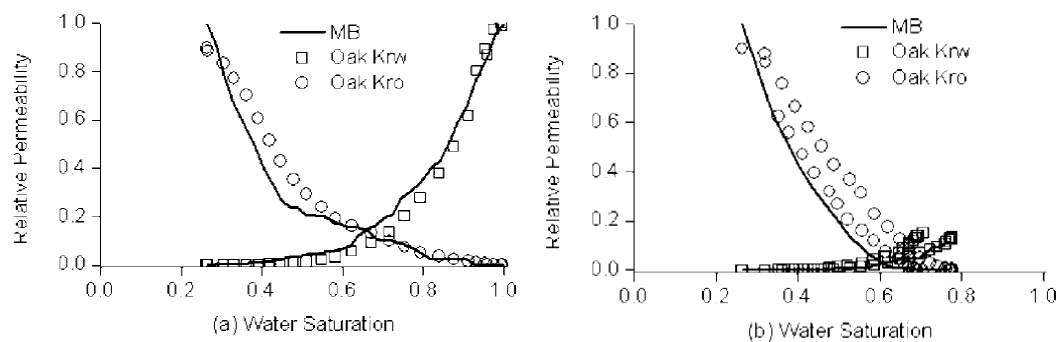


Figure 1.15: Dong and Blunt's [46] maximal ball (MB) predicted primary drainage (a) and water flooding (b) relative permeabilities for water-wet Berea sandstone compared to Oak's experimental data [48] (sample 14). Figure reproduced from Dong and Blunt, 2009 [46].

The capillary trapping curve has been measured for oil-brine and gas-brine systems (a review of the literature studies is given in Chapter 1.2.2 Previous

Experimental Studies of Capillary Trapping), although confusion remains over its exact form (bi-linear, quadratic etc). To date the trapping curve has not been measured for supercritical CO₂-brine systems, although there are limited literature measurements of the CO₂-brine end point [49]. The motivation for this work is to measure the supercritical CO₂-brine trapping curve and end point for a sandstone system. This data can then be compared with the oil-brine trapping curve and end point measured on the same sandstone to see how capillary trapping differs between the two systems.

1.2.2 Previous Experimental Studies of Capillary Trapping

Many studies have reported measurements of capillary trapping in porous media – e.g. [36], [50], [51]; however references which investigate the dependence of initial saturation upon residual saturation are more limited. Figure 1.16 shows a compilation of two-phase trapping curve data in the literature [52-60] while Table 1.3 gives a summary of the associated parameters for each study.

No clear trends emerge from a study of Figure 1.16, since the trapped saturation depends on the details of the pore structure, the experimental procedure and the contact angle between the phases. If we only consider references where saturation changes within a uniformly-wet porous media were achieved by phase on phase displacement (as opposed to other methods such as evaporation) then the list is further reduced – leaving only Kleppe *et al.*, [52] and Pickell *et al.*, [53]. The aim of this thesis is to complement this data with new coreflood and sandpack data.

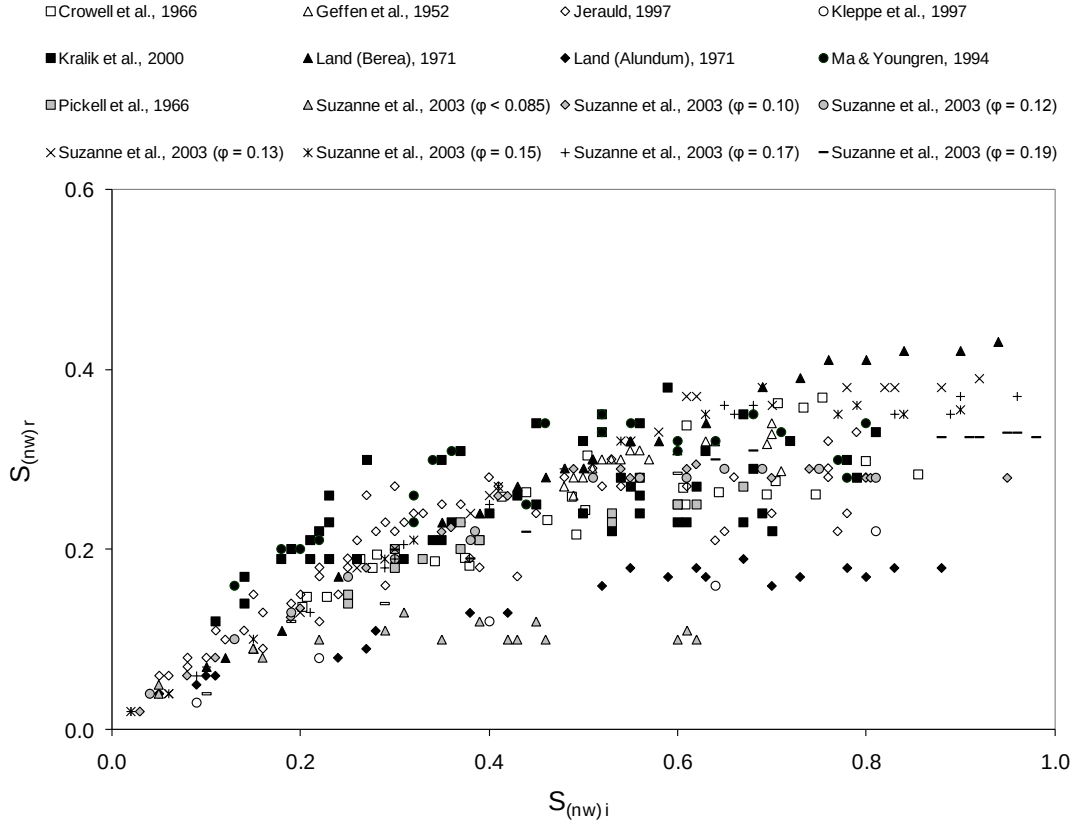


Figure 1.16: Database of residual non-wetting phase saturation $S_{(nw)r}$ versus initial non-wetting phase saturations $S_{(nw)i}$ in the literature [52-60].

Table 1.3: Parameter summary for the literature trapping curve data displayed in Figure 1.16 and Figure 1.17.

Reference	Fluid System	Porous Media
Crowell <i>et al.</i> , 1966	gas/water	consolidated sandstone ^a
Geffen <i>et al.</i> , 1952	gas/water	consolidated sandstone
Jerauld, 1997	gas/water & gas/oil	consolidated sandstone
Kleppe <i>et al.</i> , 1997	gas/water	Aerolith ^b
Kralik <i>et al.</i> , 2000	gas/water	consolidated sandstone ^a
Land, 1971	gas/oil	consolidated sandstone & Alundum ^b
Ma & Youngren, 1994	gas/water	consolidated sandstone ^a
Pickell <i>et al.</i> , 1966	oil/water & gas/mercury	consolidated sandstone
Suzanne <i>et al.</i> , 2003	gas/water	consolidated sandstone

^a Reference includes 3-phase data which is excluded from this analysis.

^b Artificial sintered ceramic materials.

For CO₂ storage applications it is not only the residual saturation that is of interest but the fraction of the gross rock volume that contains the trapped phase [61], [62]. The capillary trapping capacity (C_{trap}) is thus defined as:

$$C_{\text{trap}} = \phi S_{(nw)r} \quad (8)$$

where ϕ is the system porosity. This data is presented in Figure 1.17. There is considerable scatter in this data but if the low porosity clay rich samples from Suzanne *et al.*, [54] are excluded then it would appear that the trapping capacity increases approximately linearly with initial saturation until an initial saturation of around 50%. Beyond this there is considerable scatter, with most of the data indicating a maximum capillary trapping capacity of between 4 and 10%.

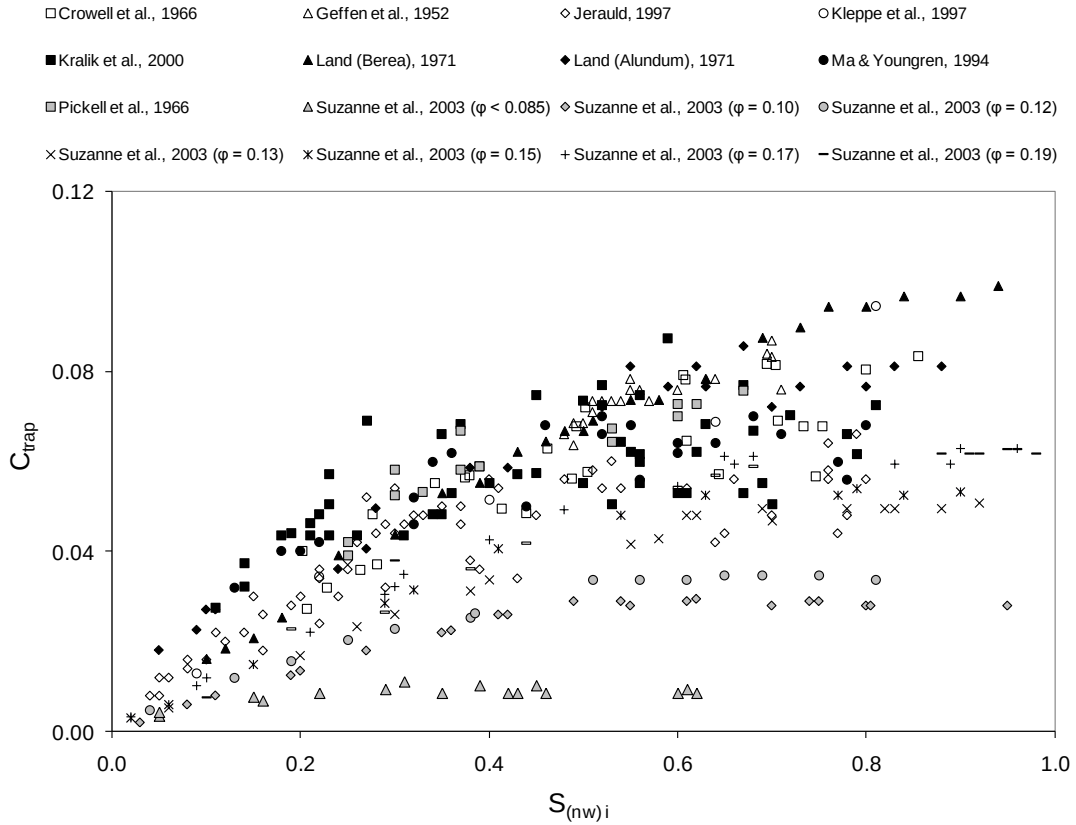


Figure 1.17: Database of trapping capacity $\phi S_{(nw)r}$ versus initial non-wetting phase saturations $S_{(nw)i}$ in the literature [52-60].

Several models have been proposed to predict the trend of trapped saturation based on this data. Land [63], building upon the work of Geffen *et al.*, [55], Naar and Henderson [64] and Agarwal [65], proposed a relationship between the trapped gas saturation and the initial gas saturation. This was based upon experimental data for consolidated media.

$$S_{gr}^* = \frac{S_{gi}^*}{1 + C S_{gi}^*} \quad (9)$$

where

$$C = \frac{1}{S_{gr}^{*\max}} - 1 \quad (10)$$

and S^* is the effective saturation: $S^* = S/(1-S_{wc})$ where S_{wc} is the connate or irreducible water saturation.

Jerauld [56] extended Land's relationship proposing a “zero slope” adaptation to match trapped gas saturation data from the mixed-wet Prudhoe Bay oil field in Alaska.

$$S_{gr}^* = \frac{S_{gi}^*}{1 + \left(\frac{1}{S_{gr}^{*\max}} - 1 \right) S_{gi}^{* \frac{1}{1-S_{gr}^{*\max}}}} \quad (11)$$

Another adaptation of Land's relationship was proposed by Ma and Youngren [57] based on an oil-wet experimental data set from the Kuparuk River Unit in Alaska. Ma and Youngren observed that at higher initial gas saturations there was a sharp levelling off of the trapped gas saturation. This led to the introduction of two empirically derived curve fitting parameters, a and b , where $b=1$ and $a=C$ in Land's original correlation:

$$S_{gr}^* = \frac{S_{gi}^*}{1 + a \left(S_{gi}^* \right)^b} \quad (12)$$

Other studies [52], [54] have questioned the validity of applying Land's trapping relationship to rock/fluid systems other than those analyzed by Land – consolidated rock with a strongly water-wet gas/liquid system where the initial saturation was established by evaporation, rather than by displacement. A shortcoming of the Land equation 9 is that it is based upon the data's ‘end point’ only ($S_{oi}^{*\max}$, $S_{or}^{*\max}$). There is no scope to tune the shape of the curve itself. Jerauld's and Ma and Youngren's adaptation of the Land curve went some way to tackling this limitation, but – as shown later – they do not match all the available data accurately.

Kleppe et al.'s [52] data, based on an artificial core (Aerolith 10, 43% porosity) did not fit to Land's trapping curve. The following linear relationship was proposed to match the experiments:

$$S_{gr} = \frac{S_{gi}}{S_{gi}^{\max}} S_{gr}^{\max} \quad (13)$$

Note that equation 13, unlike the previous correlations, is not based upon effective saturations.

Kleppe *et al.*'s proposal of a linear relationship is in agreement with the findings of Aissaoui [66]. Aissaoui's proposed trapping relationship, described below, was found to be the best match to Suzanne et al.'s [54] extensive experimental data set. It features two linear components. Initially S_{gr} increases linearly with S_{gi} before reaching a plateau at $S_{gr}^{\max}$.

$$\text{If } S_{gi} < S_{gc} \text{ then } S_{gr} = \frac{S_{gr}^{\max}}{S_{gc}} S_{gi}; \text{ else } S_{gr} = S_{gr}^{\max} \quad (14)$$

where S_{gc} is the critical gas saturation corresponding to the point where the maximum trapped saturation is reached.

Another approach to the prediction of trapped saturation is the use of pore-scale modelling. Spiteri et al. [1] used a pore-network model developed by Valvatne and Blunt [40] to predict the trapped saturation as a function of initial saturation and average contact angle. Their model matched the residual saturation measured on Berea sandstone by Oak [48]. They matched the simulated trend of trapped saturation for a given contact angle distribution as a quadratic function of initial saturation:

$$S_{or} = \alpha S_{oi} - \beta S_{oi}^2 \quad (15)$$

where α and β are contact-angle dependent coefficients.

The influence of other petrophysical properties – primarily porosity and permeability – has also been studied: Figure 1.18 shows the relationship between the maximum residual saturation and permeability, and Figure 1.19 shows the

relationship between the maximum residual saturation and porosity. Table 1.4 summarises the associated parameters of each system while Table 1.5 summarises least square fit statistics for each dataset.

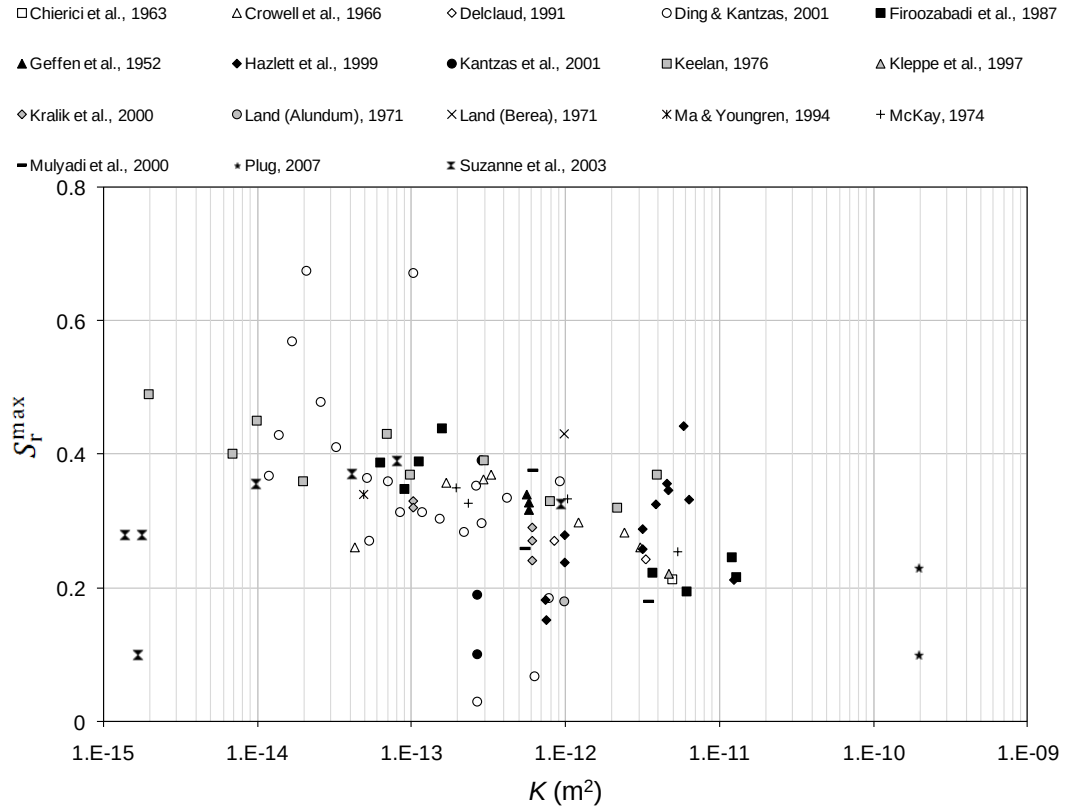


Figure 1.18: Literature data of maximum trapped saturation ($S_r^{\max}$) versus permeability (K) [52], [54], [55], [57-60], [67-76].

There is a strong trend between porosity and maximum residual saturation ($S_r^{\max}$); $S_r^{\max}$ decreases as porosity increases. This dependence is explained by higher porosity samples – such as unconsolidated sand – having lower aspect ratios (R_a) and higher coordination numbers (N_{coord}). This tends to limit pore scale trapping due to snap-off (as described in Chapter 1.2.1 Fundamentals of Immiscible Displacement). Higher porosity samples tend to have higher permeabilities [25] and a trend can be seen between permeability and $S_r^{\max}$. As with porosity the higher permeability samples tend to have lower aspect ratios and higher coordination numbers – reducing trapping by snap-off and promoting piston like displacement. The trend between permeability and $S_r^{\max}$ is weaker than the trend with porosity. The R^2 correlation coefficient of the match (Table 1.5) is significantly lower in the case of permeability.

□ Chierici et al., 1963	△ Crowell et al., 1966	◇ Delclaud, 1991
○ Ding & Kantzas, 2001	■ Firoozabadi et al., 1987	▲ Geffen et al., 1952
◆ Hazlett et al., 1999	● Jerauld, 1997 (Reservoir B-A)	□ Jerauld, 1997 (Reservoir C)
△ Jerauld, 1997 (Prudhoe-SS)	◇ Jerauld, 1997 (Frigg)	○ Jerauld, 1997 (Fontainbleau)
× Jerauld, 1997 (Reservoir B-C)	× Jerauld, 1997 (Prudhoe-cong)	+ Jerauld, 1997 (Sandstone)
— Kantzas et al., 2001	□ Katz et al., 1966	△ Keelan, 1976
◇ Kleppe et al., 1997	○ Kralik et al., 2000 (A Sand)	× Kralik et al., 2000 (C Sand)
× Kyte et al. 1956	+ Land (Alundum), 1971	— Land (Berea), 1971
● Ma & Youngren, 1994	● McKay, 1974	■ Mulyadi et al., 2000
★ Plug, 2007	★ Suzanne et al., 2003	

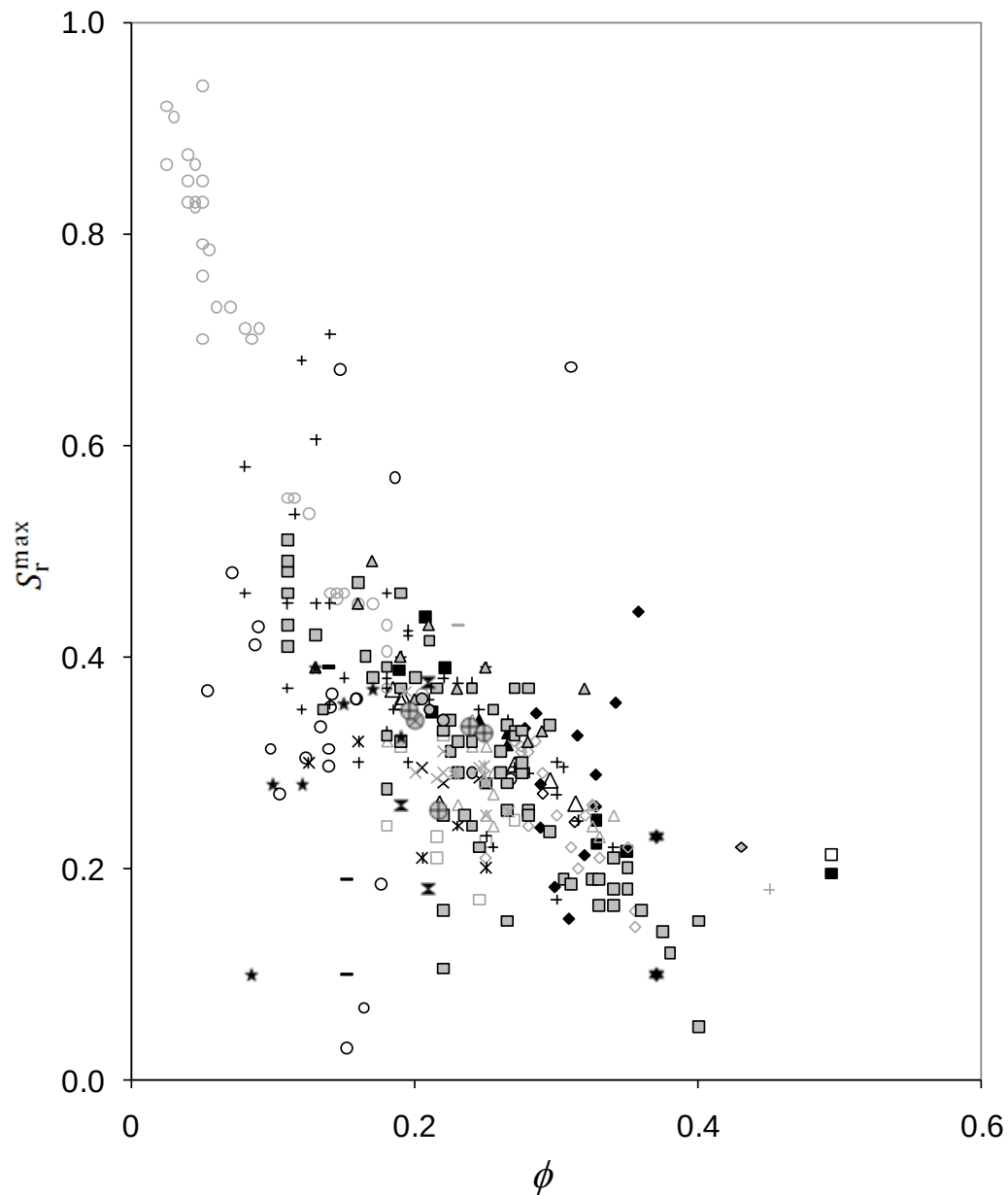


Figure 1.19: Literature data of maximum trapped saturation ($S_r^{\max}$) versus porosity (ϕ) [52], [54-60], [67-78].

Table 1.4: Parameter summary for the literature data correlating maximum trapped saturation versus porosity as displayed in as displayed in Figure 1.19.

Reference	Fluid System	Porous Media
Chierici <i>et al.</i> , 1963	gas/water	unconsolidated and consolidated sandstone ^a
Crowell <i>et al.</i> , 1966	gas/water & gas/oil	consolidated sandstone
Delclaud, 1991	gas/water	unconsolidated and consolidated sandstone
Ding & Kantzas, 2001	gas/water	consolidated ^a
Firoozabadi <i>et al.</i> , 1987	gas/water	consolidated sandstone
Geffen <i>et al.</i> , 1952	gas/water	consolidated sandstone
Hazlett <i>et al.</i> , 1999	oil/water	unconsolidated and consolidated sandstone ^b
Jerauld, 1997	gas/water & gas/oil	consolidated sandstone
Kantzas <i>et al.</i> , 2001	gas/water	consolidated sandstone
Katz <i>et al.</i> , 1966	gas/water & oil/water	consolidated sandstone
Keelan, 1976	gas/water	consolidated sandstone
Kleppe <i>et al.</i> , 1997	gas/oil	Aerolith ^c
Kralik <i>et al.</i> , 2000	gas/water	consolidated sandstone ^d
Kyte, 1956	gas/oil	Alundum ^c
Land, 1971	gas/oil	consolidated sandstone & Alundum ^c
Ma & Youngren, 1994	gas/water	consolidated sandstone ^d
McKay, 1974	gas/water	consolidated sandstone
Pickell <i>et al.</i> , 1966	oil/water & gas/mercury	consolidated sandstone
Plug, 2007	gas/water	unconsolidated sand
Suzanne <i>et al.</i> , 2003	gas/water	consolidated sandstone

^a Reference includes data from carbonate samples which are excluded from this analysis.

^b Reference includes data where initial oil saturation is achieved by the porous plate method and by unsteady state displacement. Only the porous plate data is included in this analysis.

^c Artificial sintered ceramic materials.

^d Reference includes 3-phase data which is excluded from this analysis

Table 1.5: Statistical least square fit data to the literature datasets. Permeability units are m².

Dataset	Least Square Fitting Equation	R ²
ϕ vs. $S_r^{\max}$	$S_r^{\max} = -0.2487\ln(\phi) - 0.0555$	0.65
K vs. $S_r^{\max}$	$S_r^{\max} = -0.0185\ln(K) - 0.2180^a$	0.17
F vs. $S_r^{\max}$	$S_r^{\max} = -0.0718\ln(F) + 0.1732$	0.46

^a The fit equation for mD units is: $S_r^{\max} = -0.0186\ln(K) + 0.4228$

Measuring $S_r^{\max}$ can be a costly and time consuming process – requiring core samples and specialised experimental apparatus. Being able to predict $S_r^{\max}$ from more readily available petrophysical parameters would be advantageous. Based on this analysis of literature data porosity could be used to estimate $S_r^{\max}$ – for example during an initial storage site screening study. However using permeability to estimate $S_r^{\max}$ would be unwise based on the scatter in the literature data. If a more precise understanding of capillary trapping is required then it would be recommended to run core flood experiments on the actual rock samples in question.

In addition to porosity and permeability there is limited data on the influence of formation factor (F) on $S_r^{\max}$ for sandstone samples [79]. Figure 1.20 summarises the literature measurements. The associated fitting equation and R^2 coefficient are given in Table 1.5 . Formation factor is defined as:

$$F = \frac{R_o}{R_w} \quad (16)$$

where R_o is the resistivity of a brine saturated sample and R_w is the resistivity of the brine. The formation factor of a porous medium is a function of its tortuosity and effective cross-sectional area [25].

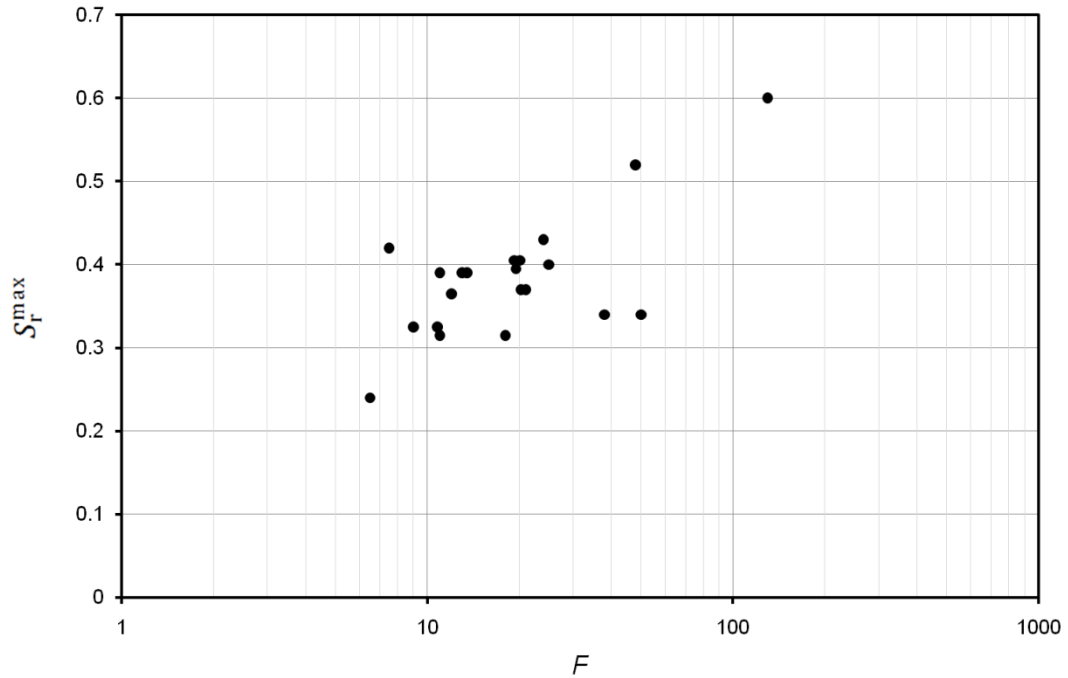


Figure 1.20: Relationship between formation factor (F) and maximum residual non-wetting phase saturation ($S_r^{\max}$). Measurements were performed on clean well sorted sandstone samples with an air-toluene fluid system, from Yuan, [79].

The complex interplay of pore structure characteristics such as aspect ratio and coordination number may provide a stronger relationship with $S_r^{\max}$. To date few literature references have reported these parameters in conjunction with capillary trapping saturation measurements for representative geological samples. Previous studies focused on micromodel and bead pack studies due to the difficulties in measuring pore structure characteristics for real rock samples [80], [81]. Increasing aspect ratio has been shown to increase capillary trapping in these idealised systems. In addition it has been proposed that coordination number has a

strong influence on residual saturation. Yuan, [79] proposed the following equation based on the percolation theory work of Shante and Kirkpatrick [82]:

$$S_{or} = \frac{1.5}{\bar{z}} \quad (17)$$

where $\bar{z}$ is the average coordination number of the rock sample.

An objective of this thesis is to complement measurements of residual saturation with a thorough characterisation of the porous media under investigation – including quantification of pore structure parameters through micro-CT scanning.

1.2.3 Previous Experimental Studies with Supercritical Carbon Dioxide

With the current interest in geological carbon dioxide storage there are a growing number of literature studies investigating supercritical CO₂ flow in porous media. The CO₂-brine trapping curve has – however – not yet been measured.

A study of the literature helps to answer a number of key questions on how best to measure the trapping curve for a CO₂-brine system. These key areas are: how *system wettability* may influence the experiments, how to *measure the CO₂ saturation* of the sample, and how to achieve a *homogeneous initial saturation distribution* throughout the core plug.

Interactions in the brine-CO₂-rock system are fundamental to how CO₂ can be stored in a geological porous medium. Interactions between the fluids and the rock will lead to dissolution and precipitation which could be beneficial or detrimental to safe storage – as highlighted previously mineral precipitation is a storage mechanism in its own right. A more subtle concern when considering capillary trapping is how the interactions between fluids and rock impact upon *system wettability*. Capillary trapping occurs when the non-wetting phase is trapped in the centre of the pore space – surrounded by the wetting phase. If CO₂ were to wet the rock surface it could not be trapped in this manner. At present there is limited evidence from measurements that this is the case. Two questions must be answered: will CO₂ preferentially wet the rock surface over brine; and if not could the wettability alter over time to become CO₂ wet. Brine-CO₂ contact angles have been measured on various substrates [29-31]. The results for untreated silicate minerals are summarised in Table 1.6. These studies show that brine will be the

wetting phase in these systems. There is conflicting evidence as to the influence of pressure or exposure time on contact angle. Chiquet *et al.*, [29] report alterations in the brine-CO₂ contact angle of 15-25° for quartz substrates between 1 and 10 MPa. Espinoza & Santamarina, [31] report alterations of less than 5° for the same substrate and pressure range, albeit at sub-critical temperature conditions. In all cases the contact angles remain in the water wet regime (defined as $\theta < 90^\circ$ [25]). Finally there is indirect evidence from coreflood experiments that CO₂ is the non-wetting phase in CO₂-brine-carbonate systems [83].

Table 1.6: Summary of brine-CO₂ contact angle measurements on silicate minerals.

Reference	Substrate	Aqueous Phase	P (MPa)	T (K)	θ (°)
Chiquet <i>et al.</i> , 2007	Mica	0.01 – 1 M NaCl	1 - 11	308 ^a	18 - 70
Chiquet <i>et al.</i> , 2007	Quartz	0.01 – 1 M NaCl	1 - 10	308 ^a	23 - 37
Espinoza & Santamarina, 2010	Quartz	0.062 M NaCl	0.1 - 10	296.5 ($\pm$ 1.5)	20 ($\pm$ 2)
Espinoza & Santamarina, 2010	Calcite	0.062 M NaCl	0.1 - 10	296.5 ($\pm$ 1.5)	39 ($\pm$ 2)

^a Private communication.

There are a number of methods to *measure saturations* in a CO₂-brine system. These include:

1. In-situ saturation monitoring
2. Volume balance measurements
3. Mass balance measurements
4. Isothermal expansion

Many modern coreflood experiments feature in-situ saturation monitoring (ISSM) where the phase saturations can be continually monitored in two or three dimensions with a radioactive source and receiver. This approach requires a coreholder with a low radiation absorption coefficient so that the core and fluids within can be imaged. Saturations can be determined by monitoring injection and effluent phase volumes and performing volume balance calculations. This approach – in a CO₂-brine context – requires a production separator where phase levels can be monitored accurately to determine effluent volumes. Injection volumes can be determined from the inlet pumps used. Mass balance calculations can be used to determine the saturation within the pore space if the phase densities and the pore volume are known. This approach has limitations if – for example – the coreholder

is at elevated pressures and/or temperatures as it must be disconnected from flowlines and placed on a balance. The isothermal expansion method can also be used to determine saturations in a CO₂-brine system [49]. Suekane *et al.* performed an isothermal expansion of the core plug pore space – using the relationship between pressure and volume to measure the saturation. Figure 1.21 illustrates the experimental design used in the experiment. To measure the phase saturations upon completion of a flow sequence the pressure cell containing the core plug was isolated from the system by closing valves 5 and 6. Valve 7 was then opened connecting the pressure cell to a pressure control syringe pump. Initially the pump cylinder volume is zero and the pressure does not change. The pump cylinder volume is then increased and the subsequent drop in pressure monitored. Knowing the solubility of CO₂ in water and the CO₂ density the original saturation of CO₂ in the core plug – prior to isothermal expansion – can be calculated (Eqn. 18).

$$V_w r(P, T) + S_{gr} V_1 \rho_g(P, T) = V_w r(P', T) + (S_{gr} V_1 + \Delta V) \rho_g(P', T) \quad (18)$$

where

$$V_w = (1 - S_{gr}) V_1 + V_2 \quad (19)$$

$$V_g = V_1 + V_2 + \Delta V - V_w = S_{gr} V_1 + \Delta V \quad (20)$$

V_w is the volume of water, V_1 the pore volume of the core, V_2 the dead volume (between valves 5 and 6 in Figure 1.21), S_{gr} the maximum trapped gas saturation, ΔV the expansion of the pump cylinder volume controlling the isothermal expansion, r the solubility of CO₂ in brine and ρ_g the CO₂ density. The expansion takes place at a constant temperature T , commences at an initial pressure P and has subsequent lower pressure steps P' .

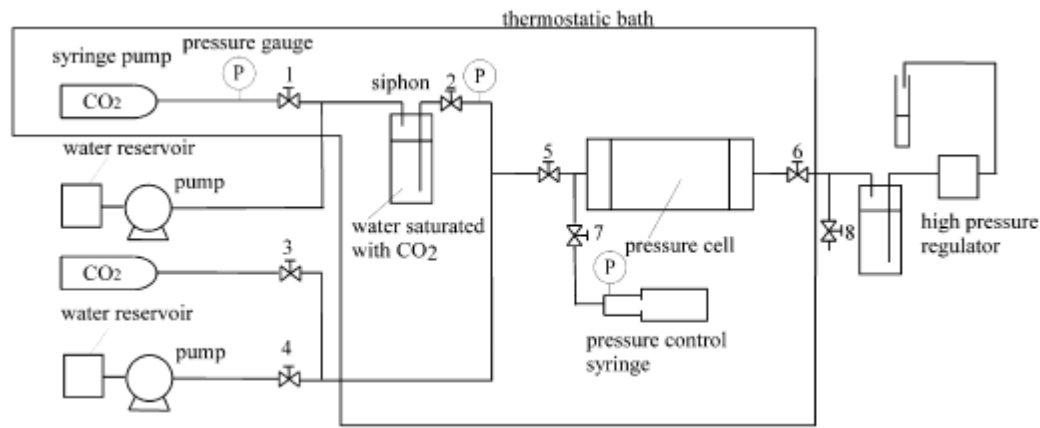


Figure 1.21: Schematic diagram of an experimental set up for measuring maximum trapped gas saturations (figure reprinted from Suekane *et al.* [49]).

Some of the saturation measurement methods outlined involve measuring an average core plug saturation (volume balance, mass balance and isothermal expansion). Alternatively it is possible to measure a saturation profile along the length of the core plug with ISSM. If an average saturation measurement is taken the nuances of any saturation profile will be averaged out. This is important to consider when planning an experiment as different core flood displacement techniques can result in different saturation profiles along the length of the core. Some core flood displacement techniques are therefore better suited to different saturation measurement techniques. Four displacement techniques could be used in a CO₂-brine system: unsteady state displacement, steady state displacement, the centrifuge method and the porous plate method. Of these methods only the porous plate method can be used to generate a *homogenous saturation profile* along the length of the core plug. In the other methods capillary end effects result in the retention of one phase at the outlet face of the core plug. The use of the porous plate method in a CO₂-brine system was first done by Plug [67]. Plug measured the capillary pressure characteristics of a CO₂-brine-sand system including at supercritical conditions. The porous plate method was used to measure both drainage and imbibition capillary pressure curves. A hydrophilic membrane (Millipore) and porous plate (SIPERM) were placed at one end of the sandpack to allow water production during drainage (Figure 1.22). A hydrophobic membrane (nylon) was placed at the opposite end to allow CO₂ production during imbibition. This approach achieves homogeneous saturation profiles along the length of the sample as capillary discontinuity at the end faces is eliminated by the presence of the porous plate. Saturations were measured by mass and volume balance.

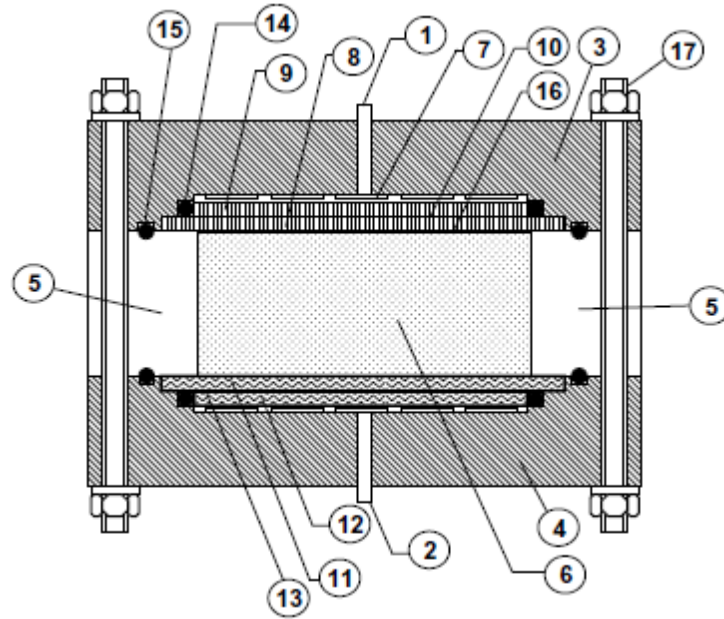


Figure 1.22: Cross section of the sampled holder used by Plug: 1. gas inlet; 2. water inlet; 3. stainless steel end piece; 4. stainless steel end piece; 5. stainless steel ring; 6. porous medium; 7. Concentric grooves; 8. perforated plate; 9. perforated plate; 10. hydrophobic filter (pore size = $0.45 \mu\text{m}$); 11. SIPERM filter; 12. SIPERM filter; 13. water-wet filter (pore size = $0.1 \mu\text{m}$); 14. o-rings; 15. o-rings; 16. nylon filter (pore size = $210 \mu\text{m}$); 17. stainless steel bolts. Reprinted from Plug [67].

Although the trapping curve for a CO_2 -brine system has not been measured Suekane *et al.*, reported maximum residual CO_2 saturations for consolidated Berea sandstone. In addition Plug's bounding capillary pressure curves yield connate water saturation and maximum residual CO_2 saturation data – in other words the end point of the CO_2 -brine-sand system investigated. Finally end-point saturations have been reported in relative permeability measurements on CO_2 -brine-sandstone systems [84], [85]. These results are summarised in Table 1.7. It should be noted that while Plug employed the porous plate method to eliminate capillary end effects, the remaining authors used the steady or unsteady state displacement methods. It is therefore likely that the average core plug saturations reported include the influence of capillary end effects.

A review of Table 1.7 shows that initial CO_2 saturations are generally low ($S_i < 0.7$) – with the exception of the unconsolidated sand and Cardium #1 data – and that there is a large variation in the reported residual saturations ($0.1 < S_r < 0.4$). In this study we investigated whether these saturations are representative of true maximum saturations (S_i^{max} , S_r^{max}) by comparing unsteady state and porous plate experiments on the same core-plug samples.

Table 1.7: Summary of capillary trapping data for CO₂-brine-silicate systems reported in the literature.

Study	Method	Sample	ϕ	T (K)	P (MPa)	S_i	S_r
Plug & Bruining (2007)	PP ^a	Unconsolidated quartz sand	0.360	313	8.5	0.85	0.23
Suekane et al. (2008)	US ^b	Berea sandstone	0.198	308-323	7.6-10.0	-	0.25-0.28
Bennion & Bachu (2008)	US	Cardium #1 sandstone	0.153	316	20.0	0.803	0.102
		Cardium #2 sandstone	0.161	316	20.0	0.575	0.253
		Viking #1 sandstone	0.125	308	8.6	0.442	-
		Viking #2 sandstone	0.195	308	8.6	0.577	0.297
		Ellerslie	0.126	313	10.9	0.341	-
Suekane et al. (2009)	US	Berea sandstone	-	318	8.0	0.66	0.40
Perrin & Benson (2010)	SS ^c	Otway Basin core-plug	0.182	336	12.4	0.56	-
		Berea sandstone	0.203	323	12.4	0.38	-

^a PP – porous plate^b US – unsteady state^c SS – steady state

1.2.4 Summary

Although there has been extensive research on capillary trapping in the past there still remain a number of key unanswered questions. For oil-brine systems with uniform wettability there is uncertainty over the shape of the capillary trapping curve. A number of influential studies – including the work of Land – achieved saturation changes by evaporation. For the systems of interest (oil-brine; CO₂-brine) saturation changes in the reservoir do not in general occur due to evaporation but by immiscible displacements. There are a limited number of literature studies that have measured the trapping curve in this manner.

The petrophysical properties that influence capillary trapping are not fully understood. Relationships with porosity (Figure 1.19), permeability (Figure 1.18) and formation factor (Figure 1.20) have been shown but the influence of pore geometry parameters such as aspect ratio and coordination number has not been studied for representative rock samples.

The shape of the trapping curve has not been measured for CO₂-brine systems. It is unknown whether the shape changes compared to an oil-brine system and whether the magnitude of the end point saturation changes.

To recap, the early studies of trapping focused primarily on gas/water systems in consolidated media. The objectives, below, of this study are applicable to CO₂ storage in siliclastic porous media:

1. Develop an understanding of the wettability characteristics of a CO₂-brine-sandstone system through petrophysical measurements.
 2. Measure the CO₂ saturation hysteresis behaviour in the form of the trapping curve – Si-Sr – through immiscible displacements inside a representative geological sample.
 3. Investigate the form of the trapping curve for different porous media (unconsolidated sand and sandstone). Determine how literature trapping equations match to the data and whether there is a best match.
 4. The petrophysical properties which influence capillary trapping will be investigated. Existing relationships with porosity and permeability will be explored in addition to geometrical properties such as coordination number and aspect ratio.
 5. Where possible capillary pressures will be measured and the saturation-capillary pressure relationship determined.
-

Chapter 2

Experiments

Three sets of capillary trapping experiments were performed during this study. The experiments investigated a range of porous media, experimental conditions and fluid types. The aim was to measure the form of the initial-residual trapping curve, quantify the end-point saturations for the systems under investigation, and investigate the influence of petrophysical parameters on capillary trapping. For consolidated samples we also measured the bounding primary drainage capillary pressure curve. Initially sandpack experiments were performed at ambient conditions before coreflood experiments with representative consolidated samples at elevated temperatures and pressures (ETP) were conducted. By performing the experiments in distinct steps lessons were learnt and expertise built up prior to attempting to measure CO₂ saturations in sandstones – experimentally the most challenging measurements performed. Table 2.1 summarises the parameters of the three experiments.

Table 2.1: A summary of the range of parameters for the three experiments performed during this study.

Experiment	Porous Media	ϕ	K (m ²)	K (D)	T (K)	P (MPa)	Phases
Sandpack	Unconsolidated sands	0.33 – 0.42	5.9×10^{-12} – 8.9×10^{-11}	6.0 – 90.2	293 (± 2)	atm	Octane- brine
ETP Oil	Sandstones & Aerolith ceramic	0.13 – 0.53	6.9×10^{-14} – 1.3×10^{-11}	0.1 – 13.2	343 (± 1)	9.0	Decane - brine
ETP CO ₂	Berea Sandstone	0.21	4.6×10^{-13}	0.5	343 (± 1)	9.0	CO ₂ - brine

2.1 Sandpack Experiments

2.1.1 Introduction

The sandpack experiments were designed to build upon the literature data (Figure 1.16; Figure 1.17). One sand (LV60) was used to probe a wide range of initial nonwetting-phase saturations ($S_{(nw)i}$) – and their corresponding residual saturations ($S_{(nw)r}$) – at one time. End-point saturations of five additional sands were also investigated. Unconsolidated sands were investigated as an analogue to shallow formations which could be used during CO₂ storage. While CO₂ is likely to be injected at depths greater than approximately 800 m to render it supercritical, it may be injected into formations that tend to have a higher porosity and permeability than deep oilfield rocks.

The experiments used unconsolidated sandpacks and analogue fluids at ambient conditions. The fluid systems investigated were oil/brine (all sands) and gas/brine (LV60 only). The initial conditions were established by injecting oil or gas into vertical or horizontal sandpacks at different flow rates and then – in the case of the oil experiments – allowing the oil to migrate due to gravity. The packs were then flooded with brine. The columns were sliced, and the residual saturation measured by gas chromatography (GC) and mass balance. The use of GC is extremely accurate and allowed low saturations to be measured reliably.

2.1.2 Equipment and Conditions

The experiments used unconsolidated sandpacks and analogue fluids at ambient conditions. Above its critical point – critical temperature = 304.13 K; critical pressure = 7.38 MPa [11] – CO₂ has unique properties with a density similar to a liquid and a viscosity more akin to a gas. For the oil/brine systems, the non-wetting phase was chosen to be *n*-octane since it has a density similar to CO₂ at reservoir conditions. Air was used as the non-wetting phase for the gas/brine systems since it has a viscosity similar to CO₂ at reservoir conditions. See Table 2.2 for details of the fluid properties; comparison with CO₂ can be made with reference to Figure 1.4. The wetting phase in both sets of experiments was brine (de-ionized water with 1 weight % Potassium Chloride, and 5 weight % Sodium Chloride). The ambient

temperature in the lab was recorded as being consistently 293.15 K (± 1 K). Ambient pressure was measured to be 0.101 MPa (± 0.003 MPa).

Six sands were studied in total – LV60 for oil/brine and gas/brine trapping curve experiments and the remaining five sands for oil/brine end-point experiments. Ottawa sands, F110, F42 and F35 were supplied by U.S. Silica (Berkley springs, WV, U.S.A). HST 95, LV60 and OMR were supplied by WBB minerals (Sandbach, Cheshire, UK). The grain size distributions measured by sieve analysis and slices of three-dimensional micro-CT scan images of the sands that illustrate the grain shapes and pore structure are included in Appendix 1. Nuclear-magnetic-resonance (NMR) scans have been published previously for the LV60 sand [86].

The sandpack was contained in a custom machined Polymethylmethacrylate column 0.6 m long, 0.04 m internal diameter. The design of the column features pre-machined grooves around the circumference every 5 cm along the column length. These grooves allowed the column to be sliced upon completion of the flow experiment such that direct samples could be taken from the sandpack for analysis using gas chromatography (GC) (oil/brine systems) or mass balance (air/brine systems). When packing the column with sand, a circular piece of wire mesh (brass) and two circular pieces of filter paper (VWR Int. Filter Papers 415) were placed between the sand face and the end cap to prevent sand production. A balance (Model S-6002, Denver Instruments, Bohemia, NY, USA) was used to measure the mass of the sand-packed column in different conditions, dry, saturated and sliced (accuracy of $\pm 1.0 \times 10^{-5}$ kg). The use of GC for direct sample measurement [87] is a precise approach that is highly accurate. A GC (PerkinElmer Autosystem XL, Waltham, MA, USA) fitted with a SGE forte capillary column (30m x 0.25mm ID, BP20 0.5 μ m, polyethylene glycol) and a thermal conductivity detector (TCD) was used to detect fluid concentrations. The GC set-up allowed detection of changes of the magnitude of 1 ppm within each GC sample vial. The GC measurement program is summarized in Appendix 1. Injection flow rates during the experiment were controlled by high precision syringe pumps (Teledyne ISCO 500D & 1000D, Lincoln, NE, USA). Flow accuracy according to technical specifications is $\pm 0.5\%$. Back pressure was applied to the pore fluids using a needle valve (Swagelok SS-SS2-KZ, Solon, OH, USA). The set-up of the oil/brine experimental apparatus is shown in Figure 2.1.

Table 2.2: Octane and brine properties at ambient conditions of 0.101 MPa and 293.15 K unless stated otherwise^a.

Property	Value
Octane Viscosity	5.1×10^{-4} Pa.s ^b
Brine Viscosity	1.085×10^{-3} Pa.s ^c
Octane Density	709 kg.m^{-3}
Brine Density	1042 kg.m^{-3}
Octane-brine interfacial tension	50.81 mN.m^{-1} ^d

^a Density figures averaged over 15 experiments.

^b Reference temperature 298.15 K [11]

^c 5 weight % NaCl Brine (no KCl present) [11]

^d [88]

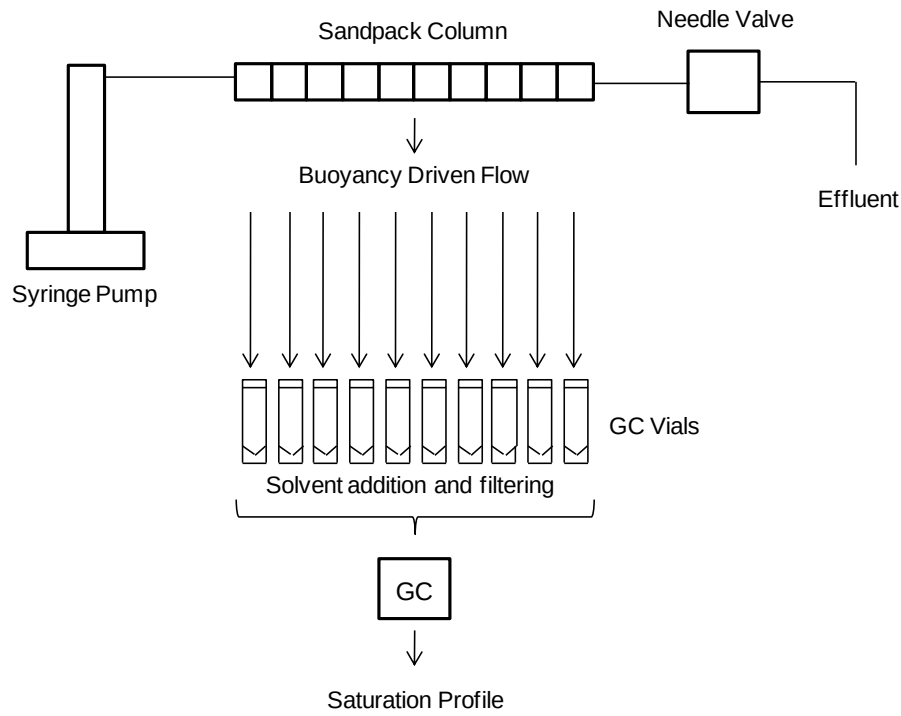


Figure 2.1: Ambient condition oil/brine sandpack experimental apparatus.

2.1.2 Experimental Procedure

In total ten experiments – comprising 37 individual columns – were performed (Table 2.3). Each individual sand-packed column would yield either an S_{oi}/S_{or} or an S_{gi}/S_{gr} set of data. Two columns – as a minimum – were required to produce a single set of S_{oi} versus S_{or} (or S_{gi} versus S_{gr}) values; additional replicates were added to assess the reproducibility of the results.

Table 2.3: Table summarising the sandpack experiments performed and their associated parameters. One pore volume (PV) was equal to 111.2±2.7 mL.

Experiment	Orientation	Data	Sand	Octane Injected (PV)	Brine Injected (PV)	Number of Replicates
1 S_{oi}	Vertical	TC ^a	LV60	0.64	0	3
1 S_{or}	Vertical	TC	LV60	0.64	8.54	3
2 S_{oi}	Vertical	TC	LV60	1.06	0	3
2 S_{or}	Vertical	TC	LV60	1.06	8.54	3
3 S_{oi}	Vertical	TC	LV60	1.70	0	1
3 S_{or}	Vertical	TC	LV60	1.70	8.54	1
4 S_{oi}	Horizontal	EP ^b	LV60	8.36	0	1
4 S_{or}	Horizontal	EP	LV60	8.36	8.54	1
5 S_{gi}	Vertical	TC	LV60	-	0	3
5 S_{gr}	Vertical	TC	LV60	-	8.54	3
6 S_{oi}	Horizontal	EP	HST 95	4.50	0	1
6 S_{or}	Horizontal	EP	HST 95	4.50	4.05	3
7 S_{oi}	Horizontal	EP	F110	4.50	0	1
7 S_{or}	Horizontal	EP	F110	4.50	4.05	3
8 S_{oi}	Horizontal	EP	OMR	4.50	0	1
8 S_{or}	Horizontal	EP	OMR	4.50	4.05	3
9 S_{oi}	Horizontal	EP	F42	4.50	0	1
9 S_{or}	Horizontal	EP	F42	4.50	4.05	1
10 S_{or}	Horizontal	EP	F35	4.50	4.05	1

^a Trapping Curve (TC).

^b End Point (EP).

The experimental procedures were as follows:

Oil/Brine System:

1. Column dry packed with sand
2. Column fully saturated with brine
3. Octane injection (primary drainage) – performed to reach S_{oi}
4. Brine injection – performed to reach S_{or}
5. Column sliced into sections for sampling
6. Addition of solvent to each sample of sand plus octane plus brine
7. Filtering of each sample removes sand, leaving a single homogeneous liquid phase
8. Injection of homogeneous liquid samples into GC for compositional analysis

Gas/Brine System:

1. Column dry packed with sand
2. Column fully saturated with brine
3. Air injection (primary drainage) – performed to reach S_{gi}
4. Brine injection – performed to reach S_{gr}
5. Column sliced into sections for sampling
6. Weigh each column section filled with sand, brine and air
7. Recover sand and wash with de-ionized water and measure sand mass
8. Weigh each empty clean column section
9. Measure bulk volume of each column section

Regardless of the fluid system or experiment type the procedure began with the packing of a column with sand. A known mass of sand was added to a column with a known bulk volume. The subsequent porosity of the sandpack was determined by mass balance. A packing density was used throughout to aid reproducibility (for example a packing density of 1654 kg/m^3 was used for the LV60 sand). The bulk volume of the columns was found by filling them with water of a known density and measuring the mass and comparing with the mass of the dry column. The packing process was performed with dry sand poured into the column in one continuous motion under vibration. Table 2.4 gives the average properties of the packs. ϕ is the porosity, K_{brine} brine permeability, F formation factor, R_a average aspect ratio and $N_{\text{coord.}}$ is the average coordination number. ϕ was measured by mass balance on a dry and saturated sandpack column. K_{brine} was measured on a packed column by injecting brine at a constant flowrate and measuring the pressure drop (equations in Appendix 1). F was measured by packing a small core-plug sized container (0.0762 m length; 0.0381 m diameter) with sand and saturating with brine. The conductivity across the sample was measured with a conductivity meter (Quadtech model 7600 RLC, Marlborough, MA, U.S.A.); further details are given in Appendix 2. The average geometric properties R_a and $N_{\text{coord.}}$ were determined from analysis of networks extracted from micro-CT images of small cylindrical (0.02 m length; 0.005 m diameter) packed samples of each sand.

Table 2.4: Average porosity (ϕ), brine permeability (K_{brine}), formation factor (F), aspect ratio (R_a), coordination number ($N_{\text{coord.}}$), and grain size of the sandpacks investigated.

Sand	ϕ	K_{brine} (m^2)	K_{brine} (D)	F	R_a	$N_{\text{coord.}}$	Avg. grain size (μm)
LV60	0.370 (± 0.002)	3.2×10^{-11} ($\pm 3 \times 10^{-13}$)	32.4 (± 0.3)	3.4	2.1	4.9	225
HST95	0.334	7.8×10^{-12}	7.9	-	2.7	5.9	136
F110	0.354	6.2×10^{-12}	6.3	-	1.9	4.3	147
OMR	0.416	8.7×10^{-11}	88.2	-	2.7	5.2	532
F42	0.350	4.2×10^{-11}	42.6	-	2.1	4.4	346
F35	0.362	4.2×10^{-11}	42.6	-	2.0	5.5	406

Establishing an initial brine saturation of 100% was accomplished in three steps. The brine was degassed by bubbling oxygen-free nitrogen gas through the brine for a minimum of 15 minutes. This decreased the likelihood of gas separating out of the liquid within the sandpack because oxygen was liberated and substituted by the agitation of the nitrogen. In addition, and before brine injection, the column was completely saturated with gaseous CO_2 . Five to ten pore volumes of brine were injected under a 0.138-MPa backpressure to displace the CO_2 . The backpressure was applied with a needle valve, forcing the brine into the smaller pores. Even so, any remaining trapped CO_2 gas dissolved in the brine, resulting in a 100%-saturated sandpack. Continued brine injection (multiple pore volumes) ensured that the sandpack was free of dissolved CO_2 before oil or air injection. This was confirmed when no trace of CO_2 was detected during GC analysis.

Primary drainage – the injection of oil or air into the sandpack – varied between the three different experiments. The following three paragraphs summarise the details of the primary drainage procedure in each case.

In the LV60 *oil/brine trapping curve experiments* it was necessary to create highly reproducible initial oil saturation (S_{oi}) profiles along the length of a column. This was achieved by injecting oil into the column and allowing it to rise under buoyancy forces. The octane was injected into the top of a column which was positioned vertically. Once the desired volume of octane had been injected, the column was inverted such that the high oil saturation interval was at the bottom. The octane subsequently migrated upwards due to buoyancy forces. Oil migration was stopped by placing the column horizontally once the first drop of octane reached the filter paper at the top end of the column. This displacement sequence

mimics upward migration of CO_2 followed by chase-brine injection. This is true for the portion of the column not invaded by oil at the point of flipping when buoyancy driven migration begins. The results from this portion of the column were of primary interest; however, as will be seen, the results from the entire length of the column describe a consistent trend and as such are included here. In each experiment the volume of octane injected varied to investigate the full range of initial oil saturations. In two experiments three replicates were performed to find both S_{oi} and S_{or} .

In the LV60 *gas/brine trapping curve experiments* three S_{gi} and two S_{gr} experiments were performed. In all experiments air was allowed to enter the top of the vertically positioned column in a gravity drainage process for 3.5 hours. The displaced brine was produced from the bottom of the column.

In the *end point experiments* an S_{oi} range was not required along the column length. Instead sufficient oil (five pore volumes) was injected horizontally such that a homogeneous S_{oi} existed along the column length. Waterflooding such a column resulted in a corresponding homogeneous S_{or} along the column length.

After primary drainage the column would either be sliced to find S_{oi}/S_{gi} or brine injection would start. To reach residual conditions, four pore volumes were injected. In the case of the oil/brine system oil production always ceased soon after brine breakthrough and long before the end of the experiment.

At the end of injection the columns were sliced into sample sections. For the oil/brine system each section was mixed with 30 g of 2-propanol solvent. This amount of solvent had been determined to be sufficient to dissolve both the octane and brine giving a single homogeneous liquid phase. The mixture of sand and liquid was then filtered to remove the sand. The liquid was sampled into vials ready for GC analysis. This process was repeated for all samples from each column.

For the air/brine experiments, each sliced section was weighed full and empty. Wet sand contained in each section was washed three times with de-ionized water to remove dissolved salt. The sand was then dried and weighed. The bulk volume of each column section was measured. This step improved the accuracy of

the results significantly as the pore volume for each column section was determined.

Table 2.5 gives the Darcy velocities, capillary numbers (Eqn. 6), and Bond number (Eqn. 7) associated with these experiments; these are typical of those likely to be found during CO₂ storage [24].

Table 2.5: Flow conditions associated with each experiment.

Experiment(s)	Phase Injected	Darcy Velocity	Capillary Number	Bond Number
1 through 3	<i>n</i> -octane	2.65×10^{-5} m/s	2.66×10^{-7}	5.3×10^{-4}
4 and 6 through 10	<i>n</i> -octane	2.65×10^{-4} m/s	2.66×10^{-6}	na
all	Brine	2.65×10^{-4} m/s	5.66×10^{-6}	na

2.1.3 Results

For LV60 sand Figure 2.2 shows the four sets of measured oil/brine trapping curve saturation profiles, while Figure 2.3 shows the inferred trapping curve. The four experiments cover different ranges of S_{oi} : in Experiment 1, it ranges from 3.4 to 52.0%; 5.6 to 73.7% in Experiment 2; 39.9 to 76.4% in Experiment 3; and 46.2 to 79.6% for Experiment 4. The error bars shown in Figure 2.3 are based on the standard deviation where three replicates were performed for each of the S_{oi} and S_{or} data sets. We also ran an additional Experiment 4 at one-quarter the flow rate and obtained the same residual saturations within experimental error; this confirmed that we performed the experiments in the capillary-controlled regime where the amount of trapping is insensitive to flow rate.

Figure 2.4 compares our data with the correlations proposed in the literature that were discussed previously: we used our data to find the parameters in the various correlations (Table 2.6). It is evident that the best fit is given by Aissaoui's law (Eqn. 14 with o for oil substituted for g) [66] and Spiteri et al.'s law (Eqn. 15) [1]. Aissaoui's correlation displays an initial linear increase in S_{or} to = 12.8% at S_{oc} = 47.6%, followed by a constant S_{or} . Spiteri et al.'s fit gives a quadratic response based on the fitting parameters α and β ; see Table 2.6. Note that the residual saturation ranges in Figure 2.3 and Figure 2.4 differ from the range shown in Figure 1.16.

When matching the trapping laws to the experimental data set, the endpoint ($S_{oimax} = 80\%$; $S_{orimax} = 12.8\%$) is fixed. Once the endpoint is fixed, some laws cannot be regressed further to match the data – they have no further degrees of freedom. Other laws can be tuned, and this is summarized in Table 2.6 along with the square of the multiple R value (R^2). R^2 gives the proportion of total variance between measured S_{or} and trapping-law-predicted S_{or} values [89]. The best matches to the data set are achieved with the equations with the highest degree of freedom, as expected. Any experimental error associated with S_{or} was ignored during the fitting process.

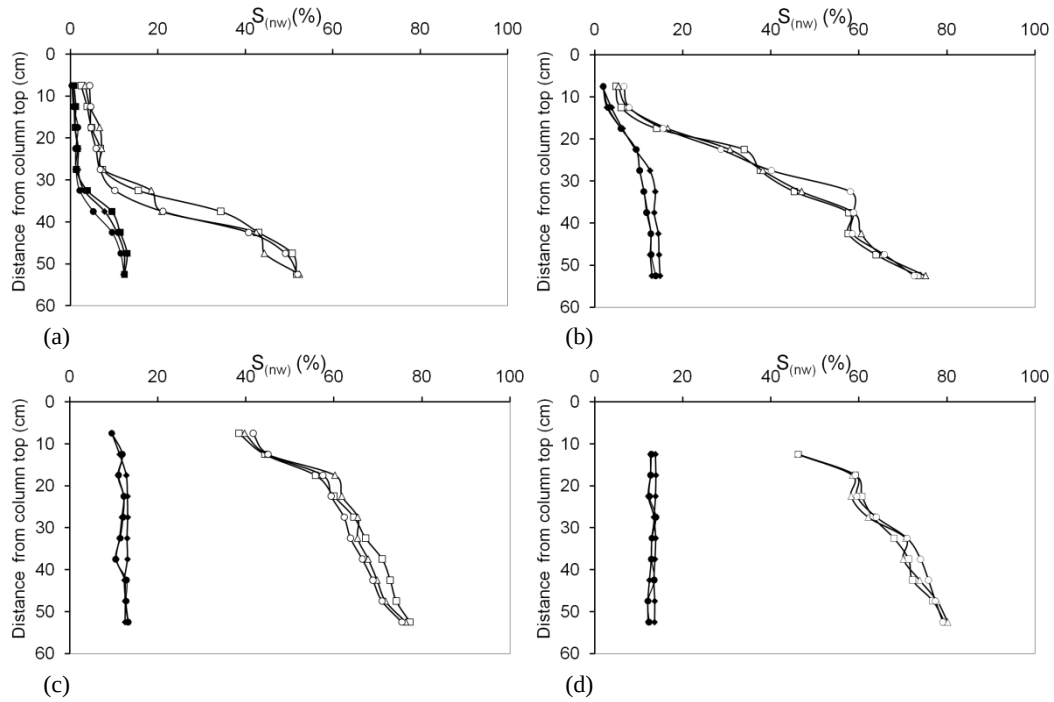


Figure 2.2: Oil saturation profiles. The lines to the right show the initial conditions, while the lines to the left show the trapped oil saturation. Three S_i replicates and three S_r replicates are shown for each experiment. (a) Experiment 1: vertical 71 ml oil injection. (b) Experiment 2: vertical 118 ml oil Injection. (c) Experiment 3: vertical 189 ml oil injection. (d) Experiment 4: horizontal 930 ml oil injection (see Table 2.3).

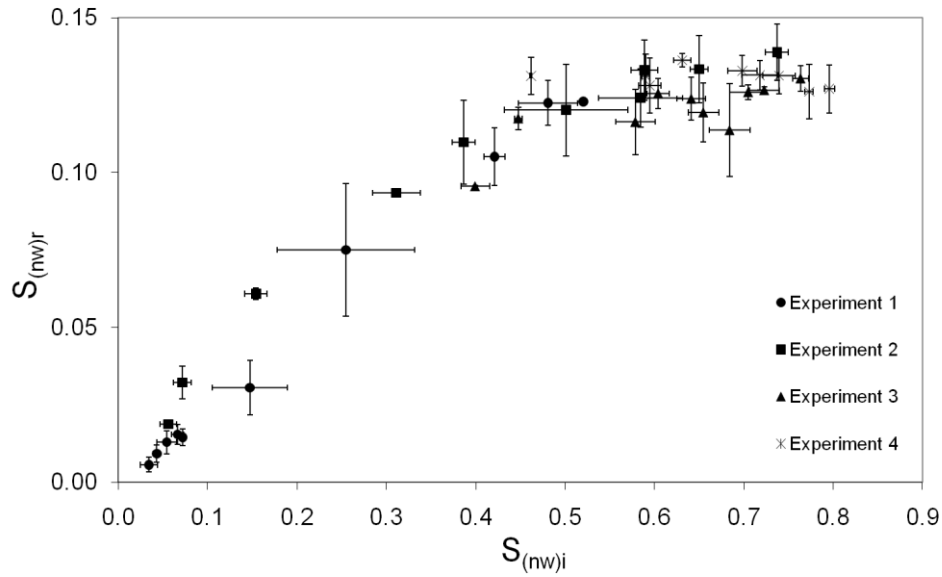


Figure 2.3: Experimental oil-brine trapping curve showing results from all four experiments (see Table 2.3).

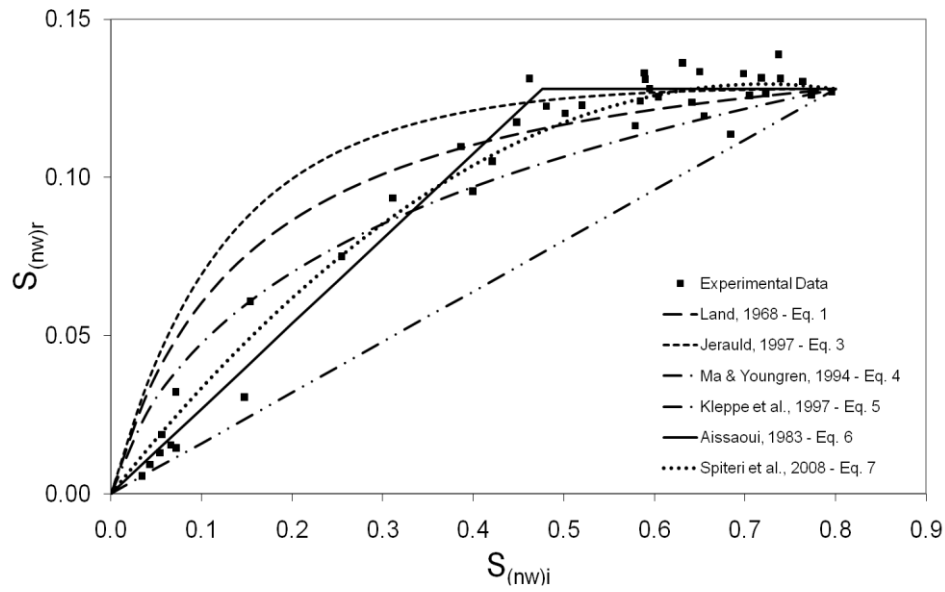


Figure 2.4: Comparison between the experimental oil-brine data and empirical trapping equations in the literature.

The gas/brine trapping curve saturation profiles are shown in Figure 2.5. The trapping curve is plotted in Figure 2.6 and the best match to the data was given by the Aissaoui correlation (Eqn. 14; R^2 of 0.974). The oil/brine and gas/brine trapping curves are displayed together in Figure 2.7.

Table 2.6: Best-fit matching parameters, including the correlation R^2 , between experimental data and empirical trapping equations in the literature.

Trapping Law	Degrees of Freedom ^a	Matching Parameters	R^2
Land (1968), Eqn. 9	0	$C = 5.25$ (fixed by endpoint)	0.766
Jerauld (1997), Eqn. 11	0	$S_{or}^{*max} = 0.16$ (fixed by endpoint)	0.627
Ma and Youngren (1994), Eqn. 12	1	$b = 0.75$; $a = C$ (Eq. 2) = 5.25 (fixed by endpoint)	0.830
Kleppe et al. (1997), Eqn. 13	0	$S_{or}^{max} = 0.128$; $S_{oi}^{max} = 0.8$ (fixed by endpoint)	0.495
Aissaoui (1983), Eqn. 14	1	$S_{oc} = 0.476$; $S_{or}^{max} = 0.128$ (fixed by endpoint)	0.974
Spiteri et al. (2008), Eqn. 15	1	$\alpha = 0.359$; $\beta = 1.25\alpha - 0.2 = 0.249$ (fixed by endpoint)	0.969

^a The degrees of freedom are those once the curve endpoint is set.

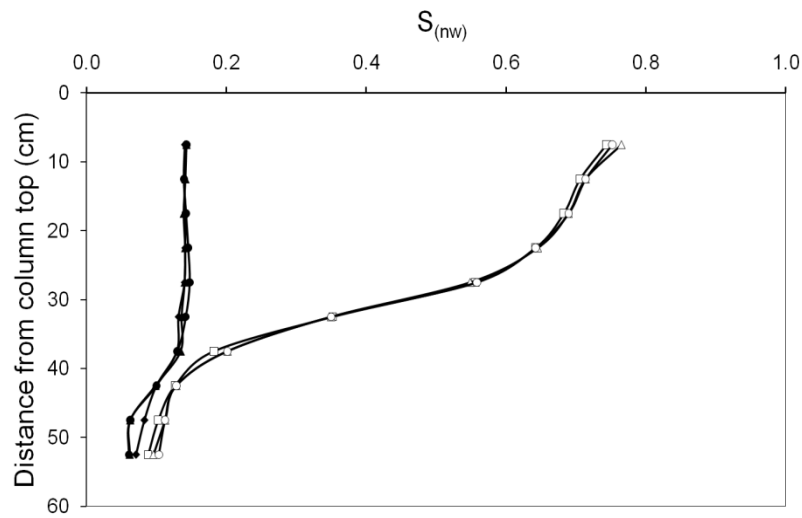


Figure 2.5: Gas Saturation profiles from the gas-brine LV60 sandpack experiment. The lines to the right show the initial conditions, while the lines to the left show the trapped gas saturation. Three S_i replicates and three S_r replicates are shown for each experiment.

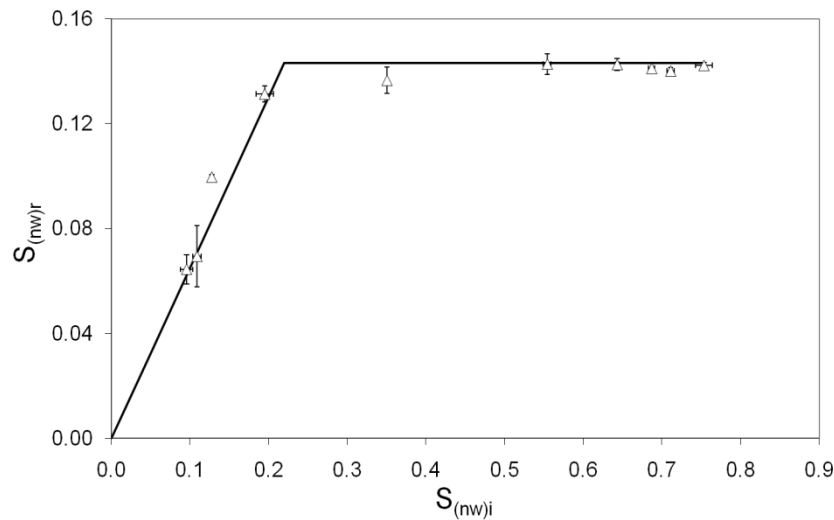


Figure 2.6: Gas-brine trapping curve data and best-fit Aissaoui correlation match (Eqn. 14).

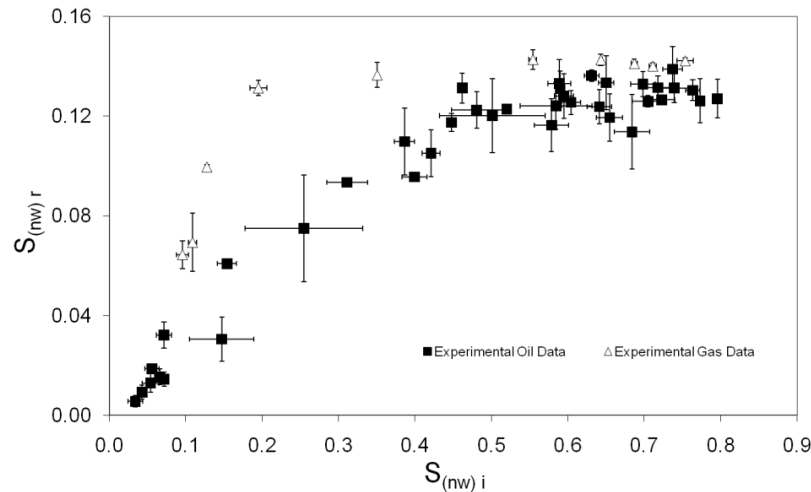


Figure 2.7: Oil/brine and gas/brine trapping curves.

The results of the oil/brine end-point experiments are summarised in Table 2.7. The table shows the full set of oil saturation results measured by both mass balance (MB) and gas chromatography (GC).

Table 2.7: Summary of end-point saturation results.

Sand	S_{oi} MB	S_{oi} GC	S_{or} MB	S_{or} GC
LV60		0.73	0.133	0.128
HST95	0.770	0.775	0.144	0.131
F110	0.766	0.780	0.140	0.135
OMR	0.643	0.620	0.122	0.114
F42	0.768	0.809	0.117	0.108
F35	0.738		0.137	0.128

There was a small difference between S_{or} and S_{oi} measured by mass balance and GC. For S_{oi} the average GC reading was approximately 1-2% higher than the mass balance calculation while GC results for S_{or} were generally around 1% lower. The GC reading is determined by measuring the saturations in each individual 0.05 m column section and averaging. No GC sampling of the end-cap sections was performed. On the other hand the mass balance measurements were made as a single average over the full length of the column, including the two end-cap sections. It is possible that a small amount of liquid was retained near the outside of the end-cap section furthest from the injection point influencing the average mass balance measurement. It is also possible that a small amount of oil may have been lost from each sample due to evaporation during the cutting and filtering procedure. Any amount lost would have been very small and would not have affected S_{oi}

readings. However, because the S_{or} readings were measuring smaller volumes of oil (around 0.5 mL in each sample as opposed to around 4 mL for S_{oi}), a small volume lost from each sample could significantly lower the S_{or} measured by GC. It is trapping in the end sections, however, that is more likely to be the main cause of the variances seen. For this reason, GC results will be taken with greater confidence and used for the analysis and discussion.

2.2 Consolidated Oil/brine Coreflood Experiments

2.2.1 Introduction

Displacement experiments using the porous plate method were conducted on consolidated sandstone and ceramic samples to measure the capillary trapping of oil by waterflooding. The form of the trapping curve was investigated in addition to the magnitude of the end point saturations. Six samples were investigated – five sandstones and one artificial ceramic – ranging in porosity from 12.2% to 53.1%. Experiments were conducted at an elevated temperature and pressure (ETP) of 343 K and 9 MPa. A confining pressure of 11.75 MPa was applied resulting in a effective radial stress of 2.75 MPa. The high permeability samples and the combination of temperature and pressure make this system analogous to a relatively warm aquifer, just below the supercritical depth, at approximately 900 m. Such formations are likely to prove attractive targets for carbon storage, as the cost of injection is likely to be lower than in deeper, less permeable formations.

2.2.2 Equipment and Conditions

Five sandstones and one ceramic sample (Aerolith 10, Pall Corporation, Crailsheim, Germany [90]) were investigated. The core-plugs were characterised prior to the coreflood experiments – Table 2.8. All core-plugs were 0.037 to 0.039 m (1.5in.) in diameter and 0.075 to 0.077 m (3.0in.) in length. Additional information and data on the characterisation of the core-plugs – including mercury injection capillary pressure measurements – are summarised in Appendix 2 and 3. The trapping curve was measured for two of the samples – Berea 11 and Clashach JP. The end point saturations were measured for the remaining samples. All of the samples are considered strongly water-wet with the exception of Doddington 4. The Doddington core-plug was a legacy sample in the Imperial College Petrophysics laboratory. As such the exact experimental history for the core-plug was not known. Upon cleaning by soxhlet extraction a discolouration of the solvents (brown colour) was noticed – indicating that the core-plug had probably been flooded with crude oil previously. With this in mind the wettability of this sample is uncertain.

Table 2.8: Petrophysical parameters of core-plug samples investigated.

Sample	ϕ	$K_{\text{brine}} (\text{m}^2)$	$K_{\text{brine}} (\text{mD})$	R_a	$N_{\text{coord.}}$	F
Aerolith 10	0.531 (± 0.041)	1.2×10^{-11}	12700	-	-	3.7
Berea 3	0.177 (± 0.005)	7.0×10^{-14}	70	16.59	2.98	28.2
Berea 11	0.228 (± 0.016)	4.6×10^{-13}	460	18.78	4.10	12.4
Berea SB	0.198 (± 0.009)	9.8×10^{-14}	100	-	-	21.0
Clashach JP	0.131 (± 0.008)	8.0×10^{-14}	70	18.56	3.1	57.5
Doddington 4	0.205 (± 0.027)	2.1×10^{-12}	1600	13.95	3.36	15.8

The experiments were conducted inside an air bath at 343 K (70 °C) with a back-pressure of 9 MPa. The non-wetting phase was *n*-decane. The wetting phase was aqueous 5wt.-%-sodium chloride, 1wt.-%-potassium chloride synthetic brine in all experiments. Table 2.9 summarises the experimental conditions and phase properties.

Table 2.9: Experimental conditions and associated phase properties. Values are laboratory measurements unless stated.

	ETP Experiments
T (K)	343
P (MPa)	9.00
Wetting Phase	5wt.-% NaCl, 1wt.-% KCl aqueous solution
Non-wetting Phase	<i>n</i> -decane
σ (mN m ⁻¹)	48.3 ^a
Wetting Phase Viscosity (Pa s)	4.554×10^{-4b}
Non-wetting phase viscosity (Pa s)	5.47×10^{-4c}
Wetting phase density (kg m ⁻³)	1020 ^d
Non-wetting phase density (kg m ⁻³)	700 ^e

^a [91]; linearly extrapolated to 343 K.

^b [92]; 5.8wt.-% NaCl aqueous solution at 10.0MPa, 343.2 K.

^c [93]; 9480 kPa, 344 K.

^d [94]; 1.027 mol/kg NaCl aqueous solution.

^e [95]

The porous plate method was identified as a method to achieve a homogeneous initial saturation distribution in a core-plug sample (Chapter 1.2.3 Previous Experimental Studies with Supercritical Carbon Dioxide). The porous plate method, in which a water-wet disk (1.5 MPa plate, Weatherford Laboratories, Stavanger, Norway) placed immediately downstream of the core-plug retains the non-wetting phase inside the sample, was used during primary drainage. With this method, equilibrium corresponds to uniform pressure distribution across the core-plug in each of the phases, with the difference in the equilibrium pressure of the two phases corresponding to the capillary pressure. Capillary end effects are eliminated, and phase saturations are assumed to be uniform across the length of the sample. The porous plate is an Alumina-silicate ceramic (0.038 m diameter; 0.007

m thickness). The small pore size (average $0.16\ \mu\text{m}$) prevents the non-wetting phase entering the plate below the breakthrough capillary pressure (1.5 MPa for an oil/water fluid system). The wetting phase is in continuum through the core-plug and plate.

The core-plug and porous plate were housed within a custom designed Hassler type core holder. The core-plug and porous plate were inserted inside a rubber sleeve (Viton[®]) around which a radial confining pressure was applied. At the end face of the core-plug was a production/injection port. At the other end of the core holder – the end face of the porous plate – there are two ports for injection and production. One port is flush with the face of the porous plate – enabling brine production during primary drainage. The other port passes through the porous plate to terminate flush with the face of the core-plug. This port was used for waterflooding the sample. It bypasses the porous plate to avoid the large pressure drops associated with flowing through the low permeability ceramic material. The port passing through the porous plate was isolated with a rubber (Viton[®]) o-ring to prevent bypassing. It could be closed with a valve to prevent production during primary drainage.

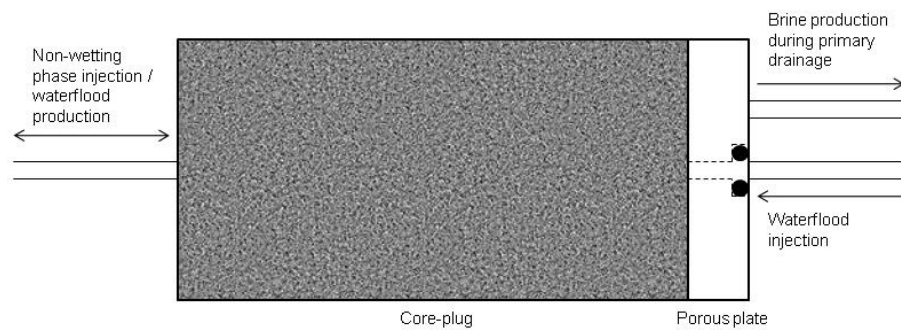


Figure 2.8: The modified porous plate design allowing for faster waterflooding of the core-plug samples. The left hand face features a single port for non-wetting phase injection during primary drainage and production during waterflooding. The right hand face has two ports: the upper port terminates flush with the face of the porous plate and allows brine to be produced during primary drainage; the lower port passes through a hole in the centre of the porous plate terminating flush with the core-plug face – this port is used during brine injection (initial saturation and waterflooding). It is sealed with o-rings to prevent bypassing.

Injection flow rates and pressures were controlled by high precision syringe pumps (Teledyne ISCO 500D & 1000D, Lincoln, NE, USA). The back pressure – which is equivalent to the wetting phase pressure during primary drainage – was

controlled by a syringe pump operating in constant pressure mode. The setup of the equipment is shown in Figure 2.9.

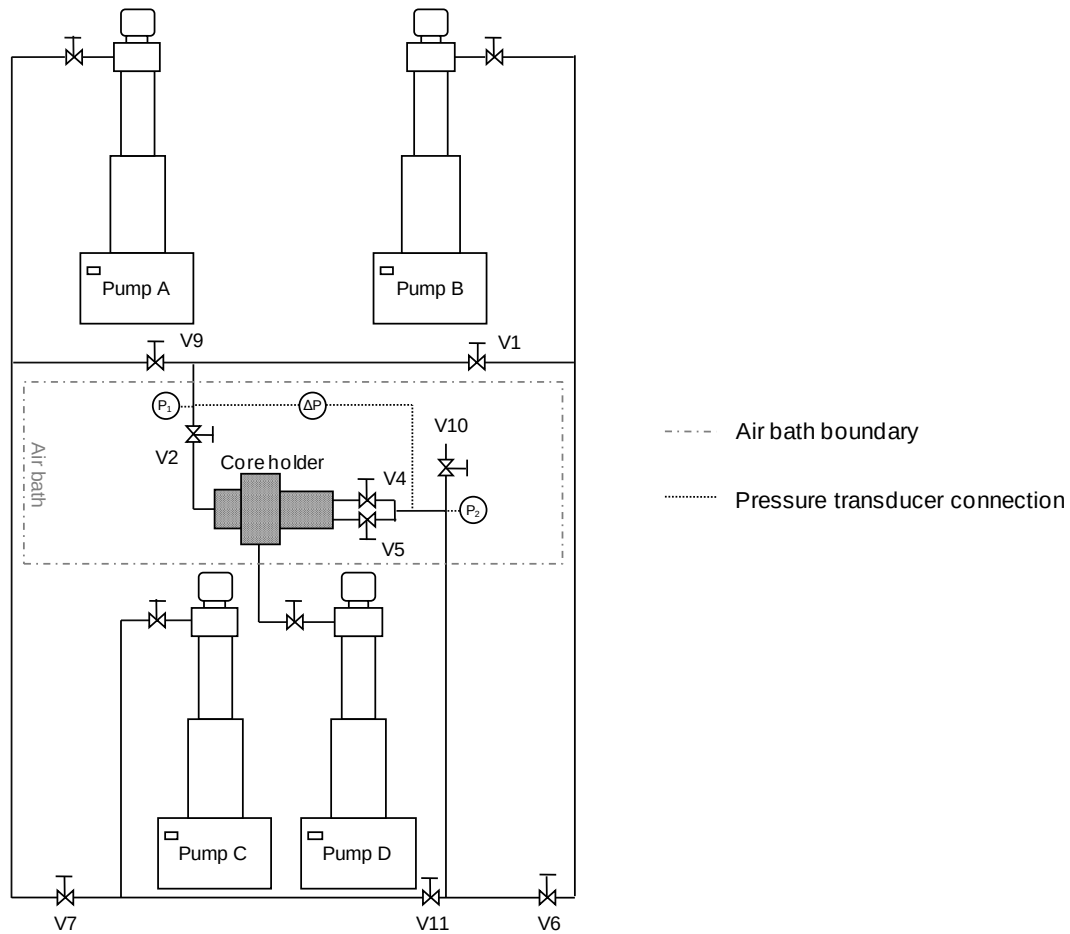


Figure 2.9: Oil/brine ETP coreflood apparatus. The porous plate was situated at the right hand end of the core holder. Valve 4 is connected to the brine production port and valve 5 is connected to the waterflood injection port (Figure 2.8). Pump A was used for oil injection; pump B for brine injection; pump C for back pressure and receiving production from the core; and pump D applied radial confining pressure to the core-plug.

2.2.3 Experimental Procedure

Initial water saturation. The test core-plug was saturated with brine at experimental conditions inside the core holder. The pore space was initially vacuumed for 30 minutes before de-gassed brine was introduced and brought up to experimental pressure. A minimum of five pore volumes of brine were injected through the core-plug against back pressure. The core holder, containing the brine-saturated core, was weighed. The pore volume was determined from the increase in mass of the core holder compared to the dry weight (once dead volumes were accounted for – see Appendix 4).

Primary drainage. The non-wetting phase was injected into the core-plug against a back-pressure using one of two methods: at constant pressure or at constant flow rate. The former was used for all end-point measurements, and for high initial non-wetting phase saturation points on the Berea and Clashach trapping curves. Here, equilibrium was considered achieved when brine production ceased and the volumetric rate of oil injection by the pump reached a constant (the pump leakage rate which was measured prior to each experiment). Capillary pressure, and hence initial saturation, was varied by changing the injection (non-wetting phase) pressure. For all other runs, a pre-determined volume of oil was injected at a constant flow rate corresponding to capillary numbers between 1.6×10^{-10} and 3.3×10^{-10} . This was necessary because at low initial saturation fluctuations in laboratory temperature caused changes in P_c of the order of 0.02 MPa when the syringe pumps were operated in constant pressure mode. Operating the pumps in constant rate mode (at very low flow-rates) resulted in the application of a more constant pressure differential to the core-plug. Once the volume necessary to achieve the target S_i was injected the injection pump was stopped and the pressure differential stabilised. The pressure differential dropped as flow ceased but it did not drop to zero. The resulting non-zero equilibrium pressure is the applied P_c . The duration of primary drainage ranged from 14 to 166 hours for Berea and 21 to 89 hours for Clashach. S_i was determined from the volume of the injected non-wetting phase and the decrease in the mass of the Hassler cell containing the core-plug from its brine-saturated state prior to oil injection.

Waterflooding. Subsequently, the core-plug was flooded with brine in the opposite direction to oil injection. The tube bypassing the porous plate was used to avoid large pressure drops across the plate. A minimum of five pore volumes of brine were injected in each run at a capillary number equal to 3.1×10^{-7} . Residual saturation was determined from the decrease in the mass of the core holder from its brine-saturated state and, in addition, from the increase in mass of the core holder during waterflooding and from the increase in the mass of the core-plug relative to its dry state.

Further details on the experimental procedure for the three flooding stages (initial saturation, primary drainage, waterflooding) – including routing of injection/production phases through the apparatus and associated valve positions – can be found in Appendix 4, along with the calculations used to determine S_i and S_r .

Core-plug Cleaning & Re-saturation. Upon completion of one set of S_i and S_r measurements the core-plug was cleaned by hot soxhlet extraction for approximately 20 hours. The solvents used were 50vol.% methanol and 50vol.% toluene. The core-plug was then dried under vacuum at a temperature of 353 K.

Once the core-plug was cleaned and dried it was inserted into the core holder and re-saturated with the same procedure described above under initial water saturation.

Pore-network simulations. A corresponding set of simulations of primary drainage and waterflooding were performed using the two-phase flow pore-network simulator developed by Valvatne and Blunt [40]. The equivalent networks used in these simulations were extracted from tomographic datasets in the same manner as outlined previously (Chapter 1.2.1 Fundamentals of Immiscible Displacement). The equivalent networks contain aspect ratio and coordination number distributions which are reported here (Table 2.8). The reported values represent average values from the network distributions. Input parameters (phase densities and interfacial tension) were matched with experimental conditions. We used networks previously extracted (Table 2.10), using Dong and Blunt's [46] algorithm, from X-ray microtomography scans of samples from the same source as the core-plugs on which the laboratory experiments were conducted (see Appendix 4). Micro-CT images were acquired with a Phoenix v/tome/x instrument (phoenix|x-ray, Wunstorf, Germany). The voxel resolution of the scans was $5.789\mu\text{m} \times 5.789\mu\text{m} \times 5.789\mu\text{m}$. Interfacial tension, brine viscosity, and oil viscosity were matched with experimental conditions, as listed in Table 2.9. A receding contact angle of 0° was assumed everywhere in the domain to describe a strongly water-wet state during primary drainage. For waterflooding, two macroscopic intrinsic contact angle cases were considered, with mean values: $\theta = 15^\circ$ and 50° . In each case a contact angle range of $\pm 15^\circ$ was used. Within this range the local intrinsic contact angle was randomly assigned, with equal probability, throughout the domain. Saturations and relative permeabilities were computed in a sequence of increasing and decreasing capillary pressures for drainage and waterflooding, respectively.

Table 2.10: Petrophysical properties of the networks used in the pore-network simulations. Clay content was set to zero in all three networks. Note that network properties differ from laboratory measurements (Table 2.8).

	Berea 11	Clashach JP
Porosity	0.21	0.14
Absolute permeability (m ²)	7.8×10^{-13}	6.1×10^{-13}
Absolute permeability (mD)	790	620
Formation factor	16.0	27.2

2.2.4 Results

Capillary pressure. Water saturation at the end of primary drainage as a function of the Leverett-J Function ($J(S_w)$) [96] is shown in Figure 2.10. $J(S_w)$ is defined, after Rose and Bruce, 1949 [97], as:

$$J(S_w) = \frac{P_c}{\sigma \cos \theta} \left(\frac{K}{\phi} \right)^{1/2} \quad (21)$$

where S_w is the wetting phase saturation at the end of primary drainage, P_c the applied capillary pressure, K and ϕ the sample permeability and porosity respectively, σ the interfacial tension and θ the contact angle between the phases and the solid rock surface. Also shown in Figure 2.10 (dashed lines) are mercury injection capillary pressure (MICP) measurements (Autopore IV 9520; Weatherford Laboratories, Stavanger, Norway). The interfacial tensions for the oil-brine and mercury-air systems are assumed to be 48.3 [91] and 485 mN m⁻¹ respectively. The contact angle during primary drainage is assumed to be 130° for mercury-air [40] and 0° for oil-brine. The $J(S_w)$ and hence P_c necessary to establish a given oil saturation during drainage at ETP was larger than values predicted by Eqn. 21 from MICP (Figure 2.10a, b). This apparent discrepancy is attributed to a shift in the MICP $J(S_w)$ - S_w curve to the left as clay bound connate water is not accounted for in mercury injection analysis [98]. Premature termination of primary drainage in the ETP experiments is another factor which may account for the apparent difference [98]. The magnitude of the discrepancy in brine saturations at a given P_c is of the same order of magnitude or smaller than the measured S_{nwi} , which indicates that the effect on the initial-residual saturation curves is negligible except at the lowest S_{nwi} (highest brine saturations). The consistent under-prediction of drainage capillary pressure by the pore network simulator, particularly at low brine saturations, has been reported in other studies [99], [100]. This is attributed to two factors. First, capillary pressure measurements do not necessarily record a position of true

capillary equilibrium and hence, for a given saturation, may record a higher value than a quasi-static displacement. Second, the resolution of the images – from which the networks were extracted – is too coarse to resolve the fine details of the pore space (cf. Appendix 4). Furthermore, the predicted network permeabilities (Table 2.10) are consistently higher than the measured permeability (Table 2.8) indicating an over-estimation of the typical pore size. Indeed, the pore-throat radius distribution estimated from MICP measurements (see Appendix 3) attributes 34.3% and 23.8% of the pore volume in Berea and Clashach respectively, to radii smaller than the corresponding voxel resolutions.

The original MICP results for all the sandstones studied are included in Appendix 3 for reference.

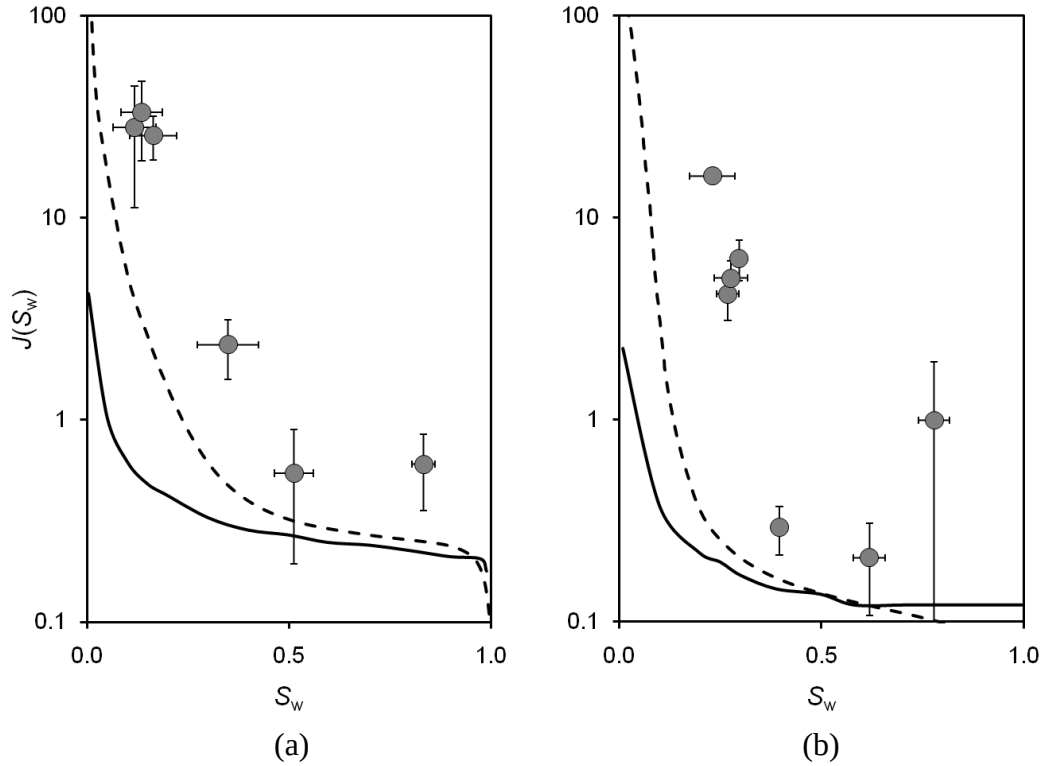


Figure 2.10: Brine saturation after primary drainage as a function of $J(S_w)$ (Eqn. 21) for (a) Berea 11 and (b) Clashach JP. Vertical bars depict the standard deviations over sampling time. Horizontal bars depict the disagreement between the different methods of saturation determination for a given run. Where the bars are not visible, they are smaller than the size of the marker. Dashed lines are translated from MICP data. Solid lines depict predictions by Valvatne and Blunt's network model [40]. Tabulated data is included in Appendix 4.

Capillary trapping. Residual oil saturations are shown as a function of initial oil saturation in Figure 2.11 and Figure 2.12. Residual saturation increases monotonically, within experimental uncertainty, with increasing initial oil saturation for all samples. The increase is most rapid at low initial saturation and asymptotes at high initial saturation, clearly deviating from a linear dependence. Empirical correlations proposed by Land [63] (Eqn. 9) and Spiteri et al. [1] (Eqn. 15) are compared with experimental data in Figure 2.11. Here, the normalised forms of $S_{or}^{\max}$ and S_{wc} in Eqn. 9 were taken as the mean residual and brine saturation of all runs for which the initial oil saturation is greater than 0.70; the coefficients α and β in Eqn. 15 were determined by least-squares fitting to data. Both functions yield good agreement with the data.

The best-fit (α , β) for Berea and Clashach are shown in Table 2.11. The Berea fitting parameters are very close to those observed in Spiteri et al.'s simulations in a Berea sandstone network (α , β) = (1.0, 0.5) with an imposed macroscopic intrinsic contact angle of $\theta = 70^\circ$ and randomly-assigned local contact angles in the range $\theta \pm 20^\circ$.

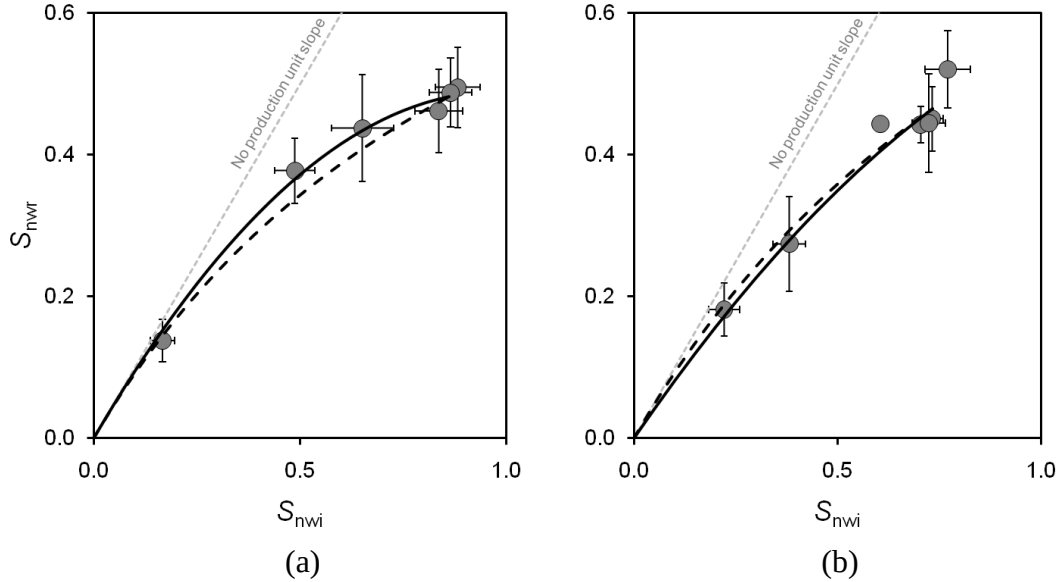


Figure 2.11: Comparison of measured (circle) $S_{nwr}(S_{nwi})$ in (a) Berea 11 and (b) Clashach JP, with empirical expressions proposed by Land (1968; Eqn. 9, dashed line) and Spiteri et al. (2008; Eqn. 15, solid line). $S_{nwr}^{\max}$ and S_{wc} in Eqn. 9 were taken as the mean S_{nwr} and S_w of all runs for which initial oil saturation is greater than 0.70. Fitting parameters C in Eqn. 9 and α and β in Eqn. 15 are listed in Table 2.11. Horizontal and vertical bars depict the disagreement between the different methods of saturation estimation for a given run. Where the bars are not visible, they are smaller than the size of the marker or are not available.

Table 2.11: Correlation coefficient of data and empirical expressions proposed by Land (1968; Eqn. 9) [63] and Spiteri et al. (2008; Eqn. 15) [1], and fitting parameters as determined by least-squares fitting to experimental data.

		Berea 11	Clashach JP
Land 1968	fitting parameter	$C = 0.79$	$C = 0.58$
	correlation coefficient	0.97	0.95
Spiteri et al. 2008	fitting parameters	$\alpha = 1.00;$ $\beta = 0.51$	$\alpha = 0.84;$ $\beta = 0.28$
	correlation coefficient	0.99	0.95

Network model simulations agree well with experimental data in Berea 11 and Clashach when the intrinsic contact angle is assigned uniformly within the range 35° to 65° (Figure 2.12a and Figure 2.12b, solid lines). These are effective local contact angles, accounting for grain roughness, converging/diverging pore geometry, and surface chemistry. This range coincides with the local contact angle distribution identified above by matching to Spiteri et al.'s simulations [1] and with those used to predict relative permeability measured by Oak [48] in Berea sandstone by Valvatne and Blunt [40].

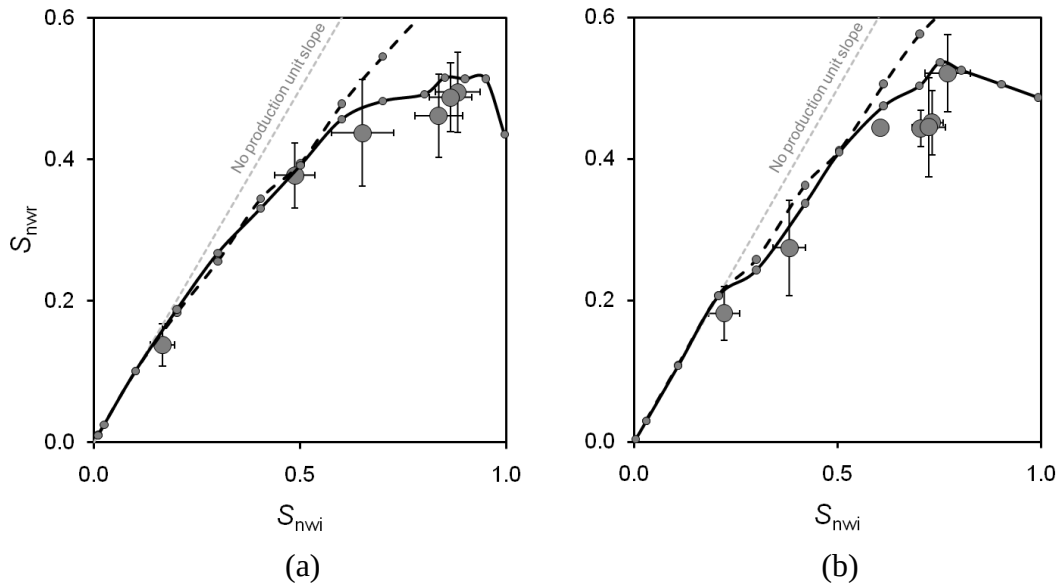


Figure 2.12: Comparison of measured (circle) and simulated $S_{nwr}(S_{nwi})$ in (a) Berea 11 and (b) Clashach JP core-plugs. Horizontal and vertical bars depict the disagreement between the different methods of saturation estimation for a given run. Where the bars are not visible, they are smaller than the size of the marker or are not available. Predictions by Valvatne and Blunt's pore-network simulator assuming intrinsic contact angles distributed in the range 0° to 30° (dashed line) and 35° to 65° (solid line) are included [40].

The end-point saturations of the remaining four samples were investigated. Table 2.12 summarises the end-point saturations, associated measurement error, P_c

applied during drainage, and the duration of primary drainage. The applied P_c target was 935 kPa for the sandstone samples. Some minor deviations from this target were seen due to fluctuations in laboratory temperature. For the Aerolith 10 sample a lower P_c was applied. The high porosity and permeability – in addition to the low tortuosity of the samples (F – Table 2.8) – resulted in large saturation changes occurring at low P_c (< 60 kPa). A large P_c was hence not required to reach S_{wc} . It is possible to compare the end-point saturation result from Aerolith 10 with the results of Kleppe et al. [52] – Figure 2.13. The end-point saturation measured in this study matches the extrapolated trend of Kleppe et al. The shift in end-point saturation is due to differences in $P_c^{\max}$ between the two studies. This comparison provided confidence in the experimental procedure as Kleppe et al. also used the porous plate method – albeit with an oil/gas system.

Table 2.12: End-point saturations – and associated primary drainage applied P_c and duration – for one ceramic Aerolith 10 and three sandstone samples. The maximum P_c applied to the sample during drainage is given along with the time averaged P_c over the drainage period.

Sample	$S_{nwi}^{\max}$	$S_{nwr}^{\max}$	$P_c^{\max}$ (kPa)	$P_c^{\text{avg.}}$ (kPa)	t (hrs)
Berea 3	0.801 (± 0.058)	0.507 (± 0.076)	938	869	24.1
Berea SB	0.753 (± 0.039)	0.478 (± 0.039)	931	869	29.3
Doddington	0.964 (± 0.026)	0.327 (± 0.032)	896	841	49.0
Aerolith 10	0.910 (± 0.022)	0.241 (± 0.026)	552	193	23.5

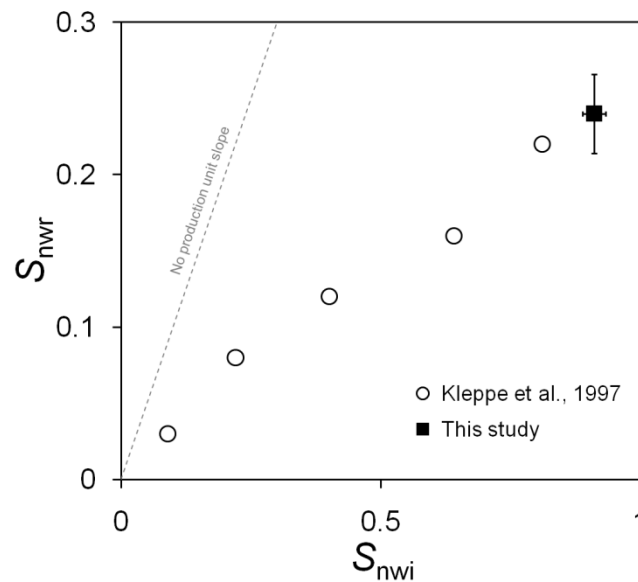


Figure 2.13: The initial versus residual non-wetting phase data of Kleppe et al., [52] compares well to the end-point saturation measured in this study. Both experiments were performed on Aerolith 10 samples using the porous plate method.

2.3 Consolidated CO₂/brine Coreflood Experiments

2.3.1 Introduction

Capillary dominated CO₂-brine porous plate experiments were conducted on a Berea sandstone core-plug at elevated temperature (343 K) and pressure (9 MPa) representative of warm consolidated aquifer formations at depths just below 800 m. A confining pressure of 11.75 MPa was applied resulting in an effective radial stress of 2.75 MPa. The primary objective was to measure the form of the capillary trapping and capillary pressure curves and compare them with oil-brine curves for the same rock type. Due to the importance of the immiscible displacement region within an injected CO₂ plume (Chapter 1.2.1 Fundamentals of Immiscible Displacement; Figure 1.6) the CO₂ and brine were pre-equilibrated before injection into the core-plug sample. Data from an un-equilibrated coreflood experiment is included to highlight this point. The solubility of CO₂ in brine was measured and the wettability characteristics of the porous plate were investigated. Finally saturation measurements from an alternative coreflood method – unsteady state – are compared to the porous plate results and the implications for coreflood design and planning are discussed.

2.3.2 Equipment and Conditions

The Berea core-plugs investigated (Berea 9 and Berea 10) were cored from the same block of sandstone as the Berea core-plug used in the ETP oil-brine experiments (Berea 11). The three core-plugs have almost identical petrophysical properties (Table 2.13). The core-plugs were 0.038 to 0.039 m in diameter and 0.075 to 0.077 m in length. Separate core-plugs were used in the oil-brine and CO₂-brine experiments to protect clay minerals present in the samples which may be damaged by continued use.

Table 2.13: Petrophysical parameters of the Berea 9 core-plug sample used in the CO₂-brine porous plate experiments. The properties were considered identical to the Berea 10 and 11 samples used in other experiments.

Sample	Experiment	ϕ	K_{brine} (m ²)	K_{brine} (mD)	R_a	$N_{\text{coord.}}$	F
Berea 9	ETP CO ₂ -brine PP ^a	0.222 ($\pm$ 0.007)	4.6×10^{-13}	460	18.78	4.1	13.7
Berea 10	ETP CO ₂ -brine US ^b	0.221 ($\pm$ 0.005)	4.6×10^{-13}	460	18.78	4.1	13.5
Berea 11	ETP oil-brine PP	0.228 ($\pm$ 0.016)	4.6×10^{-13}	460	18.78	4.1	12.4

^a PP – porous plate

^b US – unsteady state

At the experimental conditions ($T = 343$ K; $P = 9$ MPa) CO₂ is in a supercritical state (see Figure 1.3 for the CO₂ phase diagram). The aqueous phase was 5wt.-%-sodium chloride, 1wt.-%-potassium chloride synthetic brine. The phase properties at the experimental conditions were not measured but are estimated from the literature (Table 2.14).

Table 2.14: Estimated phase properties at 343 K and 9 MPa (unless stated) from literature.

	CO ₂	Brine
Density, ρ (kg m ⁻³)	208 ^a	1025 ^c
Viscosity, μ (Pa s)	2.10×10^{-5b}	5.10×10^{-4d}

^a [101]

^b [19]

^c [102]; assuming an unsaturated brine density of 1020 kg m⁻³ [94]

^d [102]; 3.0wt.-% NaCl aqueous solution at 10.0 MPa, 333 K

The coreflood apparatus for the ETP CO₂-brine experiment was based on the ETP oil-brine apparatus with some important modifications (CO₂-brine apparatus – Figure 2.14; oil-brine apparatus – Figure 2.9, Chapter 2.2.2 Equipment and Conditions;). A stirred reactor (1200mL C276 autoclave with gas entrainment stirrer – Parr Instruments Co., IL, USA) was used to agitate the phases, accelerating mass transfer in order to reach equilibrium. Once equilibrated, the phases could be contained in the reactor until required during coreflooding. An additional syringe pump (pump C - Figure 2.14) was also added for the isothermal depressurisation measurement used to determine residual CO₂ saturations within the core-plug. The modifications can be clearly identified by comparing the CO₂-brine and oil-brine experimental apparatus diagrams (Figure 2.14 and Figure 2.9 respectively).

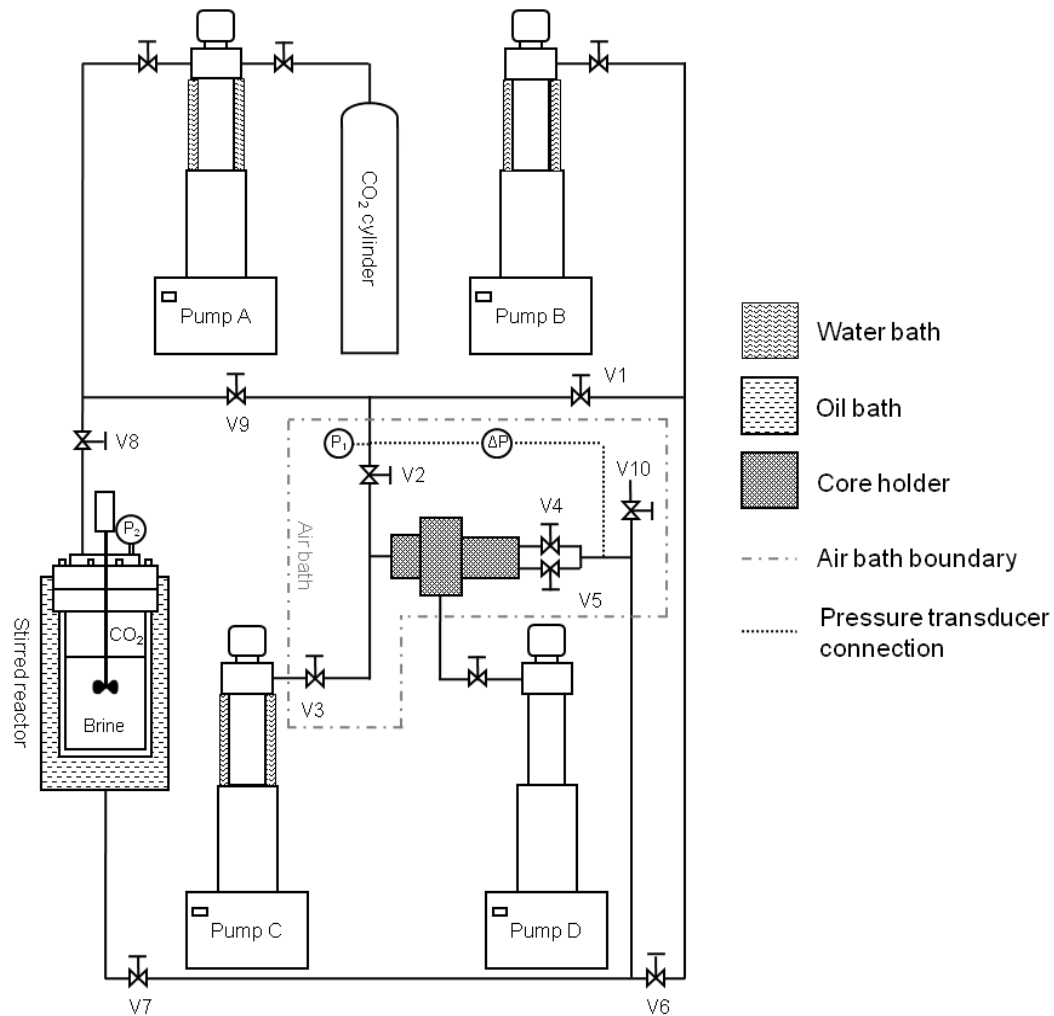


Figure 2.14: CO₂-brine ETP coreflood apparatus. The porous plate was situated at the right hand end of the core holder. Valve 4 is connected to the brine production port and valve 5 is connected to the waterflood injection port (Figure 2.8). Pump A was used for CO₂ pressurisation and injection; pump B for back pressure and receiving production from the core-plug; pump C for measuring S_r by isothermal depressurisation of the core-plug pore space; and pump D applied radial confining pressure to the core-plug.

2.3.3 Experimental Procedure

Contact Angle Measurement. Before performing saturation measurements the contact angle of the CO₂-water-porous plate system was investigated in collaboration with the Department of Chemical Engineering and Chemical Technology, Imperial College London. This was done to develop confidence in the ability of the porous plate to prevent CO₂ production during primary drainage and to investigate wettability in silicate mineral systems. A segment of porous plate was placed inside a view-cell which was filled with de-ionized water and heated to 354.5 K. The water was pressurized and CO₂ introduced onto the surface of the porous plate via a capillary tube from a screw injector. The porous plate was placed

at an angle of 21° from the horizontal to investigate advancing and receding contact angles (raindrop effect – [25]). Contact angles were measured for pressures between 26.6 MPa and 48.9 MPa. Further information on the view-cell apparatus is given elsewhere [103].

Phase Equilibration. The equilibration reactor was half filled with de-aired brine and half filled with CO_2 . The top of the autoclave was connected to a reservoir of CO_2 maintained at constant pressure by a syringe pump. The reactor's internal gas entrainment stirrer was then rotated at approximately 200 r.p.m. to mix the phases. Brine was sampled from a bottom drain valve and the solubility of CO_2 in brine measured. Equilibrium was reached when no more CO_2 entered the reactor from the reservoir with continued agitation. The equilibrated brine was stored in the reactor at constant pressure and temperature until required in the experiment. Appendix 5 contains a more detailed step by step description of the phase equilibration procedure.

Initial Saturation. The core-plug pore space was initially vacuumed for 30 minutes with the experimental temperature and confining pressure (11.72 MPa) applied. Fresh (unsaturated with CO_2) de-aired brine was then injected into the core-plug from right to left (Figure 2.14). The fresh brine was initially introduced at ambient pressure then pressurized to 9 MPa. Five pore volumes of fresh brine were injected through the core-plug. Flooding was then switched to the equilibrated brine for a further five pore volumes of injection. The flowlines connected to both valves 4 and 5 were used during injection. Valve 4 was connected to the flowline terminating at the outside face of the porous plate. Valve 5 was connected to the flowline that passed through the centre of the porous plate terminating at the face of the core-plug (Figure 2.8). Brine production was from the flowline connected to valve 2.

Primary Drainage. During primary drainage a known volume of CO_2 was injected into the brine saturated core-plug. When injection ceased the system was allowed to equilibrate. Equilibrium corresponds to a uniform pressure distribution along the core-plug length in each of the phases. The difference in the equilibrium pressure of the two phases corresponds to P_c . At equilibrium the phase saturations are assumed to be uniform along the length of the sample. No additional CO_2 enters the sample and no brine is produced. The difference in inlet and outlet pump pressures – P_c – was varied up to 160 kPa at equilibrium. This is equivalent to a CO_2 column height

of 20 m in a formation at the experimental conditions. This P_c was sufficient to desaturate the sample to irreducible water saturation. The duration of primary drainage was inversely proportional to applied P_c . The longest drainage time was 138 hours.

CO₂ injection into the pressurised, brine saturated, core-plug was achieved using one of two methods: at constant pressure or at constant flow rate. The former was used for all experiments where $P_c > 10$ kPa. Here, equilibrium was considered achieved when brine production ceased and the volumetric rate of CO₂ injection by the pump reached a constant (the pump leakage rate). P_c , and hence S_i , was varied between experiments by changing the injection pump pressure. Maximum flow rate limits were imposed on the pumps as they operated in constant pressure mode ($N_{cap} < 4.3 \times 10^{-10}$). For all other experiments ($P_c < 10$ kPa), a pre-determined volume of CO₂ was injected at a constant flow rate corresponding to $N_{cap} < 5.2 \times 10^{-11}$. This was achieved by operating the brine effluent pump in constant withdrawal mode. Once the volume necessary to achieve the target S_i was withdrawn the pump was stopped, the system equilibrated, and P_c was measured. S_i was determined from the volume of brine produced. Different injection methods were used for two reasons. At $P_c < 10$ kPa achieving equilibrium when operating both pumps in constant pressure mode was prohibitively time consuming. In addition, at low P_c , changes in laboratory temperature resulted in pressure fluctuations which became significant as a proportion of average P_c – decreasing the accuracy of the results.

Waterflooding. The core-plug was waterflooded to residual CO₂ saturation with equilibrated brine. Waterflooding took place from right to left in the same manner as initial saturation. Five pore volumes of equilibrated brine were injected at $N_{cap} = 4.2 \times 10^{-7}$.

Residual Saturation Measurement. The residual CO₂ saturation was measured by isothermal expansion of the core-plug pore space, in the same manner as Suekane *et al.*, [49] – Eqns 18-20. The pore space was initially isolated from the experimental system before connection to an empty syringe pump (via valve 3). The pump was maintained at the experimental temperature and the internal volume increased while the pressure was monitored. Knowing the pore volume, dead volume, volume of expansion, pressure, temperature, brine density [94], CO₂ density [101] and CO₂

solubility in brine [104] the CO₂ saturation was calculated. This was the same procedure used to measure the solubility of CO₂ in the equilibrated brine.

Core-plug Cleaning & Re-saturation. Upon completion of one set of S_i and S_r measurements the core-plug was re-saturated ready for the next set of measurements. Unlike in the oil-brine experiment where the core-plug was removed from the apparatus for cleaning, in the CO₂-brine experiment re-saturation occurred inside the core holder. After isothermal expansion the pore space was vacuumed and any remaining CO₂ gas was removed from the pore space. Vacuum was applied for 30 minutes before un-equilibrated brine (under-saturated with CO₂) was injected into the core-plug. The brine was then pressurised to experimental conditions and five pore volumes were injected through the sample. Injection was then switched to equilibrated brine from the stirred reactor. A further five pore volumes of equilibrated brine were injected through the core-plug. The confining pressure remained constant at experimental conditions throughout the procedure. Upon completion of this sequence of steps the core-plug was considered to be at 100% water saturation. Hot soxhlet cleaning of the core-plug was unnecessary as the non-wetting phase (CO₂) was removed by applying vacuum and flooding with under-saturated brine.

Appendix 6 contains a more detailed step by step procedure for each coreflood sequence. In addition appendix 7 includes further details on the equations used to calculate S_i and S_r .

2.3.4 Results

Contact angle. The contact angle measurements are summarized in Table 2.15. In addition Figure 2.15 shows the CO₂-water-porous plate contact angle at the maximum pressure (48.9 MPa). The contact angles on the two sides of the drop were found to be almost identical (within 1-2 degrees). Smaller contact angles at lower pressures were possibly an effect of small contact force (CO₂ drop just reached the substrate); whereas at higher pressures (39.5 – 48.9 MPa) good contact was achieved and thus contact angles remained stable at 40°. Another explanation for the observed change in contact angle with pressure is the increase of CO₂ solubility in brine and subsequent shift in the reactions $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \rightleftharpoons 2 \text{H}^+ + \text{CO}_3^{2-}$ to the right side. The drop in the pH value and an increase in HCO_3^- and CO_3^{2-} concentrations may have changed the surface chemistry of the

substrate and the electric double-layer on it, influencing the spreading of CO₂. This effect requires further study.

Table 2.15: Contact angle measurements at 354.5 K between the de-ionized water and CO₂ phase interface on a porous plate (aluminium silicate). Contact angles are reported for the denser brine phase.

Pressure (MPa)	θ (degrees)
26.6	10 ± 5
29.7	32 ± 2
32.0	30 ± 2
39.5	39 ± 2
47.0	40 ± 2
48.9	40 ± 3



Figure 2.15: A drop of CO₂ generated from a capillary tube is brought into contact with a porous plate substrate angled at 21°. The bulk phase is de-ionized water ($P = 48.9$ MPa).

CO₂-water Solubility. The solubility of CO₂ in water was measured as 0.0136 mole fraction $\pm$ 0.0020 mole fraction ($32.4 \text{ kg m}^{-3} \pm 4.8 \text{ kg m}^{-3}$) for the experimental conditions investigated. This is within the range of solubilities measured on similar systems [105], [106], [102], [107], [108]. The solubility was measured by the same isothermal expansion procedure used in pore space S_r measurement [49].

Capillary pressure. Water saturation at the end of primary drainage as a function of the Leverett-J Function ($J[S_w]$) [96], [97] – Eqn. 21 – is shown in Figure 2.16. Also shown in Figure 2.16 are MICP measurements (Autopore IV 9520; Weatherford Laboratories, Stavanger, Norway). The interfacial tensions for the CO₂-brine, oil-brine and mercury-air systems are assumed to be 36.0 [29], [109], 48.3 [91] and 485 mN m⁻¹ respectively. The contact angle during primary drainage is assumed to be 130° for mercury-air and 0° for CO₂-brine and oil-brine. There is good agreement between the mercury-air, oil-brine and CO₂-brine datasets with the exception of the irreducible water saturation measured by MICP. This is attributed to the irreducible saturation being clay bound in the presence of water. Water is not present in MICP measurements.

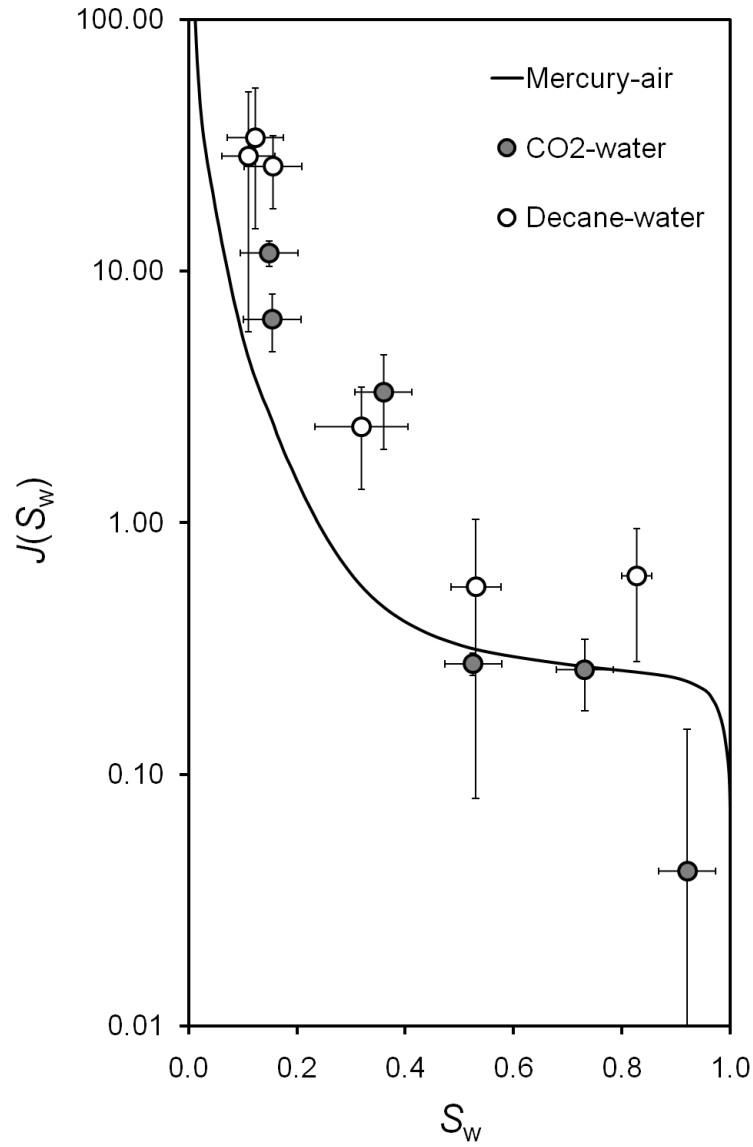


Figure 2.16: Primary drainage capillary pressure curve data measured on Berea sandstone. The three sets of data (CO₂-brine; oil-brine; mercury-air) have been normalised using the Leverett-J Function (equation 21) [96].

Capillary trapping. The capillary trapping curve – S_r as a function of S_i – is shown in Figure 2.17. Residual saturation increases monotonically deviating away from a linear dependence in the same manner as the oil-brine results which are also shown. Empirical correlations proposed by Land [63] (Eqn. 9) and Spiteri et al. [1] (Eqn. 15) are compared with the CO₂-brine experimental data. Here, the normalised forms of $S_{CO_2r}^{\max}$ and S_{wc} in Eqn. 9 were taken as the mean residual and brine saturation of all runs for which the initial CO₂ saturation is greater than 0.80; the coefficients α and β in Eqn. 15 were determined by least-squares fitting to data (experimental error associated with each data point was ignored in this process). Both functions

yield good agreement with the data. Matching parameter values, least squared regression fits for both CO₂-brine and oil-brine are summarised in Table 2.16.

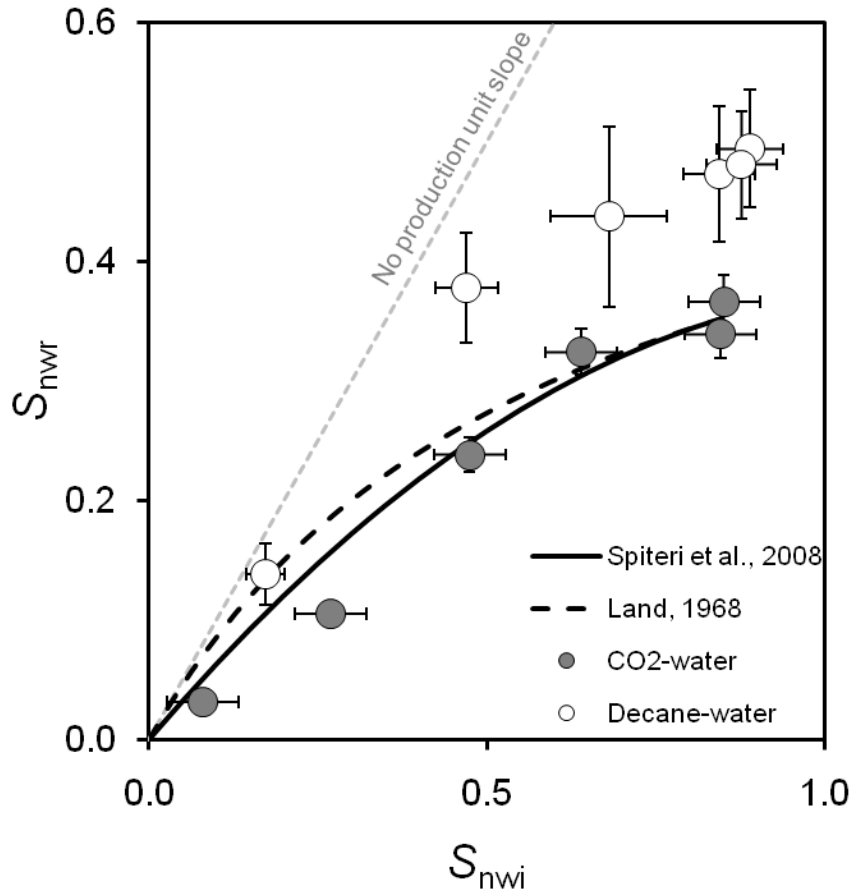


Figure 2.17: Capillary trapping curve data measured on Berea sandstone. Empirical trapping equations (Land, 1968 – Eqn. 9; Spiteri *et al.*, 2008 – Eqn. 15) matched to the CO₂-brine data are shown.

Table 2.16: Correlation coefficient of data and empirical expressions proposed by Land (1968; Eqn. 9) and Spiteri *et al.* (2008; Eqn. 15), and fitting parameters as determined by least-squares fitting to experimental data for CO₂-brine and oil-brine Berea sandstone systems.

		CO ₂ -brine	Oil-brine
Land 1968	fitting parameter	$C = 1.41$	$C = 0.79$
	correlation coefficient	0.94	0.98
Spiteri <i>et al.</i> 2008	fitting parameters	$\alpha = 0.66;$ $\beta = 0.29$	$\alpha = 0.97;$ $\beta = 0.49$
	correlation coefficient	0.97	0.91

Network modelling. Attempts were made to match the CO₂-brine capillary trapping curve with the pore scale network simulator – as done previously for the oil-brine results. A satisfactory match to the experimental data was not possible (Figure 2.18). Trapping was over-predicted when CO₂ was assumed to be the non-

wetting phase – with the same contact angle ranges used as for the oil-brine study shown in Figure 2.18 (contact angle ranges of 0-30° and 35-65°). Additional contact angle ranges were investigated and found not to provide a match (45-75°; 55-85°; 65-95°). Trapping was under-predicted if the system was assumed to be intermediate-wet, with a contact angle range of 75-105° (Figure 2.18). The phase properties input into the simulator are those listed in Table 2.14. Future work in this area would be of interest – see Chapter 3.1.3 Recommendations for Future Work.

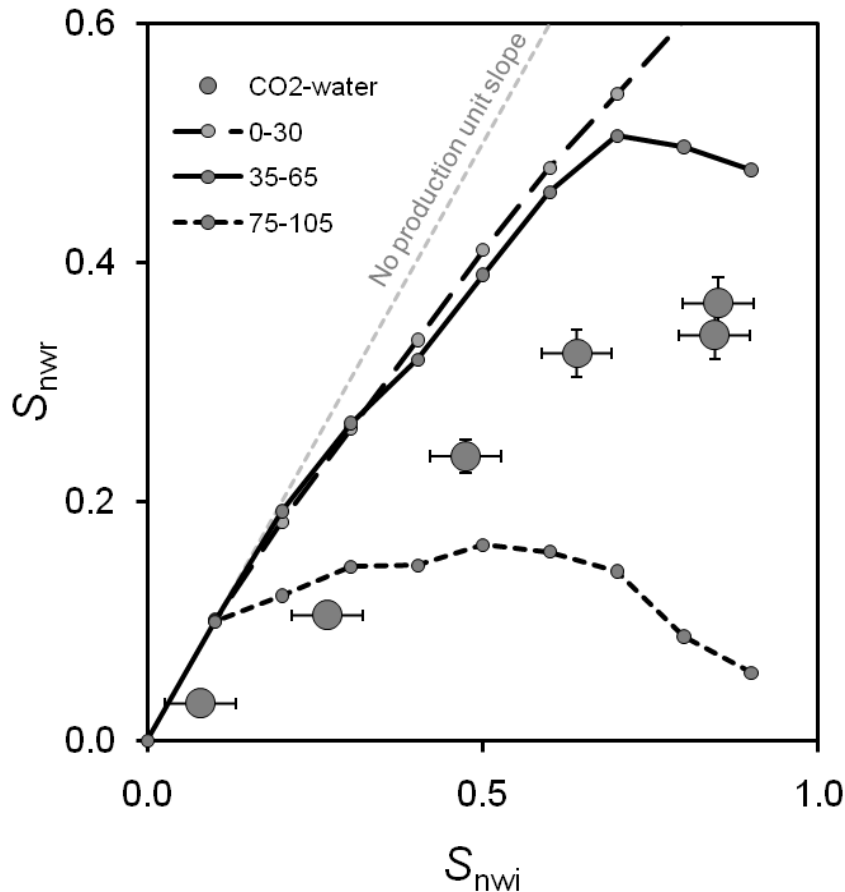


Figure 2.18: Comparison of measured (circle) and simulated $S_r(S_i)$ in Berea sandstone. Predictions by Valvatne and Blunt's pore-network simulator assuming intrinsic contact angles distributed in the range 0° to 30° (long dashed line), 35° to 65° (solid line) and 75° to 105° (short dashed line). If CO_2 is assumed to wet the surface trapping is over-predicted. If the system is assumed to be intermediate-wet trapping is under-predicted.

2.3.4 Unsteady State Collaborative Experiments

In addition to the porous plate experiments a collaborative experiment was undertaken at the Technology and Research Centre of Japan Oil, Gas and Metals National Corporation in Chiba, Japan. In this additional experiment the influence of phase equilibration and displacement methodology was investigated. These

experiments occurred prior to the porous plate experiments and influenced their planning and experimental design considerably.

As with the porous plate experiments a consolidated Berea sandstone core-plug (Berea 10) was used (Table 2.13). The Hassler type core holder containing the core-plug was placed inside a medical CT scanner (Aquilion 16, third generation scanner, Toshiba Medical Systems Corporation, Japan) for in-situ saturation monitoring (ISSM). Phase injection was controlled by high precision syringe pumps (Teledyne ISCO, Lincoln, NE, USA). Additional information on the experimental equipment is provided elsewhere [110], [111]. Experiments were performed at 313 K and 10.3 MPa. The aqueous phase was 15wt% NaI brine. CO₂ at these experimental conditions has a density of 651.5 kg m⁻³ and viscosity of 5.0 × 10⁻⁵ Pa s. The CO₂ and brine were prepared in a series of accumulators (Core Laboratories, Houston, TX, USA) and a custom designed aluminium multiphase separator to ensure mutual saturation.

The CO₂ and brine were first equilibrated by cycling the phases between the accumulators and separator three times over the course of one week. The core-plug was then saturated with equilibrated brine before more than five pore volumes of CO₂ were injected at a flow rate representative of subsurface conditions ($N_{\text{cap}} \sim 10^{-7}$). After measuring the initial CO₂ saturation by ISSM the sample was waterflooded with more than 5 pore volumes of equilibrated brine – again at a representative flow rate ($N_{\text{cap}} \sim 10^{-7}$) – to reach the residual CO₂ saturation. During coreflooding the confining pressure around the core-plug was maintained constant at 20.6 MPa. The phases were always injected from the same end of the core-plug. Further information on the unsteady state experimental procedure is given elsewhere [110], [111].

During the unsteady state coreflood experiments ISSM provided measurements of the CO₂ and brine flood front progression. This allowed the shape of the flood front to be visualized. The CO₂ and brine fronts were shown to be piston-like (Figure 2.19). ISSM also provided us with a clear indication when – in an initial experiment – the phases were not properly equilibrated. In Figure 2.20 during waterflooding a cone shaped region of 100% brine saturation can be seen. In this region the residual CO₂ phase had dissolved in under-saturated brine. Figure 2.20 clearly illustrates the problems faced when un-equilibrated phases are used in a

study of immiscible capillary trapping. The saturations shown in Figure 2.20 are not reported in this study and the figure is included here for illustrative purposes only.

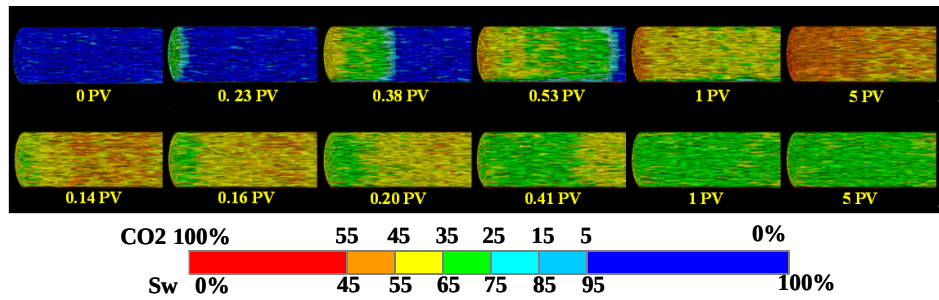


Figure 2.19: X-ray CT derived saturation distributions during CO₂ injection (upper) and brine waterflooding (lower) on a Berea sandstone sample. Phases are injected from the left hand end of the core-plug. Homogeneous piston-like immiscible displacements of the equilibrated phases are observed. After 5 pore volumes of CO₂ injection (upper right hand image), injection is switched from CO₂ to brine and 0.14PV brine injection is shown in the lower left image. A total of 5 pore volumes of brine are injected (lower right image).

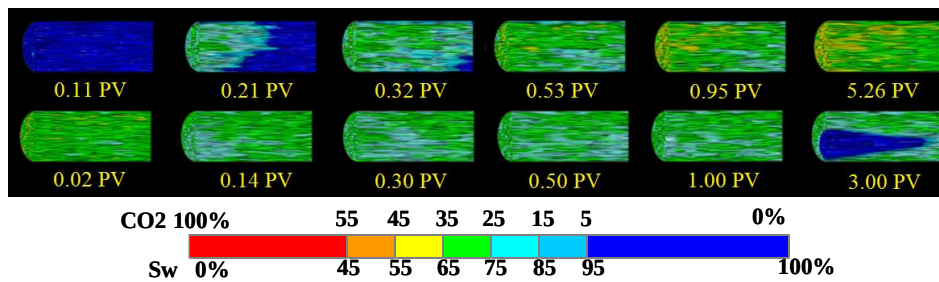


Figure 2.20: X-ray CT derived saturation distributions during CO₂ injection (upper) and brine waterflooding (lower) on a Berea sandstone sample. Phases are injected from the left hand end of the core-plug. These images are from an initial experiment when un-equilibrated brine and CO₂ were used. Note the cone-shaped region of 100% brine saturation after 3 pore volumes of brine injection (lower right hand image) indicating that the residual CO₂ has dissolved in the under-saturated brine.

After five pore volumes of CO₂ injection an S_i of 0.355 was measured by ISSM. Following the subsequent waterflood (five pore volumes brine injection) an S_r of 0.259 was measured by ISSM. This $S_i - S_r$ point is clearly lower than the maximum – or end point – values measured with the porous plate method (Figure 2.17). It does however seem to form a broadly consistent trend with the capillary trapping curve data from the porous plate experiment (Figure 2.21).

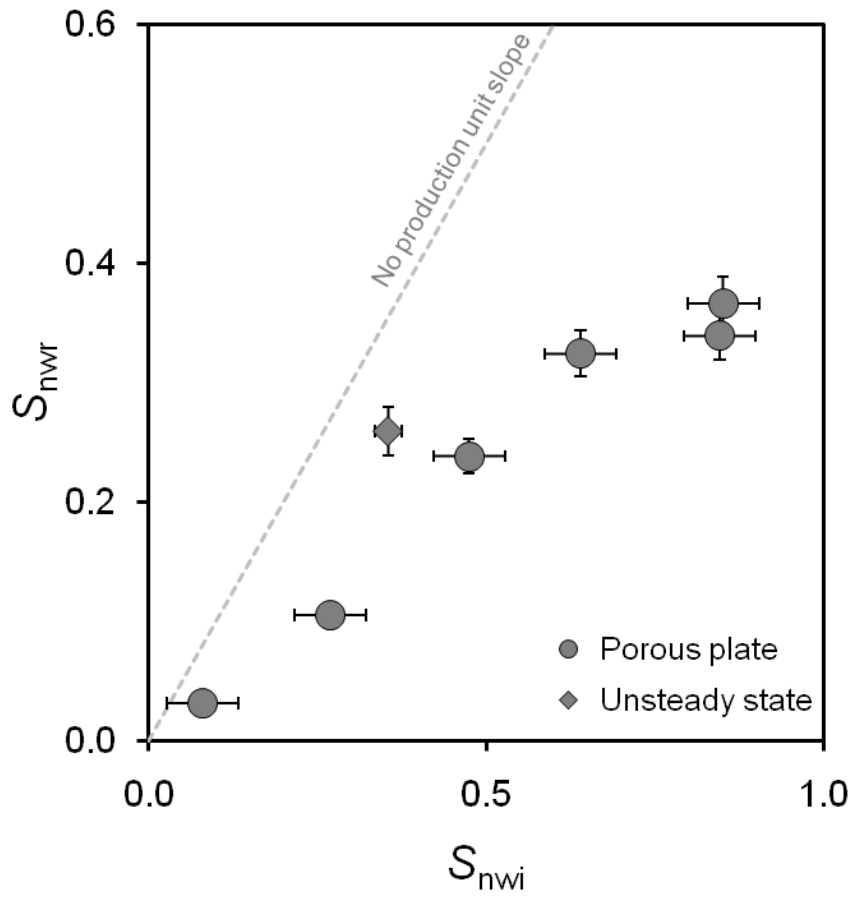


Figure 2.21: A comparison of capillary trapping curve data from porous plate and unsteady state CO_2 -brine experiments.

These results show that the unsteady state displacement method is unsuitable for de-saturating a sandstone sample to irreducible water saturation at these experimental conditions. The porous plate method is preferred when end point saturation measurements are required.

Chapter 3

Discussion and Conclusions

3.1 Discussion

The experimental results for a series of capillary controlled trapping experiments have been presented. The form of the capillary trapping curve has been measured for five systems (Figure 3.1). The capillary trapping curves for oil-brine and CO₂-brine systems in sandstones is shown to be distinctly different, but of comparable magnitude. The reasons for this difference will be considered in this section. In addition to the trapping curves end-point saturations for a further four samples have been measured. The influence of petrophysical properties on end-point saturation is also investigated in this section.

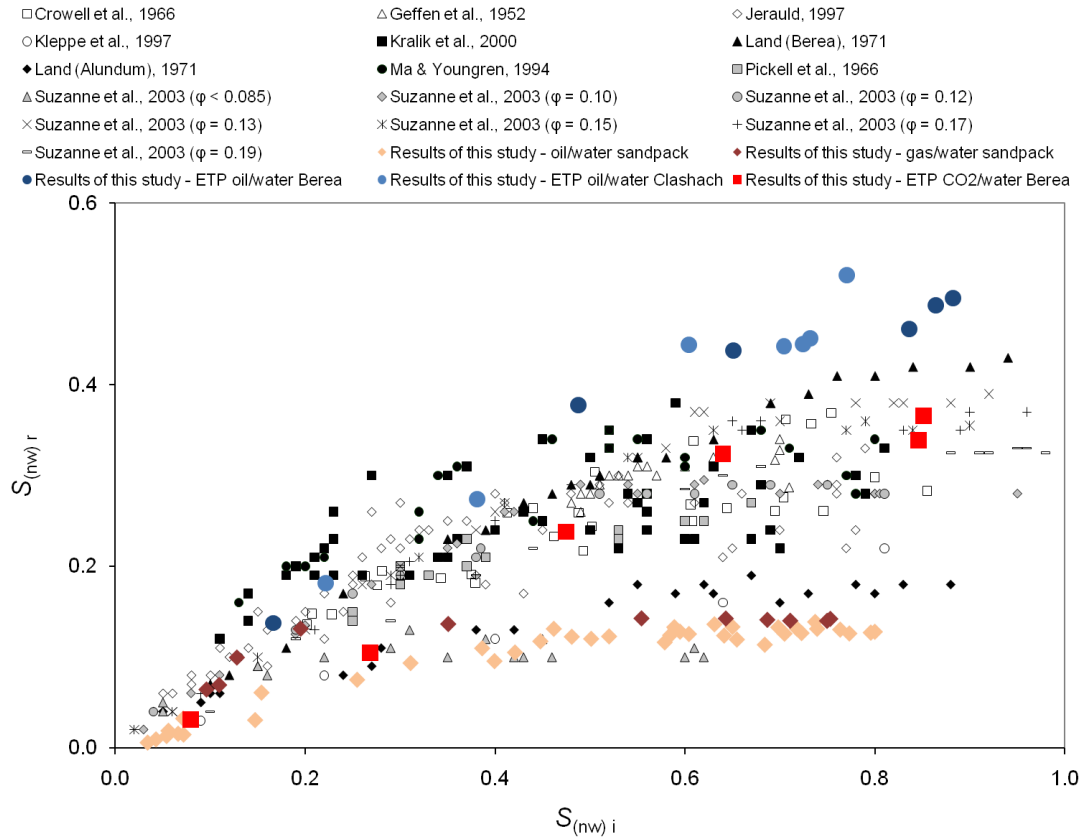


Figure 3.1: The five capillary trapping curves measured as part of this study (in colour) compared to literature data [52-60] (greyscale).

3.1.1 The Influence of Petrophysical Properties on Capillary Trapping

In Chapter 1 the influence of porosity (Figure 1.19 – page 44), permeability (Figure 1.18 – page 43) and formation factor (Figure 1.20 – page 46) on literature capillary trapping data was discussed. In this study care was taken to thoroughly characterise the porous media investigated. The full list of parameters measured during sample characterisation is:

1. Porosity (helium, brine saturation and mercury injection) – ϕ
2. Permeability (brine and air) – K_{brine} ; K_{air}
3. Formation Factor – F
4. Pore-throat aspect ratio – R_a
5. Pore-throat coordination number – N_{coord} .

The characterisation of these parameters is summarised in Table 2.4 (page 60) for unconsolidated sands and Table 2.8 (page 69) for consolidated sandstones (and ceramic) samples – a table summarising the combined data for all samples is also

included in Appendix 2 along with a summary of how the different characteristic parameters were measured.

Of initial interest is a comparison of the existing literature data – for porosity, permeability and formation factor – with the oil-brine results of this study (Figure 3.2; Figure 3.3; Figure 3.4 respectively). It is clear that the results of this study describe the same trends between maximum trapped saturations and the parameters in question. What is not initially evident is the improved match that is possible to the results of this study compared to matches to the literature data. Each of the relationships (ϕ , K , F) with maximum trapped saturation can be fitted with a least square fit logarithmic equation. Table 3.1 summarises the least square fit equations and the correlation coefficient associated with each match. It is clear that the accuracy of the match improves when only the results of this study are considered. In the case of permeability the improvement is substantial resulting in a very good match. Only geological samples were included in this analysis – the results for the Aerolith ceramic were excluded. Experimental error was ignored when finding the best fit to the data.

Table 3.1: Least square fit equations to experimental data from this study and the literature, including the correlation coefficient (R^2). Permeability units are m^2 .

Dataset	Data Source	Least Square Fit Equation	R^2
ϕ vs. $S_r^{\max}$	Literature	$S_r^{\max} = -0.2487\ln(\phi) - 0.0555$	0.65
	This study	$S_r^{\max} = -0.4456\ln(\phi) - 0.3092$	0.88
K vs. $S_r^{\max}$	Literature	$S_r^{\max} = -0.0185\ln(K) - 0.2180^a$	0.17
	This study	$S_r^{\max} = -0.0637\ln(K) - 1.4136^b$	0.92
F vs. $S_r^{\max}$	Literature	$S_r^{\max} = 0.0718\ln(F) + 0.1732$	0.46
	This study	$S_r^{\max} = 0.1419\ln(F) + 0.0066$	0.77

^a The fit equation for mD units is: $S_r^{\max} = -0.0186\ln(K) + 0.4228$

^b The fit equation for mD units is: $S_r^{\max} = -0.0637\ln(K) + 0.7887$

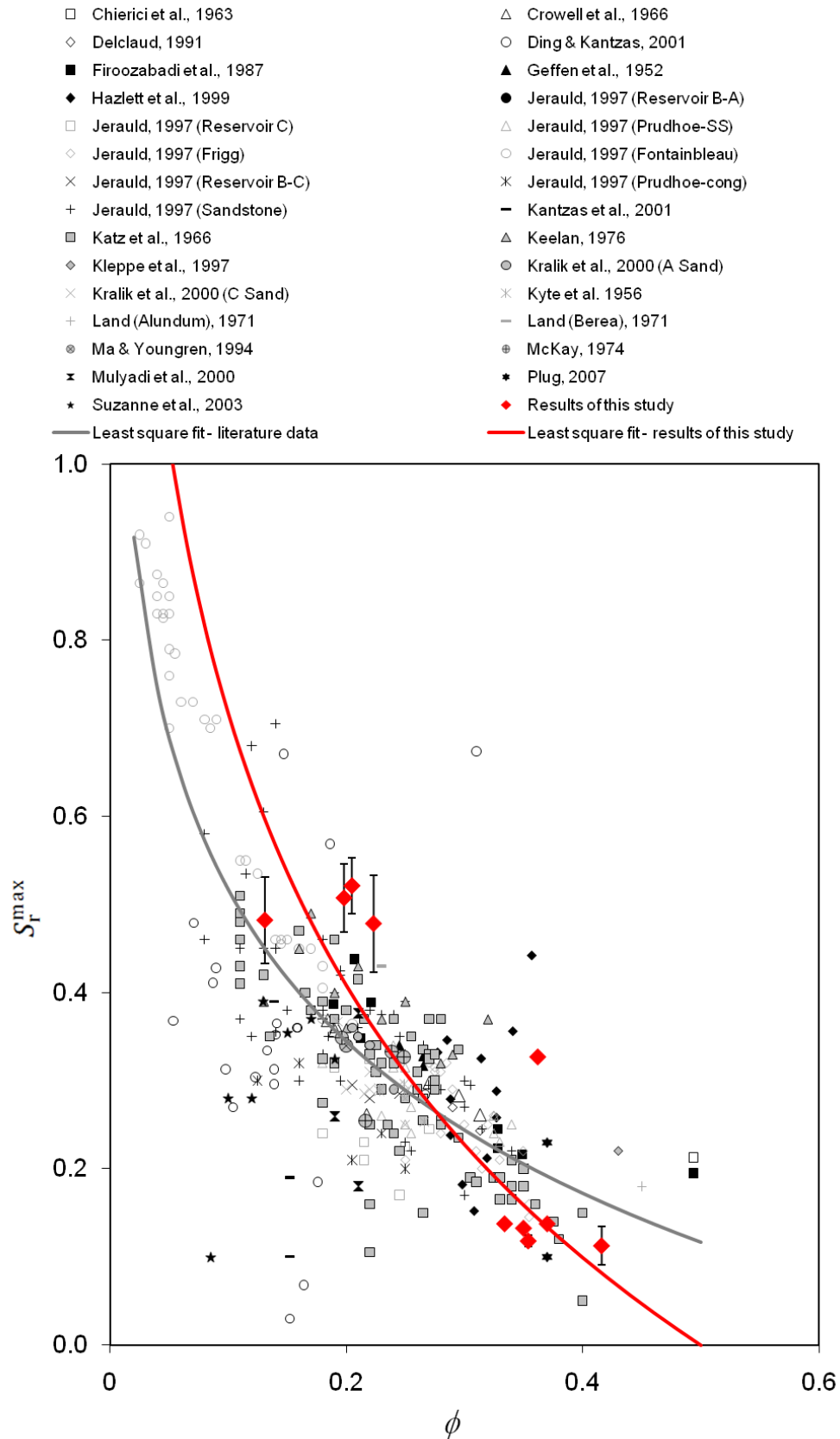


Figure 3.2: A comparison of maximum trapped saturation ($S_r^{\max}$) versus porosity (ϕ) data from this study and literature [52], [54-60], [67-78]. The results of this study clearly match the general inverse relationship between porosity and maximum trapped saturation seen in the literature. Least square fit regressions to the two sets of data (results of this study; literature) are shown. Least square fit equations and correlation coefficients are included in Table 3.1.

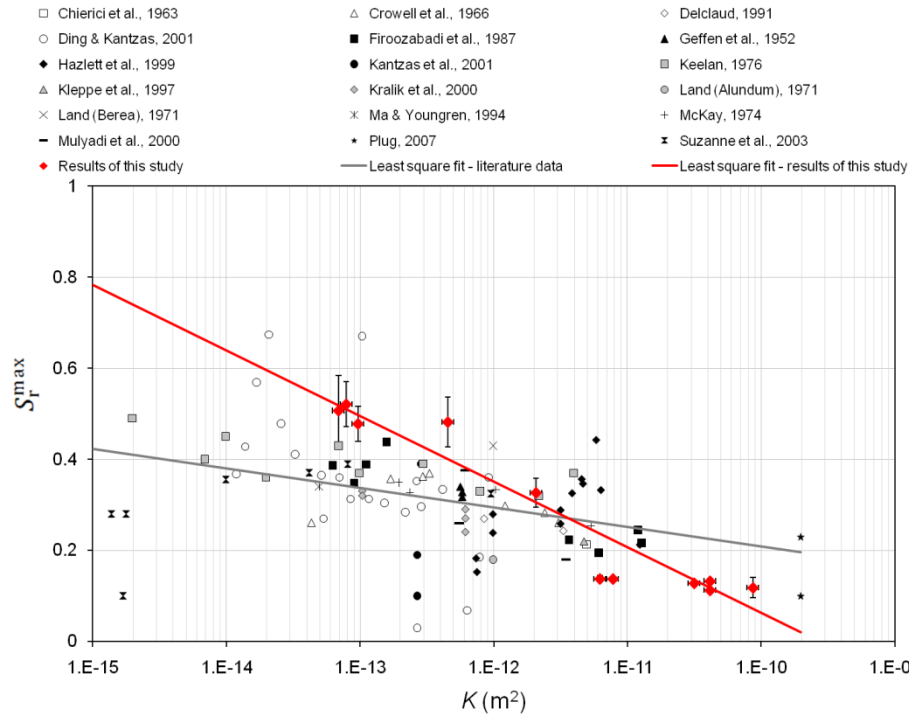


Figure 3.3: A comparison of maximum trapped saturation ($S_r^{\max}$) versus permeability (K) data from this study and literature [52], [54], [55], [57-60], [67-76]. The results of this study match the inverse relationship between permeability and maximum trapped saturation seen in the literature. Least square fit regressions to the two sets of data (results of this study; literature) are shown. Least square fit equations and correlation coefficients are included in Table 3.1. A significantly better match to the results of this study – as opposed to the literature data – is achieved.

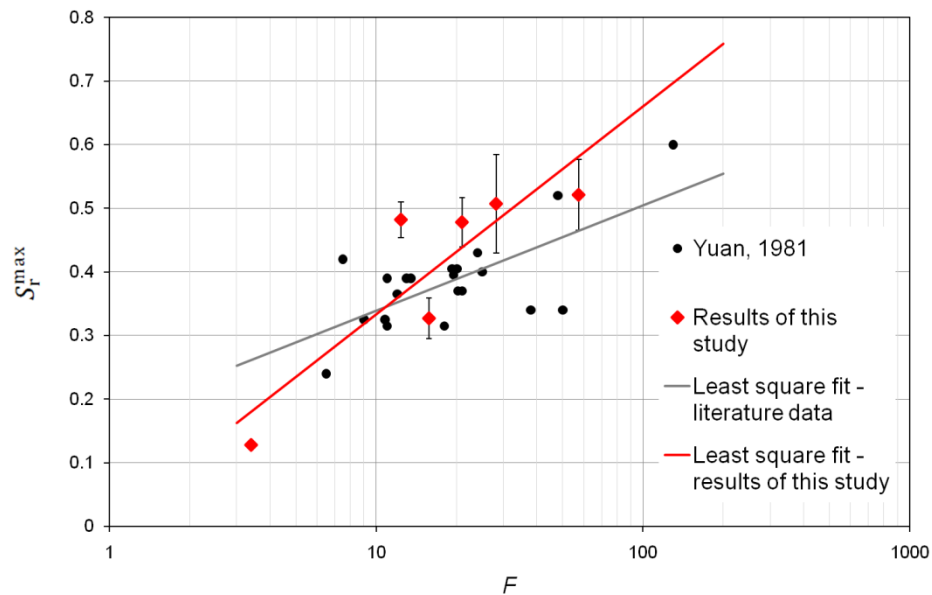


Figure 3.4: A comparison of formation factor (F) versus maximum trapped saturation ($S_r^{\max}$) data from this study and Yuan, [79]. Both sets of data describe the same trend. Least square fit regressions to the two sets of data (results of this study; literature) are shown. Least square fit equations and correlation coefficients are included in Table 3.1.

A better match to the results of this study – as opposed to the literature dataset – is due to a number of factors. The literature data includes results from different experimental procedures and a wide range of samples and, as has been shown in this study, the maximum trapped saturation is strongly dependent upon the coreflood methodology employed. In addition some experimental procedures – such as saturation changes due to evaporation [54] – are not representative of subsurface displacements. The literature data also covers a wide range of fluid systems including: gas-brine; oil-brine; and gas-oil. These factors may all add additional scatter to the literature results impacting upon the quality of any match. In this study all saturation changes were achieved by immiscible displacement in the pore space. Maximum trapped saturations were measured at irreducible water saturation and not shifted further down (in terms of S_i) the trapping curve – as is the case with unsteady state experiments. Finally all the results considered in this analysis were measured for an oil-brine system – although octane and decane were used in the sandpack and core-plug experiments respectively. The temperature and pressure of the experiments also varied but it would appear that these factors are of secondary importance.

By extracting small cylindrical (0.005 m diameter) samples from core-plug off-cuts micro-CT imaging of the pore space was possible using a Phoenix v/tome/x instrument (phoenix|x-ray, Wunstorf, Germany). The images were filtered with a 3x3 median filter and segmented according to Otsu's algorithm [112]. From the tomographic datasets equivalent networks were extracted with a maximum ball algorithm [46]. The equivalent networks contain R_a and $N_{\text{coord.}}$ distributions of the porous material. Average values of R_a and $N_{\text{coord.}}$ could be determined from these distributions [113]. Micro-CT scanning has a finite resolution – not all of the sandstone pore size distribution can be imaged. Initial research indicates that image resolution can impact on the average R_a and $N_{\text{coord.}}$ values determined [114]. For Clashach sandstone R_a decreased by 23% when image resolution decreased from 5.8 μm to 20.0 μm . Over the same range average $N_{\text{coord.}}$ values decreased by 12% [114]. The average R_a and $N_{\text{coord.}}$ data was compared with the maximum trapped saturation results from the oil-brine experiments performed on the full size core-plugs – Figure 3.5 and Figure 3.6 respectively. It is assumed that the micro-CT sample perfectly represents the core-plug in terms of pore-throat geometry. Least square fits to the data are shown in the figures and the equations and correlation

coefficient matches are included in Table 3.2. An excellent match between maximum residual saturation and R_a is seen. The match to coordination number is good. Again only geological samples were considered (the Aerolith ceramic was excluded).

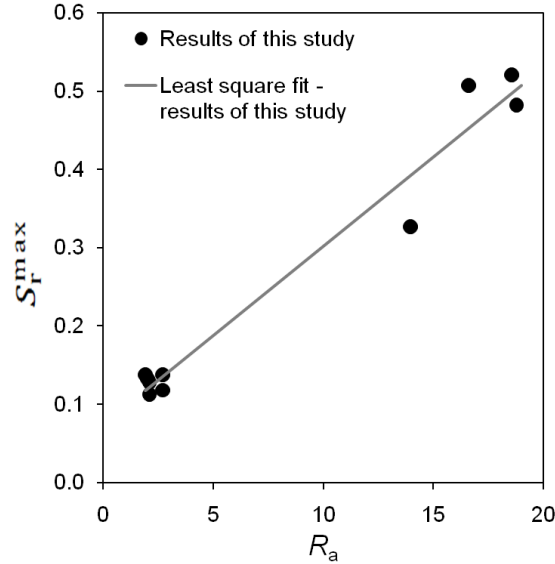


Figure 3.5: R_a versus maximum trapped saturation data (●). The least square fit to the experimental data (—) is shown ($S_r^{\max} = 0.0228[R_a] + 0.0746$). An excellent match ($R^2 = 0.97$) is achieved. The result of the Aerolith sample ($R_a = 0.39$) was excluded from the analysis as it lies outside the main trend of the data.

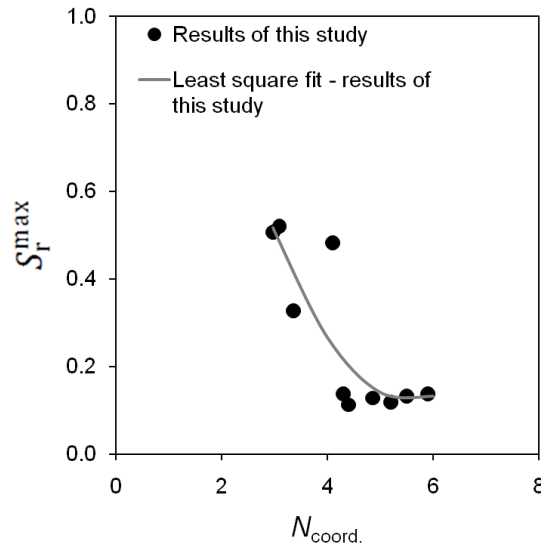


Figure 3.6: $N_{\text{coord.}}$ versus maximum trapped saturation data (●). The least square fit to the experimental data (—) is shown ($S_r^{\max} = 0.0586[N_{\text{coord.}}]^2 - 0.6537[N_{\text{coord.}}] + 1.9441$). A good match ($R^2 = 0.73$) is achieved. The result of the Aerolith sample ($N_{\text{coord.}} = 10.55$) was excluded from the analysis as it lies outside the main trend of the data.

Table 3.2: Least square fit equations to experimental data from this study, including the correlation coefficient (R^2). The result of the Aerolith sample ($N_{\text{coord.}} = 10.55$) was excluded from the analysis of coordination number as it lies outside the main trend of the data.

Dataset	Least Square Fit Equation	R^2
R_a vs. S_r^{max}	$S_r^{\text{max}} = 0.0228(R_a) + 0.0746$	0.97
$N_{\text{coord.}}$ vs. S_r^{max}	$S_r^{\text{max}} = 0.0586(N_{\text{coord.}})^2 - 0.6537(N_{\text{coord.}}) + 1.9441$	0.73

It is proposed that measurements of R_a and $N_{\text{coord.}}$ can be used to predict end point saturations with the equations given in Table 3.2. Another useful predictive tool would be a single parameter that represents the pore-scale geometry and which could also be used to predict end point saturations. In Figure 3.7 $R_a/N_{\text{coord.}}$ is plotted versus maximum trapped saturation. An excellent match ($R^2 = 0.97$) to this data is possible with a least square fit to the linear equation 22.

$$S_r^{\text{max}} = 0.0721 \left(\frac{R_a}{N_{\text{coord.}}} \right) + 0.0944 \quad (22)$$

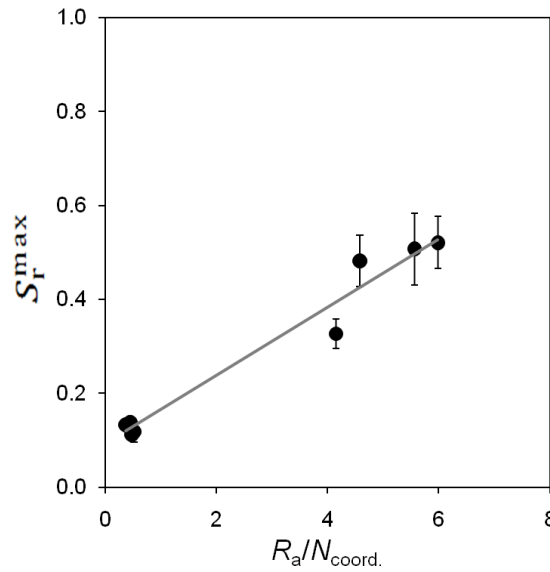


Figure 3.7: The proposed characteristic pore scale geometry term ($R_a/N_{\text{coord.}}$) versus maximum trapped saturation ($\bullet$). The least square fit to the experimental data (—) is shown ($S_r^{\text{max}} = 0.0721[R_a/N_{\text{coord.}}] + 0.0944$). An excellent match ($R^2 = 0.97$) is achieved.

The relationships between petrophysical parameters and maximum trapped saturations presented in Figure 3.2 through Figure 3.7 are consistent with our understanding of trapping in porous media – as outlined in Chapter 1.2.1 Fundamentals of Immiscible Displacement – and given by equation 5. It is worth

summarising the three effects on trapping again here. First, that as aspect ratio increases, there is more snap-off and trapping. Second, large coordination numbers tend to lead to less trapping, since there is more opportunity for the oil to be displaced through a pore before all the surrounding throats are filled. Third, an increase in contact angle suppresses snap-off compared to piston-like advance, leading to less trapping.

More consolidated media tend to have higher aspect ratios due to the process of sedimentation and compaction. Compaction and consolidation also results in lower coordination numbers as some throats are closed entirely. This can be seen from the properties of the samples investigated in this study. Unconsolidated sands have lower aspect ratios and higher coordination numbers compared to consolidated sandstones. This influence of compaction and sedimentation on the pore scale geometrical properties also explains the relationship between the remaining parameters (porosity, permeability, formation factor) and trapping. With more compaction and consolidation sample porosity and permeability decreases while tortuosity (formation factor) increases. This leads to more non-wetting phase trapping through snap-off. This is clearly illustrated by looking at how the properties and trapping differ between the unconsolidated sands and consolidated sandstones investigated.

The equations presented could be used as a useful tool to predict maximum residual saturations if, for example, the petrophysical properties of a prospective storage formation were known. The end point saturation could then be used to predict the shape of the trapping curve with a correlation such as the Land equation (Eqn. 9). This could allow site analysis and suitability studies to progress while time consuming coreflood experiments took place – ultimately providing the site specific data required for further in-depth analysis.

3.1.2 Capillary Trapping in CO₂-brine-sandstone systems

The results of this study have shown that significant quantities of CO₂ can be rendered immobile by capillary forces after waterflooding in Berea sandstone (Figure 2.17). Up to 35% of the pore space can be occupied by CO₂ trapped in this manner. This is higher than previously reported in the literature, with the exception of one data point measured on Berea Sandstone [115] (Table 1.7). It has been shown that for the same rock type more oil than CO₂ can be trapped as a residual

immobile phase – although the magnitude of the difference is not very large, consistent with both phases being non-wetting (maximum $S_r = 35.3\%$ for CO₂-brine; maximum $S_r = 48.3\%$ for decane-brine; Figure 2.17). If CO₂ had wet the rock surface then much lower residual saturations would have been expected [1].

Coreflood Methodology. The porous plate method was used in this study – the first time that this approach has been used for a CO₂-brine-sandstone system. Previous literature CO₂-brine-sandstone trapping data has been generated using the unsteady state and steady state coreflood methods. In this study results of the porous plate and unsteady state methods were compared for the same Berea rock type and maximum trapped saturations were shown to differ (unsteady state = 26%; porous plate = 35%; Figure 2.21). It is proposed that the discrepancies seen between the results of this study and literature are due to the choice of coreflood method – and more specifically the different primary drainage capillary pressures applied to the system in each instance.

Higher saturations are possible with the porous plate method due to the higher applied capillary pressures and it is proposed that this is a preferred method for determining irreducible water saturations for CO₂-brine systems. This can be seen by considering the primary drainage capillary pressure curve generated in this study (Figure 2.16). Unsteady state displacements – if end effects are accounted for – would appear to provide representative S_i , S_r measurements but at lower initial saturations due to the lower P_c applied during primary drainage. That is not to say that unsteady state corefloods are not of interest. When combined with ISSM enlightening information about core scale displacements and the role of sub-core scale heterogeneities can be produced [111], [115], [116]. Unsteady state experiments can also be used to generate relative permeability curves by numerical regression if the production and pressure drop history is known [84], [116]. It is important to thoroughly plan experiments to ensure that the correct coreflood method is used to investigate a particular area of interest. Regardless of the coreflood technique it is critically important to ensure equilibrated phases are used in any study of immiscible flow. Low residual saturations reported previously may have been caused by waterflooding with brine that was not entirely saturated with CO₂.

Oil-brine versus CO₂-brine Capillary Trapping. It has been shown in this study that the magnitude of non-wetting phase capillary trapping in Berea sandstone is influenced by the fluid system under investigation. For the same rock type and experimental methodology more oil than CO₂ was shown to be trapped by brine (Figure 2.17). The differences must therefore be caused by one or more of the rock-fluid or fluid-fluid properties which include: viscous forces; buoyancy forces; capillary forces; and wettability.

The phase properties (density, viscosity, IFT) did vary between the oil-brine and CO₂-brine experiments. It is therefore worth comparing the experiments in terms of the forces applied during entrapment (waterflooding). This is done with dimensionless ratios; the capillary number (Eqn. 6) and Bond number (Eqn. 7). Table 3.3 summarises the properties in the oil-brine and CO₂-brine experiments.

Table 3.3: Experimental properties and dimensionless numbers for oil-brine and CO₂-brine experiments on Berea sandstone. Dimensionless numbers are for waterflooding – brine is the displacing phase.

Property	Oil-brine	CO ₂ -brine
Core-plug cross sectional area (m ²)	1.16×10 ⁻³	1.16×10 ⁻³
Interfacial tension (mN m ⁻¹)	48.3 ^a	36.0 ^b
Wetting phase viscosity (Pa s)	4.55×10 ^{-4c}	5.10×10 ^{-4d}
Wetting phase density (kg m ⁻³)	1020 ^e	1025 ^f
Non-wetting phase density (kg m ⁻³)	700 ^g	208 ^h
Average pore radius (m) ⁱ	7.5×10 ⁻⁶	7.5×10 ⁻⁶
$N_{cap.}$	3.1×10⁻⁷	4.1×10⁻⁷
N_b	3.7×10⁻⁶	1.3×10⁻⁶

^a [91]; linearly extrapolated to 343 K

^b [29], [109]

^c [92]; 5.8wt.% NaCl aqueous solution at 10.0MPa, 343.2 K

^d [102]; 3.0wt.% NaCl aqueous solution at 10.0 MPa, 333 K

^e [94]; 1.027 mol/kg NaCl aqueous solution.

^f [102]; assuming an unsaturated brine density of 1020 kg m⁻³ [94]

^g [95]

^h [101]

ⁱ [46] determined from maximum ball algorithm on CT image of pore space

It has been shown that residual saturation is insensitive to capillary and Bond numbers below limiting values – typically $N_{cap.} = 10^{-6}$ for clean sandstones and $N_b = 10^{-2}$ [39], [51], [117], [118]. In these flow regimes capillary forces dominate relative to viscous and buoyancy forces respectively. It therefore seems unlikely that the differences in residual non-wetting phase saturation measured in this study are due to changes in the ratio of capillary to viscous or capillary to buoyancy forces between experiments, as the experiments were conducted below these limits.

It is proposed that initial saturations were homogeneous in the porous plate experiments. This has not been verified however – for example by use of ISSM. The presence of the porous plate will avoid capillary discontinuity at the end face of the core-plug during primary drainage but it is also worth considering saturation changes in the vertical direction. The experiments were performed with the core-plug orientated horizontally. Due to the density difference between the phases a capillary pressure gradient will exist across the height of the sample ($P_c = \Delta\rho gh$) while the phases are continuous during primary drainage. The system height is the core-plug diameter. In the CO₂-brine experiment this results in a change in P_c between top and bottom of the core-plug diameter of 0.31 kPa. This change in P_c is smaller than that applied during primary drainage due to the difference in inlet and outlet phase pressures at equilibrium ($P_c = P_{nw} - P_w$) which was $1 \text{ kPa} < P_c < 296 \text{ kPa}$. By comparison with the capillary pressure curve it is not envisaged that a change in P_c of 0.31 kPa could cause a significant saturation change over this height (0.038 m). In the unlikely event that this did occur the measured saturations should still be valid – representing an average of the saturation within the core-plug. For the oil-brine porous plate experiments the change in P_c with height is smaller – 0.12 kPa – and expected to be even less of a concern.

The final parameter which may explain the difference in trapping is system wettability. The influence of contact angle on the ratio of snap-off to piston like advance was given by equation 5. It is also well known that residual wetting phase saturations can be very low – the wetting phase being in continuum across the solid surface and able to be produced through film flow [40]. If CO₂ were to wet the rock surface, or even to be neutrally-wet, lower residual saturations may be expected. This is certainly not seen in this study – but the subtle change in the magnitude of trapping may be explained by an equally subtle change in the system wettability. Network modelling has shown that changes in the imbibition intrinsic contact angle can lead to changes in the form of the capillary trapping curve [1]. A small increase in the contact angle – possibly of the order of 10 – 20 degrees – may result in slightly less trapping in a CO₂-brine system compared to an oil-brine system. This is entirely consistent with the understanding of trapping discussed previously where an increase in contact angle suppresses snap-off compared to piston-like advance, leading to less trapping. The magnitude of the trapping measured in this study, and previous literature studies of CO₂-water contact angles [29-31], would strongly

suggest that the contact angle remains in the water-wet regime (defined as $\theta < 90^\circ$ [25]). This view is given credence by a further study of the capillary pressures measured on a CO₂-water-sand system by Plug and Bruining [67]. The primary drainage and waterflooding curves can be analysed to give a quantitative indication of system wettability with the use of wettability indices. Applying this methodology to the data of Plug and Bruining yields a USBM index of 0.48 [119], an Amott (water displacement) index of 0.55 [120], and a Hammervold-Longeron (HL) index of 0.75 [121]. All these numbers fall within the water-wet regime as defined for oil-water systems and outlined in Table 3.4. Appendix 8 contains full wettability indices equations and the data of Plug and Bruining.

Table 3.4: Approximate relationship between wettability and wettability indices for oil-water systems.

Index	Water-wet	Neutrally-wet	Oil-wet
Amott (displacement by water ratio)	Positive	0	0
Hammervold-Longeron	1	0	-1
USBM	near 1	near 0	near -1

It is speculated that the small changes in contact angle proposed may be due to mineral-water interactions in the presence of dissolved CO₂. This may be especially important for rocks containing clays and cements. The brine pH and salinity play an important role in system wettability due to their influence on rock surface charge [26]. This is an interesting area for future study, as discussed in the next section.

Also the small differences in the degree of trapping observed in unconsolidated systems between gas/brine and oil/brine could be caused by the gas/brine systems being slightly more water-wet.

3.1.3 Recommendations for Future Work

An understanding of non-wetting phase trapping in porous media has been developed in this thesis – with new insights into CO₂ trapping and the petrophysical properties that influence it – but there are many areas for further work.

Wettability is a topic of great interest for CO₂ storage. The results of this study would strongly indicate that CO₂ is the non-wetting phase in a CO₂-brine-sandstone system. However there is a tantalising indication that CO₂-brine

wettability within the water-wet domain is not as simple as an equivalent refined oil-brine system – as illustrated by the differences in the respective trapping curves and the inability of the pore network model to match the CO₂-brine results. Further insights into CO₂-brine wettability may be possible by investigating methods of quantifying wettability such as wettability indices and contact angle measurements as well as qualitative approaches such as CT imaging.

The use of wettability indices would require the waterflood capillary pressure curve to be measured. This type of experiment is common in oil-brine applications and its development and application to CO₂ storage would be welcome. CO₂-brine-rock contact angles have already been measured [29-31], [122-124] but further research in this area would be welcome, especially if contact angle measurements on an idealised substrate are combined with coreflood experiments on the same rock type. The measurement of contact angle was an area of interest in this study however time constraints prevented further research of the type that led to the contact angle measurements on the porous plate. Enlightening wettability insights would also be possible through the CT imaging of CO₂ and brine phase distribution on the pore scale at reservoir conditions. This continues to be an area of ongoing research at Imperial College London.

The influence of brine pH and salinity on wettability should also be investigated further. Different brine compositions – including different ionic valencies – could be investigated in addition to the role of pH, possibly through the influence of temperature and pressure on CO₂ solubility in water and subsequent brine pH. Once saturated with CO₂ brine pH is likely to be low – possibly of the order of pH 3 [125], close to the zero surface charge of quartz (pH ~ 2) [126] where contact angles between brine and non-aqueous phase liquids (NAPL) have been calculated and measured to reach a maximum [127]. The influence of brine salinity on contact angle has also been measured for a brine-NAPL-quartz system [127]. Contact angle was shown to decrease with increasing brine salinity. In this study only one brine salinity – comprising monovalent ions – was investigated. The influence of brine composition, the measurement of pH, and the influence of pH on wettability for CO₂-brine systems would be welcome additions to the literature.

Wettability alteration with time, or aging, is another area of interest. It is known that some hydrocarbon accumulations experience wettability alterations

over time – caused by the adsorption of polar compounds or the precipitation of organic material. It would be interesting to investigate whether rocks in contact with CO₂ and water experience similar changes in wettability state with time. This could have significant consequences for long term CO₂ storage security.

The use of pore network simulation for CO₂-brine systems should be investigated further in order to accurately predict CO₂ trapping behaviour. It may be necessary to incorporate the behaviour of subtle wettability changes into the code. These studies could also be expanded to consider different rock types and brines – possibly allowing for research on the role of clays, cements and brine composition on wettability. Carbonate rocks should also be investigated as surface chemistry is likely to be much more important in these systems.

The porous plate experiment method used in this study would benefit from an additional study of initial saturation distribution. There is confidence that initial saturations were homogeneous but this could be verified by in-situ saturation monitoring methods. Additionally it would be preferential in future to conduct experiments at higher T and P conditions – beyond those possible with this experimental apparatus. Figure 1.4 showed that CO₂ density and viscosity is quasi constant at depths below approximately 1500 m ($\rho \approx 650 \text{ kg m}^{-3}$; $\mu \approx 5 \times 10^{-5}$). If coreflood experiments were to replicate these conditions they could be of direct applicability to a greater number of storage projects.

Finally pore network simulation could also be used to further investigate the parameter space in the relationship between geometric rock properties (aspect ratio and coordination number) and trapping, without resort to time consuming coreflood experiments.

3.2 Conclusions

This thesis presents a suite of capillary trapping data. Capillary trapping curves have been measured on two different porous media – unconsolidated sand and sandstones – while oil-brine and CO₂-brine systems have been investigated at both ambient and elevated temperature and pressure conditions. End-point saturations have been measured for additional systems and these results used to investigate the petrophysical influences on non-wetting phase capillary trapping. A simple term – the capillary trapping capacity – has been developed to aid estimates of subsurface storage capacities.

In ***unconsolidated sands*** the degree of capillary trapping was shown to be relatively low and the form of the trapping curve was poorly predicted by common literature correlations. The residual saturation increased linearly as a function of initial saturation before reaching a maximum of 12.8% for oil and 14.3% for gas at initial saturations of 47.6% and 20.0% respectively. The best match to this behaviour was with the correlation proposed by Aissaoui [66]. The low maximum residual saturations are a result of the unconsolidated nature of the medium where the majority of the larger pores can be invaded easily at low water saturations. The small aspect ratios and high coordination numbers dissuade non-wetting phase snap-off compared to more consolidated media. The difference in maximum saturations between the oil-brine and gas-brine systems can be explained by small changes in wettability and contact angle. In the gas-brine system brine is likely to be more wetting resulting in more snap-off during secondary imbibition.

The observed maximum capillary trapping capacities were 4.9% for oil and 5.3% for gas. This indicates that CO₂ storage in poorly consolidated, shallow sediments would likely lead to low storage efficiencies.

For ***consolidated sandstones*** correlations between maximum residual (end-point) oil saturation and petrophysical properties (K , ϕ , F , R_a , $N_{\text{coord.}}$) have been presented. Good predictions of residual saturation are possible within the parameter ranges investigated. In the absence of coreflood data these correlations may provide useful insights into how much non-wetting phase may be trapped. Of specific interest is the new relationship proposed between pore scale geometric properties –

aspect ratio and coordination number – and trapped saturations. This parameter – the ratio of aspect ratio to coordination number – gives the best match to the residual saturation results ($R^2=0.97$), followed by aspect ratio ($R^2=0.97$), permeability ($R^2=0.92$) and porosity ($R^2=0.88$).

CO₂-brine and oil-brine capillary trapping in Berea sandstone has been shown to be different. The maximum residual non-wetting phase saturation is larger in oil-brine systems – 48.3% versus 35.3%. This is likely to be due to subtle changes in imbibition intrinsic contact angle which leads to less snap-off in a CO₂-brine system where the brine is slightly less wetting. The shape of the capillary trapping curve is also shown to be different which again is probably due to subtle changes in system wettability.

Carbon dioxide does not wet the rock surface. This has important implications for storage efficiency both in terms of cap-rock integrity (capillary entry) and capillary trapping in reservoir rocks. Significant quantities of CO₂ are rendered immobile proving that capillary trapping is a secure method to store CO₂ in sandstones. The observed maximum capillary trapping capacity is 7.8%, higher than gas-brine trapping in unconsolidated sands (5.3%). This indicates that significant quantities of CO₂ could be stored securely in sandstones by capillary trapping.

The primary drainage capillary pressure curve is also reported. This data allows the de-saturation of water from a storage formation to be calculated for a given height of CO₂ column. An irreducible water saturation of 15.2% is reached at a column height of only 20 m for the conditions investigated. This data may prove important for field scale CO₂ drainage studies and calculations of structural and stratigraphic trapping capacity.

Finally a number of interesting and significant areas for future study have been highlighted. System wettability continues to be an area of interest in CO₂ storage and the suggestion is to study this in terms of wettability indices and pore-scale imaging.

Bibliography

- [1] E. Spiteri, R. Juanes, M. J. Blunt, and F. Orr, "A New Model of Trapping and Relative Permeability Hysteresis for All Wettability Characteristics," *SPE Journal*, vol. 13, no. 3, pp. 277-288, 2008.
 - [2] S. Iglauer, S. Favretto, G. Spinelli, G. Schena, and M. Blunt, "X-ray tomography measurements of power-law cluster size distributions for the nonwetting phase in sandstones," *Physical Review E*, vol. 82, no. 5, 2010.
 - [3] Solomon, *Intergovernmental Panel on Climate Change*, 2007th ed. 2007.
 - [4] P. Falkowski, "The Global Carbon Cycle: A Test of Our Knowledge of Earth as a System," *Science*, vol. 290, no. 5490, pp. 291-296, 2000.
 - [5] T. M. L. Wigley, R. Richels, and J. A. Edmonds, "Economic and environmental choices in the stabilization of atmospheric CO₂ concentrations," *Nature*, vol. 379, no. 6562, pp. 240-243, 1996.
 - [6] M. I. Hoffert et al., "Advanced Technology Paths to Global Climate Stability: Energy for a Greenhouse Planet," *Science*, vol. 298, no. 5595, pp. 981-987, Nov. 2002.
 - [7] "Scottish Centre for Carbon Storage." [Online]. Available: <http://www.geos.ed.ac.uk/scs/>. [Accessed: 05-May-2010].
 - [8] F. M. Orr Jr., "Storage of Carbon Dioxide in Geologic Formations," *Journal of Petroleum Technology*, vol. 56, no. 9, pp. 90-97, 2004.
 - [9] K. S. Lackner, "CLIMATE CHANGE: A Guide to CO₂ Sequestration," *Science*, vol. 300, no. 5626, pp. 1677-1678, Jun. 2003.
 - [10] C. Hawkes, P. Mclellan, and S. Bachu, "Geomechanical Factors Affecting Geological Storage of CO₂ in Depleted Oil and Gas Reservoirs," *Journal of Canadian Petroleum Technology*, vol. 44, no. 10, pp. 52-61, 2005.
 - [11] D. R. Lide, *CRC Handbook of Chemistry and Physics*, 87th Edition, 87th ed. CRC Press, 2006.
 - [12] S. Bachu, W. D. Gunter, and E. H. Perkins, "Aquifer disposal of CO₂: Hydrodynamic and mineral trapping," *Energy Conversion and Management*, vol. 35, no. 4, pp. 269-279, Apr. 1994.
 - [13] E. Lindeberg and D. Wessel-Berg, "Vertical convection in an aquifer column under a gas cap of CO₂," *Energy Conversion and Management*, vol. 38, pp. 229-234, 1997.
 - [14] J. Ennis-King and L. Paterson, "Role of Convective Mixing in the Long-Term Storage of Carbon Dioxide in Deep Saline Formations," *SPE Journal*, vol. 10, no. 3, pp. 349-356, 2005.
 - [15] W. D. Gunter, E. H. Perkins, and T. J. McCann, "Aquifer disposal of CO₂-rich gases: Reaction design for added capacity," *Energy Conversion and Management*, vol. 34, no. 9, pp. 941-948, 1993.
 - [16] W. D. Gunter, B. Wiwehar, and E. H. Perkins, "Aquifer disposal of CO₂-rich
-

- greenhouse gases: Extension of the time scale of experiment for CO₂-sequestering reactions by geochemical modelling,” *Mineralogy and Petrology*, vol. 59, no. 1, pp. 121-140, 1997.
- [17] J. Ennis-King and P. Lincoln, “Engineering Aspects of Geological Sequestration of Carbon Dioxide,” in *Proceedings of SPE Asia Pacific Oil and Gas Conference and Exhibition*, SPE Paper 77809, 2002.
- [18] Z. Duan, N. Møller, and J. H. Weare, “An equation of state for the CH₄-CO₂-H₂O system: I. Pure systems from 0 to 1000 C and 0 to 8000 bar,” *Geochimica et Cosmochimica Acta*, vol. 56, no. 7, pp. 2605–2617, 1992.
- [19] A. Fenghour, W. A. Wakeham, and V. Vesovic, “The Viscosity of Carbon Dioxide,” *Journal of Physical and Chemical Reference Data*, vol. 27, no. 1, p. 31, 1998.
- [20] W. Brock and L. Bryan, “Summary Results of CO₂ EOR Field Tests, 1972-1987,” in *Proceedings of Low Permeability Reservoirs Symposium*, 1989.
- [21] R. Hadlow, “Update of Industry Experience With CO₂ Injection,” in *Proceedings of SPE Annual Technical Conference and Exhibition*, 1992.
- [22] International Energy Agency, “Energy Policies of IEA Countries Norway: 2005 Review Complete Edition ISBN 9264109358.”
- [23] “Bellona Foundation - Bellona.” [Online]. Available: <http://www.bellona.org/>. [Accessed: 04-May-2010].
- [24] R. Qi, T. C. LaForce, and M. J. Blunt, “Design of carbon dioxide storage in aquifers,” *International Journal of Greenhouse Gas Control*, vol. 3, no. 2, pp. 195-205, 2009.
- [25] J. Bear, *Dynamics of fluids in porous media*. Courier Dover Publications, 1988.
- [26] W. Anderson, “Wettability Literature Survey- Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability,” *Journal of Petroleum Technology*, vol. 38, no. 10, pp. 1125-1144, 1986.
- [27] W. Anderson, “Wettability Literature Survey- Part 2: Wettability Measurement,” *Journal of Petroleum Technology*, vol. 38, no. 11, pp. 1246-1262, 1986.
- [28] W. Anderson, “Wettability Literature Survey-Part 3: The Effects of Wettability on the Electrical Properties of Porous Media,” *Journal of Petroleum Technology*, vol. 38, no. 12, pp. 1371-1378, 1986.
- [29] P. Chiquet, D. Broseta, and S. Thibeau, “Wettability alteration of caprock minerals by carbon dioxide,” *Geofluids*, vol. 7, no. 2, pp. 112-122, 2007.
- [30] J. L. Dickson, G. Gupta, T. S. Horozov, B. P. Binks, and K. P. Johnston, “Wetting Phenomena at the CO₂/Water/Glass Interface,” *Langmuir*, vol. 22, no. 5, pp. 2161-2170, Feb. 2006.
- [31] D. N. Espinoza and J. C. Santamarina, “Water-CO₂-mineral systems: Interfacial tension, contact angle, and diffusion—Implications to CO₂ geological storage,” *Water Resources Research*, vol. 46, p. 10 PP., Jul. 2010.
- [32] L. P. Dake, *Fundamentals of Reservoir Engineering*, New impression. Elsevier Science, 1983.
- [33] L. E. Treiber and W. W. Owens, “A Laboratory Evaluation of the Wettability of Fifty Oil-Producing Reservoirs,” *Society of Petroleum Engineers Journal*, vol. 12, no. 6, pp. 531-540, 1972.
- [34] M. Blunt and H. Scher, “Pore-level modeling of wetting,” *Physical Review E*, vol. 52, no. 6, pp. 6387-6403, 1995.
- [35] G. R. Jerauld and S. J. Salter, “The effect of pore-structure on hysteresis in relative permeability and capillary pressure: Pore-level modeling,” *Transport in Porous Media*, vol. 5, no. 2, pp. 103-151, 1990.
-

- [36] A. Abrams, "The Influence of Fluid Viscosity, Interfacial Tension, and Flow Velocity on Residual Oil Saturation Left by Waterflood," *Society of Petroleum Engineers Journal*, vol. 15, no. 5, pp. 437-447, 1975.
 - [37] T. F. Moore and R. L. Slobod, "The effect of viscosity and capillarity on the displacement of oil by water," *Producers Monthly*, vol. 20, pp. 20-30, 1956.
 - [38] J. Taber, "Dynamic and Static Forces Required To Remove a Discontinuous Oil Phase from Porous Media Containing Both Oil and Water," *Society of Petroleum Engineers Journal*, vol. 9, no. 1, pp. 3 - 12, 1969.
 - [39] N. Morrow, I. Chatzis, and J. Taber, "Entrapment and Mobilization of Residual Oil in Bead Packs," *SPE Reservoir Engineering*, vol. 3, no. 3, pp. 927-934, 1988.
 - [40] P. H. Valvatne and M. J. Blunt, "Predictive pore-scale modeling of two-phase flow in mixed wet media," *Water Resources Research*, W07406, vol. 40, no. 7, p. 21, 2004.
 - [41] M. Piri and M. J. Blunt, "Three-dimensional mixed-wet random pore-scale network modeling of two- and three-phase flow in porous media. II. Results," *Physical Review E*, vol. 71, no. 2, p. 026302, Feb. 2005.
 - [42] M. Piri and M. J. Blunt, "Three-dimensional mixed-wet random pore-scale network modeling of two- and three-phase flow in porous media. I. Model description," *Physical Review E*, vol. 71, no. 2, p. 026301, Feb. 2005.
 - [43] S. Chen and G. D. Doolen, "Lattice Boltzmann Method for Fluid Flows," *Annual Review of Fluid Mechanics*, vol. 30, no. 1, pp. 329-364, 1998.
 - [44] P. Øren and S. Bakke, "Reconstruction of Berea sandstone and pore-scale modelling of wettability effects," *Journal of Petroleum Science and Engineering*, vol. 39, no. 3, pp. 177-199, 2003.
 - [45] P. Øren and S. Bakke, "Process Based Reconstruction of Sandstones and Prediction of Transport Properties," *Transport in Porous Media*, vol. 46, pp. 311-343, 2002.
 - [46] H. Dong and M. Blunt, "Pore-network extraction from micro-computerized-tomography images," *Physical Review E*, 036307, vol. 80, no. 3, 2009.
 - [47] D. Silin and T. Patzek, "Pore space morphology analysis using maximal inscribed spheres," *Physica A: Statistical and Theoretical Physics*, vol. 371, no. 2, pp. 336-360, Nov. 2006.
 - [48] M. J. Oak, L. Baker, and D. Thomas, "Three-Phase Relative Permeability of Berea Sandstone," *Journal of Petroleum Technology*, vol. 42, no. 8, pp. 1054-1061, 1990.
 - [49] T. Suekane, T. Nobuso, S. Hirai, and M. Kiyota, "Geological storage of carbon dioxide by residual gas and solubility trapping," *International Journal of Greenhouse Gas Control*, vol. 2, no. 1, pp. 58-64, Jan. 2008.
 - [50] C. Agbalaka, A. Dandekar, S. Patil, S. Khataniar, and J. Hemsath, "Coreflooding Studies to Evaluate the Impact of Salinity and Wettability on Oil Recovery Efficiency," *Transport in Porous Media*, vol. 76, no. 1, pp. 77-94, Jan. 2009.
 - [51] I. Chatzis and N. Morrow, "Correlation of Capillary Number Relationships for Sandstone," *Society of Petroleum Engineers Journal*, vol. 24, no. 5, pp. 555-562, 1984.
 - [52] J. Kleppe, P. Delaplace, R. Lenormand, G. Hamon, and E. Chaput, "Representation of Capillary Pressure Hysteresis in Reservoir Simulation," in *Proceedings of SPE Annual Technical Conference and Exhibition, SPE Paper 38899, San Antonio, Texas, USA*, 1997.
 - [53] J. J. Pickell, B. F. Swanson, and W. B. Hickman, "Application of Air-Mercury and Oil-Air Capillary Pressure Data In the Study of Pore Structure
-

- and Fluid Distribution,” *Society of Petroleum Engineers Journal*, vol. 6, no. 1, pp. 55-61, 1966.
- [54] K. Suzanne, G. Hamon, J. Billiotte, and V. Trocme, “Experimental Relationships Between Residual Gas Saturation and Initial Gas Saturation in Heterogeneous Sandstone Reservoirs,” in *Proceedings of SPE Annual Technical Conference and Exhibition, SPE Paper 84038, Denver, Colorado, U.S.A., 2003*.
- [55] T. M. Geffen, D. R. Parrish, G. W. Dean, and R. A. Morse, “Efficiency of gas displacement from porous media by liquid flooding,” *Trans. AIME*, vol. 195, pp. 29-38, 1952.
- [56] G. R. Jerauld, “Prudhoe Bay Gas/Oil Relative Permeability,” *SPE Reservoir Engineering*, vol. 12, no. 1, pp. 66-73, 1997.
- [57] T. D. Ma and G. K. Youngren, “Performance of Immiscible Water-Alternating-Gas (IWAG) Injection at Kuparuk River Unit, North Slope, Alaska,” in *Proceedings of SPE Annual Technical Conference and Exhibition, SPE Paper 28602, New Orleans, Louisiana, U.S.A., 1994*.
- [58] C. Land, “Comparison of Calculated with Experimental Imbibition Relative Permeability,” *Society of Petroleum Engineers Journal*, vol. 11, no. 4, pp. 419-425, 1971.
- [59] D. C. Crowell, G. W. Dean, and A. G. Loomis, *Efficiency of gas displacement from a water-drive reservoir*. US Department of the Interior, Bureau of Mines, Washington, DC, 1966.
- [60] J. Kralik, L. Manak, G. Jerauld, and A. Spence, “Effect of Trapped Gas on Relative Permeability and Residual Oil Saturation in an Oil-Wet Sandstone,” in *Proceedings of SPE Annual Technical Conference and Exhibition, SPE Paper 62997, Dallas, Texas, U.S.A., 2000*.
- [61] M. H. Holtz, “Reservoir characterization applying residual gas saturation modeling, example from the Starfak T1 reservoir, Middle Miocene Gulf of Mexico,” Master of Science, The University of Texas at Austin, 2005.
- [62] S. Iglauer, W. Wüling, C. H. Pentland, S. Al Mansoori, and M. J. Blunt, “Capillary Trapping Capacity of Rocks and Sandpacks,” in *Proceedings of SPE EUROPEC/EAGE Conference and Exhibition, SPE Paper 120960, Amsterdam, The Netherlands, 2009*.
- [63] C. Land, “Calculation of Imbibition Relative Permeability for Two- and Three-Phase Flow From Rock Properties,” *Society of Petroleum Engineers Journal*, vol. 8, no. 2, pp. 149 - 156, 1968.
- [64] J. Naar and J. H. Henderson, “An Imbibition Model - Its Application to Flow Behavior and the Prediction of Oil Recovery,” *Society of Petroleum Engineers Journal*, vol. 1, no. 2, pp. 61-70, 1961.
- [65] R. G. Agarwal, “Unsteady-state performance of water-drive gas reservoirs,” Texas A&M university, 1967.
- [66] A. Aissaoui, “Etude théorique et expérimentale de l’hystérésis des pressions capillaires et des perméabilités relatives en vue du stockage souterrain de gaz,” PhD thesis, Ecole des Mines de Paris, 1983.
- [67] J. Plug, “Measurements of capillary pressure and electric permittivity of gas-water systems in porous media at elevated pressures: application to geological storage of CO₂ in aquifers and wetting behavior in coal,” PhD thesis, Delft University of Technology, 2007.
- [68] Chierici, “Experimental research on gas saturation behind the water front in gas reservoirs subjected to water drive,” 1963. [Online]. Available: <http://www.onepetro.org/mslib/servlet/onepetropreview?id=WPC-10134&soc=WPC&speAppNameCookie=ONEPETRO>. [Accessed: 04-May-
-

- 2010].
- [69] J. Delclaud, "Laboratory measurements of the residual gas saturation," in *Laboratory measurements of the residual gas saturation*, p. 431, 1991.
- [70] M. Ding and A. Kantzas, "MEASUREMENTS OF RESIDUAL GAS SATURATION UNDER AMBIENT CONDITIONS," in *Proceedings of SCA Annual Symposium*, 2001.
- [71] A. Firoozabadi, G. Olsen, and T. van Golf-Racht, "Residual Gas Saturation in Water-Drive Gas Reservoirs," in *Proceedings of SPE California Regional Meeting*, 1987.
- [72] R. Hazlett, M. Honarpour, J. Bulau, and R. Vaidya, "Residual Oil Saturation Dependence on Initial Water Saturation in Clean Water-Wet Sandstone," in *Proceedings of SCA Annual Symposium*, 1999.
- [73] A. Kantzas, M. Ding, and J. Lee, "Residual Gas Saturation Revisited," *SPE Reservoir Evaluation & Engineering*, vol. 4, no. 6, 2001.
- [74] D. Keelan, "A Practical Approach to Determination of Imbibition Gas-Water Relative Permeability," *Journal of Petroleum Technology*, vol. 28, no. 2, pp. 199-204, 1976.
- [75] B. A. McKay, *Laboratory studies of gas displacement from sandstone reservoirs having strong water drive. [Australia]*. 1974.
- [76] H. Mulyadi, R. Amin, T. Kennaird, I. Palmer, and D. Van Nispen, "Measurement of Residual Gas Saturation in Water-Driven Gas Reservoirs : Comparison of Various Core Analysis Techniques," in *Proceedings of SPE International Oil and Gas Conference and Exhibition in China*, 2000.
- [77] D. Katz, "How Water Displaces Gas from Porous Media," *Oil and Gas Journal*, vol. 2966, pp. 55-60, 1966.
- [78] J. Kyte, R. Stanclift Jr., S. Stephan Jr., and L. Rapoport, "Mechanism of Water Flooding in the Presence of Free Gas," *Trans. AIME*, vol. 207, pp. 215-221, 1956.
- [79] H. Yuan, "The Influence of Pore Coordination on Petrophysical Parameters," in *Proceedings of SPE Annual Technical Conference and Exhibition, SPE Paper 10074, San Antonio, Texas, U.S.A.*, 1981.
- [80] N. Wardlaw, "The Effects of Pore Structure on Displacement Efficiency in Reservoir Rocks and in Glass Micromodels," in *Proceedings of SPE/DOE Enhanced Oil Recovery Symposium, SPE Paper 8843, Tulsa, Oklahoma, U.S.A.*, 1980.
- [81] N. Wardlaw, "The Effects of Geometry, Wettability, Viscosity And Interfacial Tension On Trapping In Single Pore-throat Pairs," *Journal of Canadian Petroleum Technology*, vol. 21, no. 3, pp. 21-27, 1982.
- [82] V. K. S. Shante and S. Kirkpatrick, "An introduction to percolation theory," *Advances in Physics*, vol. 20, no. 85, pp. 325-357, 1971.
- [83] P. Egermann, C. Chalbaud, J. Duqueroix, and Y. Le Gallo, "An Integrated Approach to Parameterize Reservoir Models for CO₂ Injection in Aquifers," in *Proceedings of SPE Annual Technical Conference and Exhibition, SPE Paper 102308, San Antonio, Texas, U.S.A.*, 2006.
- [84] D. B. Bennion and S. Bachu, "Drainage and Imbibition Relative Permeability Relationships for Supercritical CO₂/Brine and H₂S/Brine Systems in Intergranular Sandstone, Carbonate, Shale, and Anhydrite Rocks," *SPE Reservoir Evaluation & Engineering*, vol. 11, no. 3, pp. 487-496, 2008.
- [85] J. Perrin and S. Benson, "An Experimental Study on the Influence of Sub-Core Scale Heterogeneities on CO₂ Distribution in Reservoir Rocks," *Transport in Porous Media*, vol. 82, no. 1, pp. 93-109, Mar. 2010.
- [86] O. Talabi, S. AlSayari, S. Iglaier, and M. J. Blunt, "Pore-scale simulation of
-

- NMR response,” *Journal of Petroleum Science and Engineering*, vol. 67, no. 3, pp. 168-178, 2009.
- [87] D. DiCarlo, S. Akshay, and M. Blunt, “Three-Phase Relative Permeability of Water-Wet, Oil-Wet, and Mixed-Wet Sandpacks,” *SPE Journal*, vol. 5, no. 1, pp. 82-91, 2000.
- [88] E. Washburn, “International Critical Tables of Numerical Data, Physics, Chemistry and Technology (1st Electronic Edition),” Knovel.
- [89] R. Woodhouse, *Statistical regression line-fitting in the oil & gas industry : a descriptive guide with Microsoft Excel examples*. Tulsa Okla.: PennWell Corp., 2003.
- [90] “Aerolith® Material.” [Online]. Available: http://www.pall.com/industrialmaterials_43632.asp. [Accessed: 03-Oct-2010].
- [91] S. Zeppieri, J. Rodríguez, and A. L. López de Ramos, “Interfacial Tension of Alkane + Water Systems†,” *Journal of Chemical & Engineering Data*, vol. 46, no. 5, pp. 1086-1088, 2001.
- [92] J. Kestin, H. E. Khalifa, and R. J. Correia, “Tables of the dynamic and kinematic viscosity of aqueous NaCl solutions in the temperature range 20–150 °C and the pressure range 0.1–35 MPa,” *Journal of Physical and Chemical Reference Data*, vol. 10, no. 1, pp. 57-70, 1981.
- [93] A. L. Lee and R. T. Ellington, “Viscosity of n-Decane in the Liquid Phase.,” *Journal of Chemical & Engineering Data*, vol. 10, no. 4, pp. 346-348, 1965.
- [94] S. Mao and Z. Duan, “The P,V,T,x properties of binary aqueous chloride solutions up to T=573K and 100MPa,” *The Journal of Chemical Thermodynamics*, vol. 40, no. 7, pp. 1046-1063, 2008.
- [95] T. Banipal, S. Garg, and J. Ahluwalia, “Heat capacities and densities of liquid -octane, -nonane, -decane, and -hexadecane at temperatures from 318.15 K to 373.15 K and at pressures up to 10 MPa,” *The Journal of Chemical Thermodynamics*, vol. 23, no. 10, pp. 923-931, 1991.
- [96] M. C. Leverett, “Capillary Behavior in Porous Solids,” *Petroleum Transactions, AIME*, vol. 142, pp. 152-169, 1941.
- [97] W. Rose and W. Bruce, “Evaluation of Capillary Character in Petroleum Reservoir Rock,” *Trans. AIME*, vol. 186, pp. 127-142, 1949.
- [98] Z. Omoregle, “Factors Affecting the Equivalency of Different Capillary Pressure Measurement Techniques,” *SPE Formation Evaluation*, vol. 3, no. 1, pp. 147-155, 1988.
- [99] A. Cense and F. Marcelis, “A comparative study of three pore-scale reconstruction and pore-network extraction techniques,” presented at the International Symposium of the Society of Core Analysts, Abu Dhabi, UAE, 2008.
- [100] M. Touati, S. Suicmez, J. Funk, Y. Cinar, and M. Knackstedt, “Pore Network Modeling of Saudi Aramco Rocks: A Comparative Study,” in *Proceedings of SPE Saudi Arabia Section Technical Symposium, SPE Paper 126043, AlKhobar, Saudi Arabia*, 2009.
- [101] R. Span and W. Wagner, “A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa,” *Journal of Physical and Chemical Reference Data*, vol. 25, no. 6, pp. 1509-1596, 1996.
- [102] S. Bando, F. Takemura, M. Nishio, E. Hihara, and M. Akai, “Solubility of CO₂ in Aqueous Solutions of NaCl at (30 to 60) °C and (10 to 20) MPa,” *Journal of Chemical & Engineering Data*, vol. 48, no. 3, pp. 576-579, May. 2003.
-

- [103] A. Georgiadis, G. Maitland, J. P. M. Trusler, and A. Bismarck, "Interfacial Tension Measurements of the (H₂O + CO₂) System at Elevated Pressures and Temperatures," *Journal of Chemical & Engineering Data*, vol. 55, no. 10, pp. 4168-4175, 2010.
 - [104] Z. Duan and R. Sun, "An improved model calculating CO₂ solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar," *Chemical Geology*, vol. 193, no. 3, pp. 257-271, 2003.
 - [105] J. A. Nighswander, N. Kalogerakis, and A. K. Mehrotra, "Solubilities of carbon dioxide in water and 1 wt. % sodium chloride solution at pressures up to 10 MPa and temperatures from 80 to 200.degree.C," *Journal of Chemical & Engineering Data*, vol. 34, no. 3, pp. 355-360, Jul. 1989.
 - [106] J. Kiepe, S. Horstmann, K. Fischer, and J. Gmehling, "Experimental Determination and Prediction of Gas Solubility Data for CO₂ + H₂O Mixtures Containing NaCl or KCl at Temperatures between 313 and 393 K and Pressures up to 10 MPa," *Industrial & Engineering Chemistry Research*, vol. 41, no. 17, pp. 4393-4398, 2002.
 - [107] A. N. Sabirzyanov, R. A. Shagiakhmetov, F. R. Gabitov, A. A. Tarzimanov, and F. M. Gumerov, "Water Solubility of Carbon Dioxide under Supercritical and Subcritical Conditions," *Theoretical Foundations of Chemical Engineering*, vol. 37, no. 1, pp. 51-53, Jan. 2003.
 - [108] D. Koschel, J. Coxam, L. Rodier, and V. Majer, "Enthalpy and solubility data of CO₂ in water and NaCl(aq) at conditions of interest for geological sequestration," *Fluid Phase Equilibria*, vol. 247, no. 1, pp. 107-120, Sep. 2006.
 - [109] C. Chalbaud, M. Robin, J. Lombard, F. Martin, P. Egermann, and H. Bertin, "Interfacial tension measurements and wettability evaluation for geological CO₂ storage," *Advances in Water Resources*, vol. 32, no. 1, pp. 98-109, 2009.
 - [110] H. Okabe, Y. Tsuchiya, K. Oseto, and K. Okatsu, "Development of X-ray CT Coreflood System for High Temperature Condition," in *Advances in X-ray Tomography for Geomaterials*, 2006, pp. 309-314.
 - [111] H. Okabe, Y. Tsuchiya, C. H. Pentland, S. Iglauer, and M. J. Blunt, "Residual CO₂ saturation distributions in rock samples measured by X-ray CT," in *Proceedings of the 3rd International Workshop on X-Ray CT for Geomaterials*, 2010.
 - [112] N. Otsu, "A Threshold Selection Method from Gray-Level Histograms," *IEEE Transactions on Systems, Man, and Cybernetics*, vol. 9, no. 1, pp. 62-66, 1979.
 - [113] H. Dong, "Micro-CT Imaging and Pore Network Extraction," PhD thesis, Imperial College London, 2007.
 - [114] N. Al-Ansi, "Influence of Micro-Computed Tomography Images Resolution on Computed Single-Phase Permeability," MSc thesis, Imperial College London, 2010.
 - [115] T. Suekane, N. H. Thanh, T. Matsumoto, M. Matsuda, M. Kiyota, and A. Ousaka, "Direct measurement of trapped gas bubbles by capillarity on the pore scale," *Energy Procedia*, vol. 1, no. 1, pp. 3189-3196, Feb. 2009.
 - [116] J. Shi, Z. Xue, and S. Durucan, "Supercritical CO₂ core flooding and imbibition in Tako sandstone--Influence of sub-core scale heterogeneity," *International Journal of Greenhouse Gas Control*, 2010.
 - [117] I. Chatzis, M. Kuntamukkula, and N. Morrow, "Effect of Capillary Number on the Microstructure of Residual Oil in Strongly Water-Wet Sandstones," *SPE Reservoir Engineering*, vol. 3, no. 3, pp. 902-912, 1988.
-

- [118] N. Morrow, "Interplay of Capillary, Viscous And Buoyancy Forces In the Mobilization of Residual Oil," *Journal of Canadian Petroleum Technology*, vol. 18, no. 3, pp. 35-46, 1979.
 - [119] E. Donaldson, R. Thomas, and P. Lorenz, "Wettability Determination and Its Effect on Recovery Efficiency," *Society of Petroleum Engineers Journal*, vol. 9, no. 1, pp. 13-20, 1969.
 - [120] E. Amott, "Observations Relating to the Wettability of Porous Rock," *Trans. AIME*, vol. 216, pp. 156-162, 1959.
 - [121] D. Longeron, W. Hammervold, and S. Skjaeveland, "Water-Oil Capillary Pressure and Wettability Measurements Using Micropore Membrane Technique," in *Proceedings of International Meeting on Petroleum Engineering, SPE Paper 30006, Beijing, PR China*, 1995.
 - [122] V. Shah, D. Broseta, and G. Mouronval, "Capillary Alteration of Caprocks by Acid Gases," in *Proceedings of SPE/DOE Symposium on Improved Oil Recovery*, 2008.
 - [123] N. Tonnet, D. Broseta, and G. Mouronval, "Evaluation of the Petrophysical Properties of a Carbonate-rich Caprock for CO₂ Geological Storage Purposes," in *SPE EUROPEC/EAGE Annual Conference and Exhibition*, 2010.
 - [124] D. Yang, Y. Gu, and P. Tontiwachwuthikul, "Wettability Determination of the Reservoir Brine-Reservoir Rock System with Dissolution of CO₂ at High Pressures and Elevated Temperatures," *Energy & Fuels*, vol. 22, no. 1, pp. 504-509, 2008.
 - [125] H. T. Schaef and B. P. McGrail, "Direct Measurements of pH and Dissolved CO₂ in H₂O-CO₂ Brine Mixtures to Supercritical Conditions."
 - [126] E. Matijević, *Surface and colloid science*. New-York: Plenum Press, 1982.
 - [127] F. T. Barranco, H. E. Dawson, J. M. Christener, and B. D. Honeyman, "Influence of Aqueous pH and Ionic Strength on the Wettability of Quartz in the Presence of Dense Non-Aqueous-Phase Liquids," *Environmental Science & Technology*, vol. 31, no. 3, pp. 676-681, Mar. 1997.
 - [128] L. J. Klinkenberg, "The Permeability Of Porous Media To Liquids And Gases," *Drilling and Production Practice (A.P.I.)*, vol. 41, pp. 200-213, 1941.
 - [129] B. Swanson, "A Simple Correlation Between Permeabilities and Mercury Capillary Pressures," *Journal of Petroleum Technology*, vol. 33, no. 12, pp. 2498-2504, 1981.
 - [130] W. Plug and J. Bruining, "Capillary pressure for the sand-CO₂-water system under various pressure conditions. Application to CO₂ sequestration," *Advances in Water Resources*, vol. 30, no. 11, pp. 2339-2353, 2007.
-

Appendices

Appendix 1 – Sandpack Experiments

This appendix contains equipment and material properties of the sandpack experiments. Figure A. 1 illustrates the grain size distributions of the sands investigated. These were measured by sieve analysis.

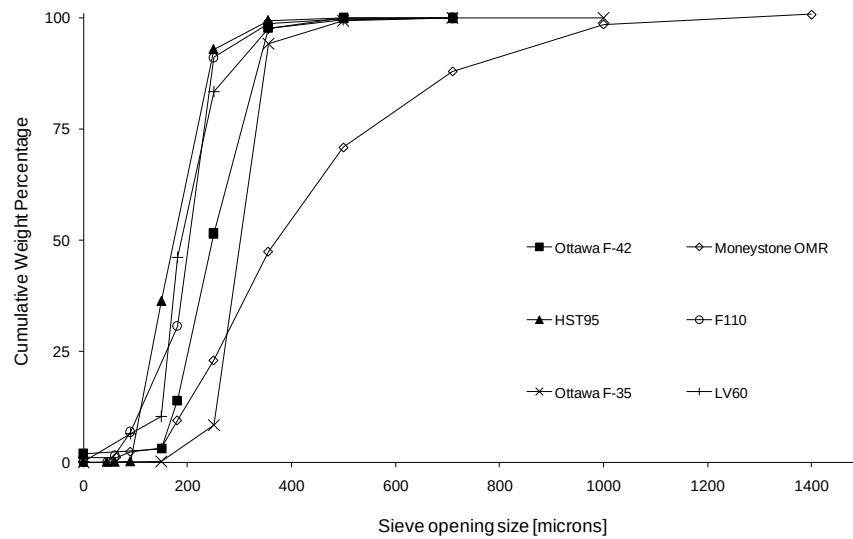


Figure A. 1: Grain size distributions of the sands investigated in the sandpack experiments. Grain size distributions were determined by sieve analysis.

Figure A. 2 shows 2D slices of three-dimensional micro-CT scan images of the sands that illustrate the grain shapes and pore structure. Micro-CT images were acquired with a Phoenix v/tome/x instrument based in the Imperial College London Materials Department. The images were filtered with a 3x3 median filter and segmented according to Otsu's algorithm [112].

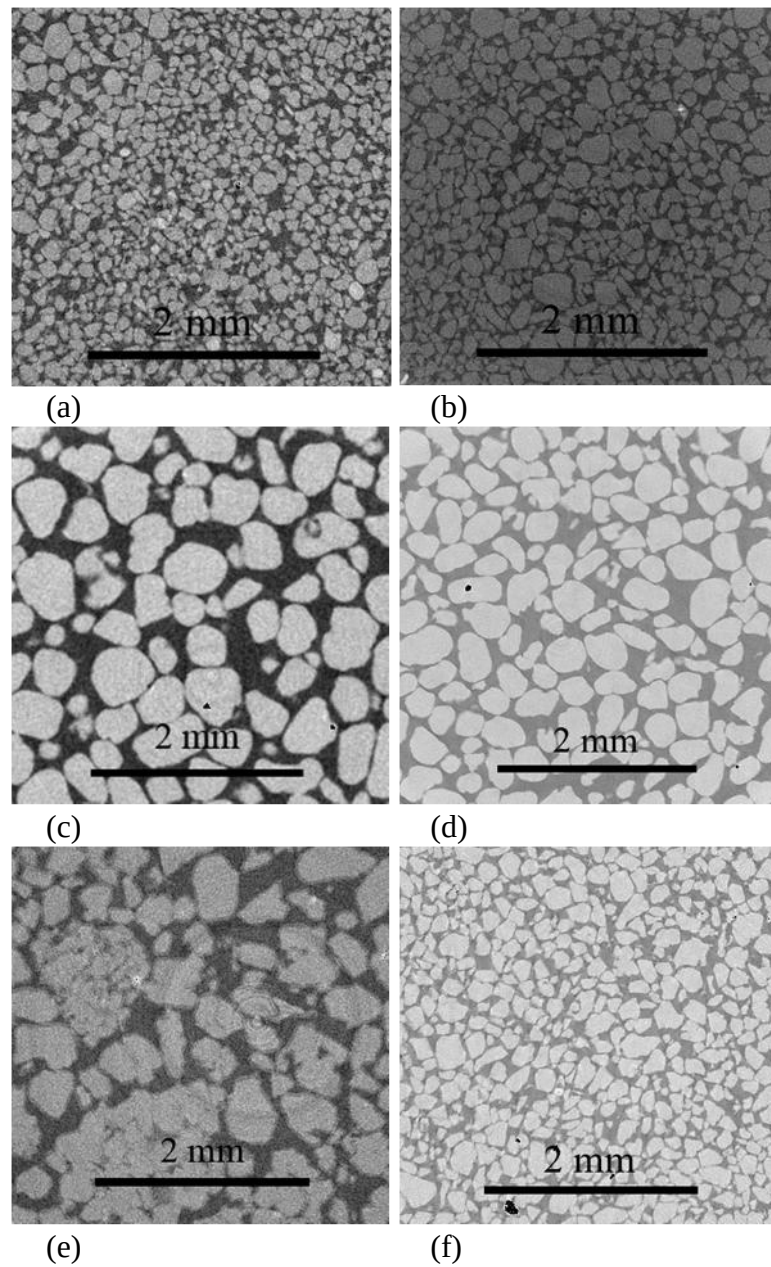
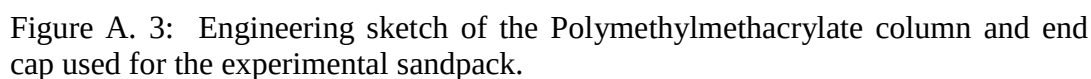


Figure A. 2: Two-dimensional image slices from three-dimensional micro-CT scans performed on: (a) HST-95; (b) F110; (c) Ottawa F-35; (d) Ottawa F-42; (e) Moneystone OMR; (f) LV60.

The custom-machined polymethylmethacrylate column used to contain the sandpack is shown in Figure A. 3. The measurement programme of the GC used to determine saturation measurements is given in Table A. 1.

The sandpack results relied upon a series of additional equations not reported in the main body of the text. These are included below for each of the parameters measured.



Parameter	Value
Run time	3 minutes
Sampling rate	12 readings per second
Oven temperature	Initial: 353.15 K, increase to 443.15 K at a rate of 30 K per minute
Injector temperature	473.15 K
Detector temperature	513.15 K
Carrier gas	Helium, 2mL/min flow rate
Detector gas	Helium, 18 mL/min; reference gas: Helium 20 mL/min; split flow = 50 mL/min; total flow rate = 54 mL/min
Retention time <i>n</i> -octane	1.344 minutes
Retention time 2-propanol	1.496 minutes
Retention time water	1.734 minutes

The **permeability** of each sand type was calculated after initial saturation. This was done for oil-brine and gas-brine experiments alike. Once saturated a constant flowrate of brine passed through the column and the pressure drop was recorded. The sample permeability (K) in m^2 is given by:

$$K = \frac{q\mu\Delta L}{A\Delta P} \quad (23)$$

where q is the linear flow velocity (m.s^{-1}) along the column length L (m), μ is the brine viscosity ($\text{kg.m}^{-1}.\text{s}^{-1}$), A the column's cross sectional area (m^2) and ΔP is the pressure drop ($\text{kg.m.s}^{-2}.\text{m}^{-2}$). The common oilfield unit of permeability is the Darcy: $1 \text{ Darcy} = 1.0133 \times 10^{-12} \text{ m}^2$.

Trapping curves were generated by relating the initial saturation from one column to the residual saturation from a second column for the same distance along the column length. Where **error bars** are shown these correspond to the standard deviation between three replicates for either the initial or residual saturation. The standard deviation is given by:

$$s = \sqrt{\frac{\sum(X - M)^2}{N - 1}} \quad (24)$$

where s is the unbiased estimation of standard deviation, X is the measured saturation value, M the mean of the saturation values and N the number of saturation measurements.

Oil-brine Experiments

The initial and residual oil saturations were measured by GC. The molar ratio of oil to water was determined by measuring the area under the oil and water response peaks:

$$m_{\text{GCO}} = \frac{a_o}{A_o} \quad (25)$$

where m_{GCO} is the number of moles of octane, a_o is the area under the GC octane peak ($\mu\text{V.s}$), and A_o is the average area under the GC octane peak ($\mu\text{V.s}$). Then using:

$$M_{GCO} = m_{GCO}M_O \quad (26)$$

where M_{GCO} is the mass of octane (kg) and M_O is the molar mass of octane (kg/mol). Finally:

$$V_{GCO} = \frac{M_{GCO}}{\rho_o} \quad (27)$$

where V_{GCO} is the volume of octane (m^3) and ρ_o is the density of octane ($kg.m^{-3}$).

The calculation steps are identical for water with the relevant subscripts updated to read w for water instead of o for oil. This resulted in the saturation (S_o) being given by:

$$S_o = \frac{V_{GCO}}{V_{GCO} + V_{GCW}} \quad (28)$$

Gas-brine Experiments

Bulk Volume. In the gas-brine experiments the bulk volume of each column section was incorporated into the determination of section saturation to reduce experimental error. This proved a more accurate approach than assuming that each column section had the same bulk volume. The bulk volume was measured by mass balance. The empty section was weighed then one end was sealed with parafilm and the section filled with liquid of a known density. The full weight was then recorded. The bulk volume is given by the change in weight (mass full minus mass empty) divided by the density of the liquid used to fill the section.

Pore Volume. The mass of sand from each column section was weighed. Assuming a density for sand (taken to be pure quartz) the volume of sand could be calculated. This sand volume could be subtracted from the bulk volume (above) to yield the pore volume.

Gas Saturation. The gas saturation of each section at either initial or residual conditions is given by:

$$S_{(g)i} = 1 - S_{(w)i} \quad (29)$$

where $S_{(g)i}$ is the saturation of gas in section i and $S_{(w)i}$ is the saturation of water in the same section. Note that the subscript i does not denote the initial state in this instance but rather a section of the column. $S_{(w)i}$ is given by:

$$S_{(w)i} = \left(\frac{M_{(s)i} - M_{(e)i}}{\rho_w V_{(b)i}} \right) \quad (30)$$

where $M_{(s)i}$ is the mass of the section saturated with air and water, $M_{(e)i}$ is the mass of the dry section (mass of plastic column plus mass of sand), ρ_w is the water density and $V_{(b)i}$ is the section bulk volume. The mass of air is assumed to be zero.

Appendix 2 – Core-plug Characterisation

Table A. 2 below summarises the petrophysical properties of each sample used during this study.

Helium Porosity. A Robertson Research Helium gas expansion volume meter (Model HGEVM/PG; Serial No. 823/M/0011) was used to measure sample effective porosities.

Mercury Injection Porosity. Mercury injection capillary pressure (MICP) data was gathered for all of the sandstones and the Aerolith ceramic sample. As part of the MICP dataset porosity measurements were provided. Appendix 3 provides further information on the MICP measurements.

Brine Porosity. The porosity of the samples was also measured by brine saturation. The weight of the dry core-plug or sandpack was measured. The pore space was then fully saturated with brine of a known density. The weight of the fully saturated sample was measured and the pore volume calculated.

Matrix Density Porosity. As a quick check the porosity of the sandstone samples was determined by a matrix density calculation. The bulk volume of the core-plug was measured with vernier callipers. The dry weight of the core-plug was measured (Model S-6002, Denver Instruments, Bohemia, NY, USA) Assuming that the matrix of the rock was pure quartz ($\rho = 2,650 \text{ kg/m}^3$) the pore volume could be determined. This value of porosity was only used for quick checks and was not used subsequently in calculations or in reporting results. It is considered more inaccurate than other methods as generally the matrix of the sandstones used was not pure quartz.

Brine Permeability. Brine permeability was measured using the same Hassler type core holders as used during the oil-brine and CO₂-brine capillary trapping experiments. The cell was removed from the experimental set-up along with the differential pressure transducer (3051S2CD2A2E12A1BD2I1M5Q4, Scalable Classic Differential Pressure Transmitter, Emerson Process Management Ltd., St. Louis, MO, U.S.A.). The differential pressure transducer was connected to the end

platens at either end of the core-plug. The core-plug was saturated by vacuuming the pore space for 30 minutes before brine was introduced from a syringe pump (Teledyne ISCO 500D & 1000D, Lincoln, NE, USA). Five pore volumes of brine were flooded through the core-plug to ensure complete saturation. A series of differential pressure measurements were then taken for corresponding flow rates. Measurements were taken at 1, 2, 5, 10 and 20 mL/min. Knowing the dimensions of the core-plug and assuming a brine viscosity from literature [11] the permeability of the core-plug could be calculated using Darcy's Law (Eqn. 23).

Air Permeability. Using the same Hassler type core holder and differential pressure transducer described above the air permeability of the core-plug samples was measured. The gas used was not infact air but high purity oxygen free nitrogen (55bar bottle, B.O.C., Middlesex, U.K.). The nitrogen bottle was connected to the core-holder via a regulator and 1/8" 316 stainless steel tubing. The gas flowrate was controlled with the bottle regulator and measured with a gas flow meter (Agilent Flow Tracker 1000 Series, Agilent Technologies, Wilmington, DE, U.S.A.). The Klinkenberg correction for gas permeability was applied [128].

Mercury Injection Permeability. Mercury injection capillary pressure (MICP) data was gathered for all of the sandstones and the Aerolith ceramic sample. As part of the MICP dataset permeability measurements were provided. Appendix 3 provides further information on the MICP measurements.

Formation Factor. The formation factor is an electrical measurement and is defined as the resistivity of a brine saturated sample divided by the resistivity of the brine (Eqn. 16). The conductivity of the brine saturated core-plug was determined with a conductivity meter (Quadtech model 7600 RLC, Marlborough, MA, U.S.A.). The core-plug was initially saturated with brine inside a vacuum chamber. The core-plug was then removed and placed in the apparatus. A sweep test frequency was applied and the resistance measured. Knowing the core-plug dimensions the conductivity was calculated. Resistivity is simply the reciprocal of conductivity. The brine conductivity was measured separately with a conductivity meter (712 Conductometer, Metrohm AG, Herisau, Switzerland).

Coordination Number and Aspect Ratio. Small cylindrical samples of all of the materials studied were used for micro-CT scans. This allowed the pore-matrix

structure to be imaged in three dimensions. Through image analysis and network extraction statistics on the pore structure were generated. This included the average coordination number and average aspect ratio of the scan volume.

Table A. 2: Petrophysical characterisation of the samples investigated in this study.

Sample Name	Sample Type	L (m)	D (m)	$\phi_{m.d.}$	ϕ_{He}	ϕ_{brine}	ϕ_{MCP}	$K_{gas} (m^2)$	$K_{brine} (m^2)$	$K_{MCP} (m^2)$	$N_{coord.}$	R_a	F
LV60	Unconsolidated sand	-	-	-	-	0.370	-	-	3.2×10^{-11}	-	4.9	2.1	3.4
HST95	Unconsolidated sand	-	-	-	-	0.334	-	-	7.8×10^{-12}	-	5.9	2.7	-
F110	Unconsolidated sand	-	-	-	-	0.354	-	-	6.2×10^{-12}	-	4.3	1.9	-
OMR	Unconsolidated sand	-	-	-	-	0.416	-	-	8.7×10^{-11}	-	5.2	2.7	-
F42	Unconsolidated sand	-	-	-	-	0.350	-	-	4.2×10^{-11}	-	4.4	2.1	-
F35	Unconsolidated sand	-	-	-	-	0.362	-	-	4.2×10^{-11}	-	5.5	2.0	-
Berea 3	Sandstone	0.075	0.038	0.181	0.176	0.182	0.172	3.0×10^{-13}	7.0×10^{-14}	8.1×10^{-14}	3.0	16.6	28.2
Berea 9	Sandstone	0.075	0.038	0.235	0.227	0.217	0.213	1.1×10^{-12}	4.4×10^{-13}	4.3×10^{-13}	4.1	18.8	13.7
Berea 11	Sandstone	0.075	0.039	0.248	0.242	0.214	0.213	1.1×10^{-12}	4.6×10^{-13}	4.3×10^{-13}	4.1	18.8	12.4
Clashach JP	Sandstone	0.077	0.039	0.143	0.135	0.122	0.137	-	8.0×10^{-14}	3.2×10^{-13}	3.1	18.6	57.5
Doddington 4	Sandstone	0.076	0.037	0.223	0.204	0.232	0.179	-	1.6×10^{-12}	5.4×10^{-13}	3.4	14.0	15.8
Aerolith 10	Ceramic	0.076	0.038	-	0.502	0.560	-	-	1.2×10^{-11}	-	10.6	0.4	3.7

X-ray Diffraction. Two of the sandstone samples – Berea and Clashach – were chosen for compositional analysis. This was performed by x-ray diffraction (XRD). The semi-quantitative results are summarised in Table A. 3 and Table A. 4.

Table A. 3: XRD compositional analysis of dry Clashach sandstone.

Material	Weight %
Quartz	96
K-feldspar	2
Calcite	1
Ankerite	<1
Illite	trace

Table A. 4: XRD compositional analysis of dry Berea sandstone.

Material	Weight %
Quartz	95
Anhydrite	1
Total Clay	1
Siderite	trace

Appendix 3 – Mercury Injection Capillary Pressure

Trim samples of the porous media considered in this study were supplied for mercury injection measurements. The trims were generally off-cuts from the end of the core-plug that were removed during sample machining.

Procedure. An Autopore IV 9520 (Micrometrics, Norcross, GA, U.S.A.) situated in Weatherford Laboratories, Stavanger, Norway, was used for the mercury injection analysis. The measurements were performed by Weatherford employees and the following information – which is based on communications with Weatherford Norway – is included for completeness.

The selected mercury injection samples were cleaned with solvents by soxhlet extraction then oven dried at 95 °C prior to analysis. The samples were weighed and loaded into the selected penetrometers. The desired number of pressure steps, from vacuum to 413.7 MPa, was selected. The pressure steps are automatically distributed over a logarithmic scale. Air was then evacuated from the penetrometers to a pressure equivalent to 50µmHg. After 15 minutes at this pressure the penetrometers were back filled with mercury. The mercury pressure was then increased up to the last low pressure point specified.

Data Analysis. As the mercury pressure is increased it invades into the sample pore structure. The volume of mercury invasion is determined by an electrical capacitance measurement on the mercury reservoir. Mercury porosimetry is expressed by the Young-Laplace Equation (Eqn. 2) which governs the liquid penetration into the pore space. For a cylindrical pore tube the two radii of curvature are equal, reducing the Young-Laplace equation to:

$$P_c = \frac{2\sigma}{R} \quad (31)$$

The radius of the capillary tube (r) is related to the radius of curvature (R) by:

$$\cos \theta = \frac{r}{R} \quad (32)$$

Substituting eqn. 32 into eqn. 31 reduces the Young-Laplace equation to :

$$P_c = \frac{2\sigma \cos \theta}{r} \quad (33)$$

The capillary pressure (P_c) is equal to the difference between the mercury phase pressure (P_{Hg}) and the air pressure (P_{air}), and if the air pressure is zero (vacuum), this gives:

$$P_c = P_{Hg} = \frac{2\sigma_{Hg-air} \cos \theta}{r_i} \quad (34)$$

where r_i is the pore radii. This equation can be solved for r_i as the other terms can be assumed or measured.

The results of mercury intrusion can be used to approximate sample permeability based on the empirical correlation between mercury and brine permeability data proposed by Swanson [129]:

$$K_{MICP} = 399 \left(\frac{S_b}{P_c} \right)_A^{1.691} \quad (35)$$

where P_c is measured in psia, S_b is the mercury saturation and the subscript A denotes the maximum value of S_b / P_c derived from the intersection between a 45° line drawn at a tangent to the hyperbolic plot of S_b versus P_c . There is a high degree of uncertainty associated with this approximation and as such these values of permeability were not reported in the main results of this study.

Mercury intrusion also provides a measurement of porosity. This is a simple volume balance calculation if the sample bulk volume and the maximum intruded mercury volume are known. The mercury porosity measurements were not used when reporting sample porosities in the results of this study but are included here for completeness. They were considered less accurate than direct measurements on the actual core-plugs (helium porosity, brine porosity).

A large database of sandstone samples has been built up including sandstones not investigated as part of this study. Figure A. 4 illustrates the Leverett-J profiles (Eqn. 21) of the sandstones in the database. The data supplied by

Weatherford assumed the contact angles and interfacial tensions listed in Table A. 5. The pore-throat radius distributions for the sandstones used in the trapping curve studies (Berea 400 and Clashach) are shown in Figure A. 5 and Figure A. 6.

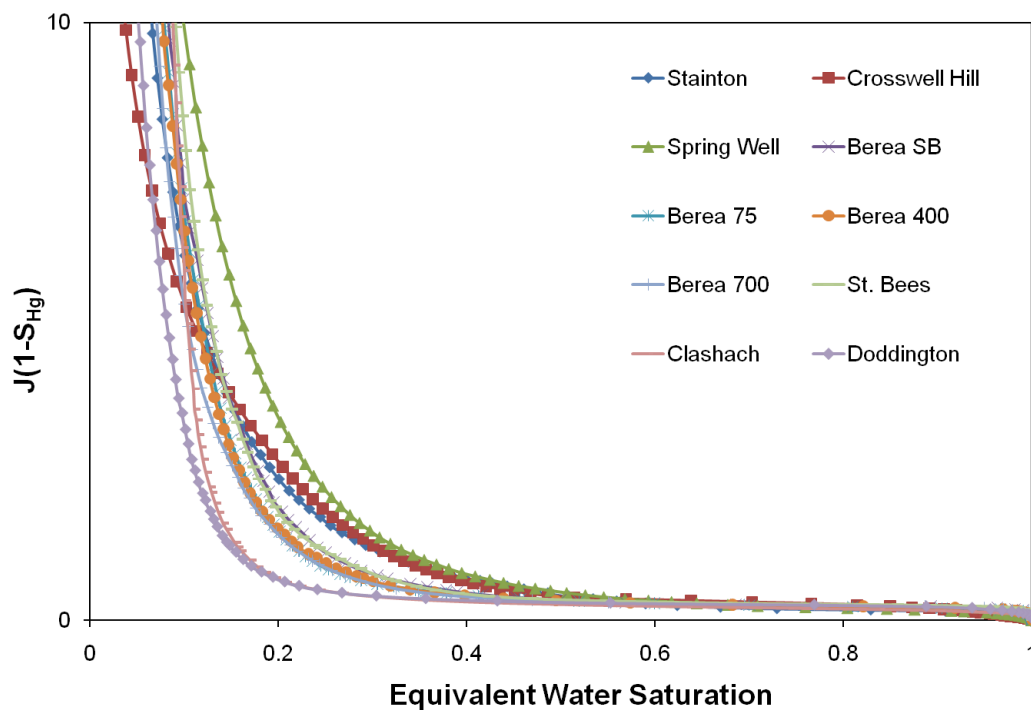


Figure A. 4: Mercury injection capillary pressure database of sandstones – including those studied as part of this research (Stainton, Berea 700, Clashach).

Table A. 5: Interfacial tensions and primary drainage contact angles assumed by Weatherford Laboratories in MICP data.

System	σ (mN.m ⁻¹)	θ (°)
Hg-air	485	130
Gas-brine	72	0
Gas-oil	24	0
Oil-brine	32	30

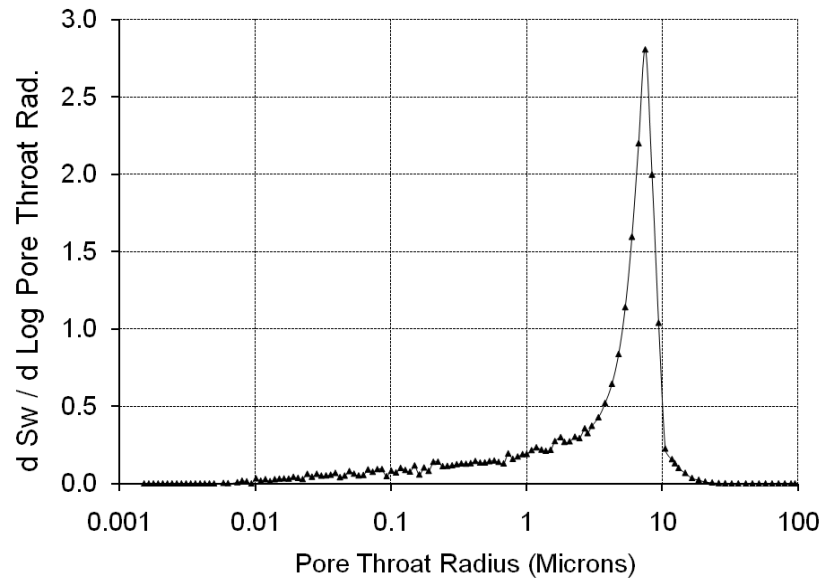


Figure A. 5: Pore-throat radius distribution for Berea 400 sandstone – from MICP analysis.

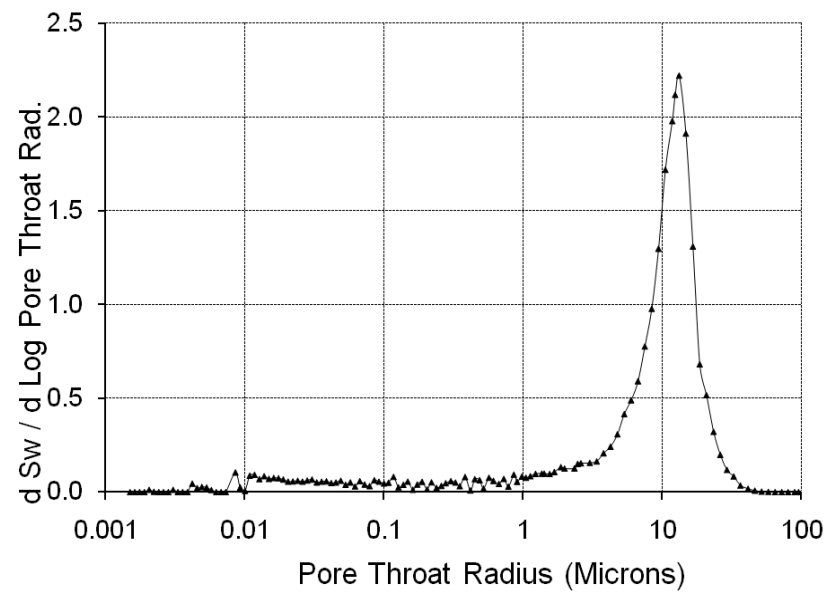


Figure A. 6: Pore-throat radius distribution for Clashach sandstone – from MICP analysis.

Appendix 4 – ETP Oil-brine Experiments

This appendix contains additional information relating to the consolidated oil/brine coreflood experiments. Micro CT scans of the two sandstones used in the trapping curve experiments are shown in Figure A. 7. Micro-CT images were acquired with a Phoenix v/tome/x instrument based in the Imperial College London Materials Department. The images were filtered with a 3x3 median filter and segmented according to Otsu's algorithm [112].

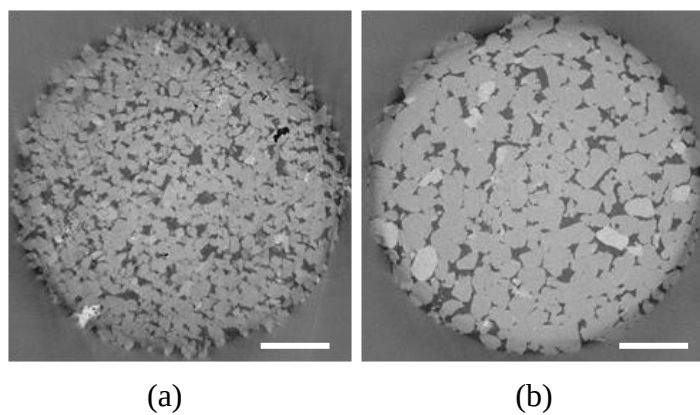


Figure A. 7: A two-dimensional section of X-ray microtomography scans of (a) Berea and (b) Clashach samples. Voxel volume (resolution) is $5.789\mu\text{m} \times 5.789\mu\text{m} \times 5.789\mu\text{m}$. The white horizontal bar in each image depicts 1.00mm.

The three flow sequences in the experiment are: initial saturation (primary imbibition); primary drainage; and waterflooding. The injection of the brine and oil phases was controlled and directed by opening and closing various valves in the experimental apparatus. The phases were injected from syringe pumps (Teledyne ISCO 500D & 1000D, Lincoln, NE, USA). In the oil-brine experiment there was one dedicated pump for oil injection, one dedicated pump for brine injection and one dedicated pump for back pressure and effluent collection. This was in addition to a fourth pump used for confining pressure. In Figure A. 8 (a-d) the valve positions and tubing used in each injection sequence is illustrated.

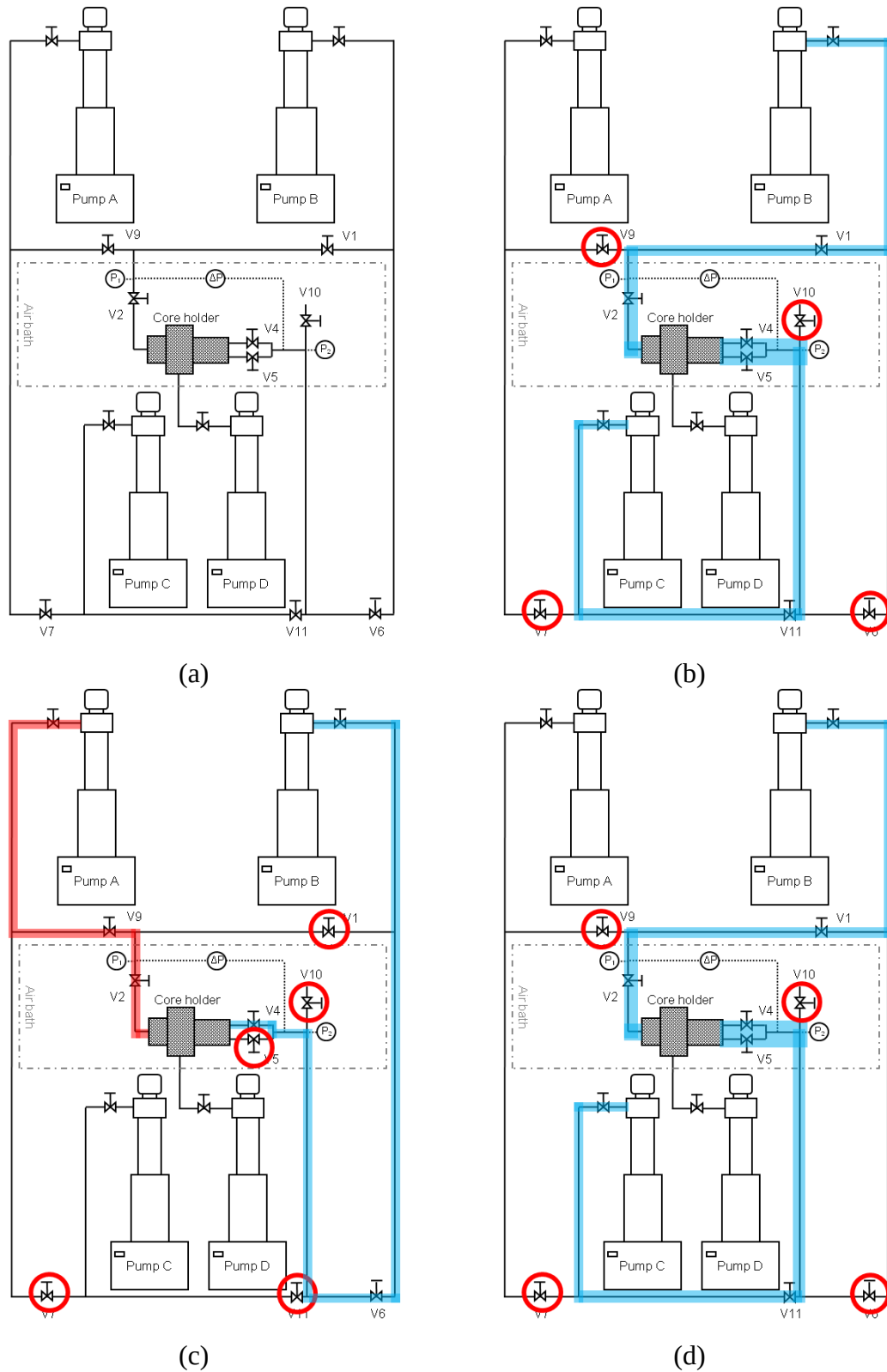


Figure A. 8: (a) ETP oil-brine coreflood apparatus. (b) Closed valves (○) and tubing used for the initial saturation of the sample. Brine is injected from pump C, back pressure and effluent collection is controlled by pump B (tubing used is highlighted in blue) (c) Closed valves and tubing used for the primary drainage of oil (tubing containing oil is highlighted in red) into the sample. Oil injection is controlled by pump A. Brine production from the core-plug is controlled by pump B (tubing containing brine is highlighted in blue). (d) Closed valves and tubing used during waterflooding.

Dead Volume. Mass and volume balance methods – which were used to measure S_i and S_r – were highly sensitive to dead volume. Dead volume is defined as a volume other than the pore volume that contributes to a mass or volume measurement. The design of the Hassler type core holder meant that there were some tube volumes – in-between the core-plug and the valves that isolated the core-plug from the remainder of the system – that were considered during measurements. These volumes had to be measured and in some cases a judgment had to be made as to whether a given volume contained oil or brine at each measurement time. Table A. 6 summarises the dead volume components measured. After initial saturation all dead volumes were considered to be saturated with brine (components 1 through 11). After primary drainage all dead volume upstream of the porous plate was considered to be saturated with oil (components 7, 8, 10 and 11). After waterflooding all dead volume was once again considered to be saturated with brine (components 1 through 11). These were assumptions based on experimental experience and knowledge of the core holder design. Dead volume certainly contributed to the relatively large experimental error seen on most oil-brine data points.

Table A. 6: Dead volume components for the oil-brine ETP experiments.

Component	Description	Dead Volume (mL)
1	Core-holder tube 1 (right hand fitting - Figure 2.8); 207.94 mm.	0.319
2	Core-holder tube 1 NPT fitting	0.289
3	Core-holder tube 2 (right hand fitting - Figure 2.8); 159.00 mm.	0.244
4	Core-holder tube 2 NPT fitting	0.329
5	Platten grooves – right	0.100
6	Porous plate	2.884 or 3.641 (depending on type used; 5 bar or 15 bar)
7	Core-holder tube 3 (left hand fitting - Figure 2.8); 97.00 mm.	0.149
8	Core-holder tube 3 NPT fitting	0.136
9	Core-holder blanked off connection number 4 (left hand fitting – not shown in Figure 2.8) NPT fitting	0.233
10	Platten grooves – left	0.100
11	Half of a 1/8" H800 Hamlet ball valve	0.150

During primary drainage the oil volume injected into the core-plug pore space was not exactly equal to the brine volume produced through the porous plate. The dead volume in the oil injection tubing was initially filled with brine. The oil

had to displace this brine and travel through the tube before entering the core-plug. As such the oil volume injected into the core-plug was equal to the brine production volume minus this inlet dead volume (components 7, 8, 10 and 11). In summary:

$$V_{(DV)} = \sum \text{components 1 through 11}$$

$$V_{(DV)o} = \sum \text{components 7, 8, 10, 11}$$

where $V_{(DV)}$ is the total dead volume and $V_{(DV)o}$ is the volume of oil within $V_{(DV)}$ after primary drainage.

Dead volumes were determined by calculating volumes based on dimensions or – in the case of the ball valve and the porous plate – mass balance measurements with a component being weighed dry and saturated with a liquid of a known density.

Saturation Measurements. Mass balance and volume balance measurements were used to determine core-plug saturations. There were five separate measurements taken during each experiment, three mass and three volume measurements:

1. Volume of oil injected into the core-plug during primary drainage ($V_{(oi)}$)
2. Mass of core-holder at the end of primary drainage (M_2)
3. Volume of oil produced during waterflooding ($V_{(op)}$)
4. Mass of core-holder at the end of waterflooding (M_3)
5. Mass of core-plug after waterflooding ($M_{(c-p)s}$)

The volume of oil injected is measured from the oil injection syringe pump. The mass of the core-holder is measured by disconnecting it from the experimental flow lines, removing it from the oven, and weighing on a balance. The effluent is collected during waterflooding and the amount of oil measured in a measuring cylinder. The mass of the core-plug after waterflooding is measured by removing the core-plug from the core-holder and submerging it in a beaker of brine of a known weight. The beaker containing the core-plug is then weighed on a balance.

Of the six measurements two can be used to calculate the initial oil saturation directly once dead volumes have been accounted for. The volume of oil injected is given by:

$$V_{(o)i} = V_1 - V_2 - V_{(DV)o} \quad (36)$$

therefore

$$S_{oi_1} = \frac{V_{(o)i}}{PV} \quad (37)$$

where V_1 is the initial volume of oil in the pump before injection, V_2 the volume of oil remaining in the pump after injection, $V_{(DV)o}$ the dead volume containing oil after injection, and PV the core-plug pore volume. The mass of the core-holder after oil injection is M_2 and this is related to S_{oi} by:

$$S_{oi_2} = \frac{(M_1 - M_{(DV)w}) - (M_2 - M_{(DV)o/w})}{PV(\rho_w - \rho_o)} \quad (38)$$

where M_1 is the initial mass of the core-holder filled with brine, $M_{(DV)w}$ is the mass of the dead volume filled with brine, $M_{(DV)o/w}$ the mass of the dead volume where some of the volume is occupied by oil and some by brine (see above for volumes).

Two of the six measurements – $M_{(c-h)r}$ and $M_{(c-p)r}$ – can be used to calculate the residual saturation. Once again dead volumes are accounted for.

$$S_{or_1} = \frac{([M_1 - M_{(DV)w}] - [M_3 - M_{(DV)w}])}{PV(\rho_w - \rho_o)} \quad (39)$$

where M_3 is the mass of the cell at the end of waterflooding. After waterflooding the dead volume is once again assumed to be fully saturated with brine. The residual saturation based on the measurement of core-plug mass after waterflooding is:

$$S_{or_2} = \frac{M_{(c-p)d} + (\rho_w PV) - M_{(c-p)s}}{PV(\rho_w - \rho_o)} \quad (40)$$

Where $M_{(c-p)d}$ is the mass of the dry core-plug.

The difference between initial and residual saturation ($S_i - S_r$) is related to the volume of oil produced:

$$\Delta S_1 = (S_{oi} - S_{or}) = \frac{(V_{(o)p} - V_{(DV)o})}{PV} \quad (41)$$

where $V_{(DV)o}$ is the dead volume containing oil (which is also produced during waterflooding). Similarly the difference between initial and residual saturation is related to the change in mass of the cell ($M_3 - M_2$):

$$\Delta S_2 = (S_{oi} - S_{or}) = \frac{(M_3 - M_2)}{(\rho_w - \rho_o)} \frac{1}{PV} \quad (42)$$

Equation 41 is derived from the measured oil volume change and equation 42 is derived from the measured change in mass of the core-holder. This data can be combined with equations 37-40 giving additional initial and residual saturations. This is done by combining volumetric saturation changes (ΔS_1) with initial and residual saturations measured by mass balance (S_{oi2} , S_{or1} , S_{or2}). Similarly mass balance saturation changes (ΔS_2) are combined the volumetric initial saturation – S_{oi1} .

$$S_{oi3} = S_{or1} + \Delta S_1 \quad (43)$$

$$S_{oi4} = S_{or2} + \Delta S_1 \quad (44)$$

$$S_{or3} = S_{oi1} - \Delta S_2 \quad (45)$$

$$S_{or4} = S_{oi2} - \Delta S_2 \quad (46)$$

This now yields a total of four initial and four residual saturation values. An arithmetic average was taken of the four values to get an averaged saturation value. The error associated with the saturation was equal to the standard deviation between the four values (Eqn. 24).

Due to experimental difficulties some data points did not include the full suite of four initial and four residual saturation values. Measuring oil production proved problematic due to evaporation and the transfer of the oil to an accurate measuring cylinder. Measuring the mass of the core-plug was at times difficult if it became stuck in the viton sleeve. If too much time elapsed before the core-plug could be submerged in brine inside the measuring beaker then the measurement was discarded. It was found that air could easily enter the pore space replacing liquid

that drained out under gravity. Erroneously high residual oil saturations were possible if air had entered the core. Measuring the mass of the Clashach core-plug was especially difficult – its small pore volume making it more sensitive to the duration outside the core-holder or measuring beaker. Table A. 7 summarises the calculated saturations based on the mass and volume balance measurements as outlined in the equations above.

Capillary Pressure Measurements. The capillary pressure was measured with a differential pressure transducer connected to the inlet and outlet of the core holder. The reported P_c is the average value applied to the core-plug during primary drainage. The reported error associated with P_c is the standard deviation of the recorded P_c dataset. The P_c data is summarised in Table A. 8.

Table A. 7: Calculated saturations based on mass balance and volume balance measurements for the oil-brine ETP experiments.

Experiment	S_{oi1}	S_{oi2}	S_{oi3}	S_{oi4}	S_{or1}	S_{or2}	S_{or3}	S_{or4}	$\overline{S_{oi}}$	$\overline{S_{or}}$	S_i	S_r
Berea 11 - 1	0.89	0.83	0.86	0.95	0.47	0.56	0.52	0.43	0.88	0.50	0.05	0.06
Berea 11 - 2	0.89	0.78	0.79	0.88	0.41	0.50	0.52	0.41	0.84	0.46	0.06	0.06
Berea 11 - 3	0.83	0.84	0.85	0.94	0.47	0.56	0.47	0.46	0.86	0.49	0.05	0.05
Berea 11 - 4	-	0.63	0.59	0.74	0.38	0.52	-	0.41	0.65	0.44	0.08	0.08
Berea 11 - 5	0.52	0.45	-	-	0.36	0.34	0.43	-	0.49	0.38	0.05	0.05
Berea 11 - 6	0.17	0.14	0.15	0.20	0.12	0.17	0.15	0.11	0.17	0.14	0.03	0.03
Clashach - 1	0.74	0.74	0.83	-	0.55	-	0.55	0.46	0.77	0.52	0.06	0.05
Clashach - 2	0.71	0.69	0.72	-	0.45	-	0.42	0.47	0.70	0.44	0.02	0.03
Clashach - 3	0.73	0.76	0.71	-	0.44	-	0.41	0.50	0.73	0.45	0.03	0.05
Clashach - 4	0.71	0.77	0.69	-	0.44	-	0.38	0.52	0.72	0.44	0.04	0.07
Clashach - 5	0.61	0.60	-	-	0.44	-	0.45	-	0.60	0.44	0.00	0.00
Clashach - 6	0.40	0.34	0.41	-	0.28	-	0.34	0.21	0.38	0.27	0.04	0.07
Clashach - 7	0.25	0.20	-	-	0.15	-	0.21	-	0.22	0.18	0.04	0.04

Table A. 8: Capillary pressure data for the ETP oil-brine coreflood experiments.

Coreflood	P_c (kPa)	Error $_{Pc}$ (kPa)	Drainage time (hrs)
Berea 11 - 1	296.1	33.5	22.0
Berea 11 - 2	161.3	41.4	23.1
Berea 11 - 3	82.7	33.8	21.1
Berea 11 - 4	6.9	0.7	14.1
Berea 11 - 5	6.6	2.1	165.7
Berea 11 - 6	1.0	2.8	45.8
Clashach - 1	993.5	82.7	21.0
Clashach - 2	389.6	88.9	24.3
Clashach - 3	258.6	66.9	24.0
Clashach - 4	310.1	68.4	65.9
Clashach - 5	18.1	4.9	88.6
Clashach - 6	12.8	6.2	69.6
Clashach - 7	61.4	57.9	41.7

Appendix 5 – CO₂-brine Mixing

This appendix details the steps involved in equilibrating brine and CO₂ for use in the ETP CO₂-brine coreflood experiments. Saturating the brine with CO₂ – and the CO₂ with brine – is necessary to ensure that immiscible displacements occur in the core-plug pore space.

The equilibration process can be split into the following three main steps.

Fill reactor with brine. Sufficient brine to fill the stirred reactor was de-gassed overnight under vacuum. The reactor volume is listed as 1200 mL but through the fitting of a pressure transducer and other ancillary flowlines the total process volume was measured as 1350 mL. A syringe pump was filled with the de-gassed brine and connected to the base of the reactor. The reactor internal volume was vacuumed to remove air. The brine was then introduced into the reactor under vacuum. Once the reactor was filled the brine was pressurised to 9 MPa by the attached syringe pump.

The reactor was situated inside an oil bath at 343 K. Some time was required for the brine to stabilise at the experimental temperature before proceeding.

CO₂ introduced into the reactor – displacing brine. A syringe pump was connected to a CO₂ gas bottle. With the pump piston at the top of the barrel (pump volume $\approx$ 0 mL) the CO₂ bottle was opened and the pump is pressurised to the bottle pressure (5.5 MPa). The pump barrel is contained within a water jacket at 343 K. The pump piston was then withdrawn, introducing CO₂ from the bottle into the pump barrel. Once filled the CO₂ bottle is closed and isolated from the pump. The pump is then pressurised from 5.5 MPa to the experimental pressure – 9 MPa.

The pump filled with CO₂ was connected to the top of the stirred reactor. A second pump – used to fill the reactor with brine – was still connected to the base of the reactor. By operating the brine pump in constant withdrawal model – and the CO₂ pump in constant pressure mode – CO₂ displaced brine from the reactor in a

controlled manner. The transfer of phases was stopped when the desired volume of brine (600 mL) and CO₂ (750 mL) was inside the reactor.

Phase mixing. Once the reactor was filled with the correct volumes of brine and CO₂ the bottom valve of the reactor (that connects to the brine pump) was closed. The valve at the top of the reactor (that connects to the CO₂ pump) remained open. The CO₂ syringe pump was set to constant pressure mode (9 MPa) and the pump volume recorded through a data logger connected to a PC.

The internal stirrer inside the reactor was connected to a motor through a magnetic coupling. The motor was turned on and the stirrer shaft rotated at 200 r.p.m.. The stirrer was a special gas entrainment (GE) design whereby the less dense CO₂ phase was sucked down the stirrer shaft – through a hole situated in the CO₂ phase – and expelled through the stirrer blades in the denser brine phase. The GE stirrer created an aggressive mixing environment with a large surface area between the phases to promote mass transfer.

As CO₂ dissolved in the brine more CO₂ entered the reactor from the attached pump. The pump CO₂ volume hence decreased. CO₂ continued to enter the reactor from the pump until the phases were mutually saturated. No more CO₂ dissolved in the brine and hence the CO₂ pump volume stabilised. Figure A. 9 illustrates one such set of CO₂ pump volume versus time data.

In total CO₂-brine mixing was performed six times. The average time to reach equilibration was 1 hour. In three of the mixing experiments a sample of the equilibrated brine was taken from the base of the reactor. This was done using a syringe pump to maintain the sample pressure. Once the sample was extracted and isolated within the pump an isothermal depressurisation measurement was performed to determine the solubility of CO₂ in the water. The solubility was measured to be 0.0136 mole fraction $\pm$ 0.0020 mole fraction (32.4 kg m⁻³ $\pm$ 4.8 kg m⁻³). Further details on the isothermal depressurisation procedure are given in Appendix 7.

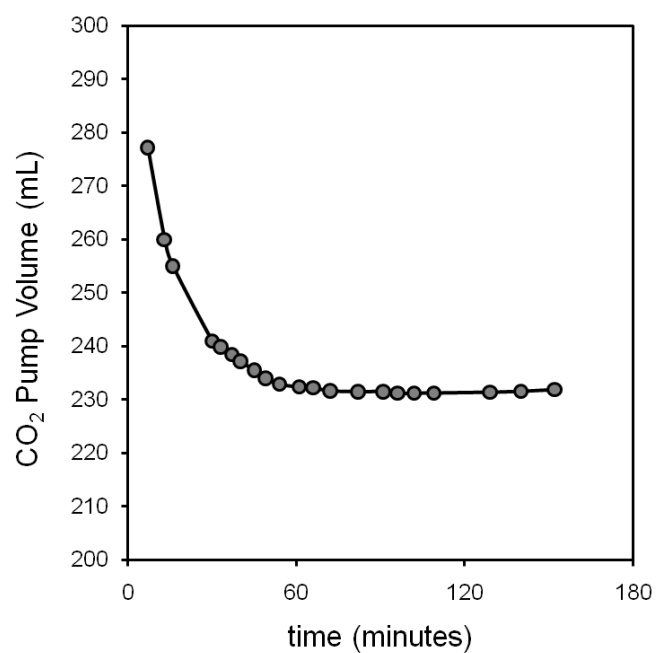
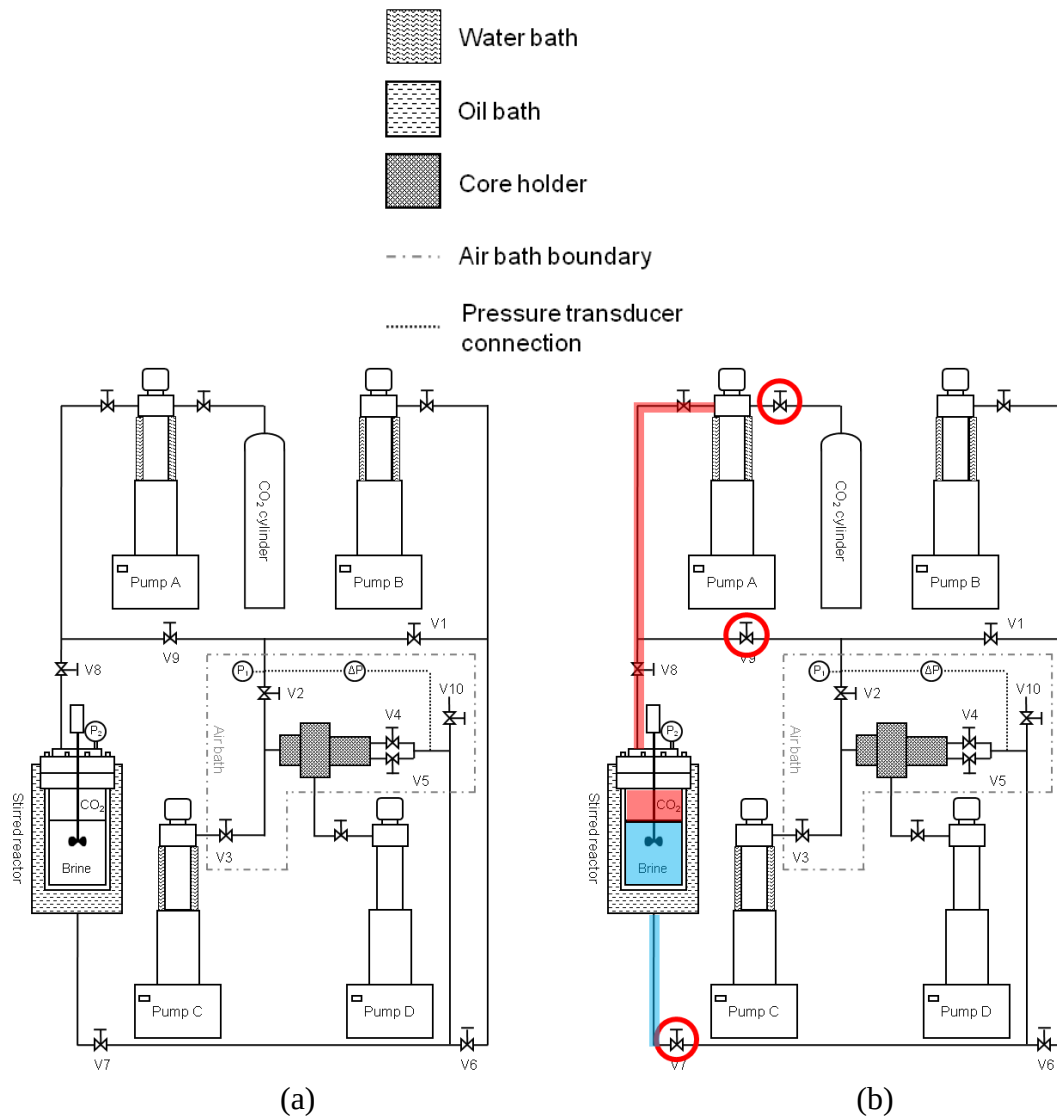


Figure A. 9: CO₂ pump volume versus time. As CO₂ dissolves into brine within the reactor the pressure is maintained by injecting additional CO₂ from an attached pump. As the brine becomes saturated with CO₂ the rate of injection slows and finally stops when the phases are equilibrated.

Appendix 6 – ETP CO₂-brine Coreflood Procedure

This appendix contains additional information on the ETP CO₂-brine coreflood experiments. Additional detail relating to the experimental flow sequences is given in addition to the saturation calculations used to determine S_i and S_r .

The five main experimental steps in the CO₂-brine experiment were highlighted in the main body of the text as being: CO₂-brine mixing, initial saturation, primary drainage, waterflooding; and residual saturation measurement. To help understand the procedure the experimental diagram has been modified to highlight the valves closed – and tubing used for phase injection – in each case (Figure A. 10).



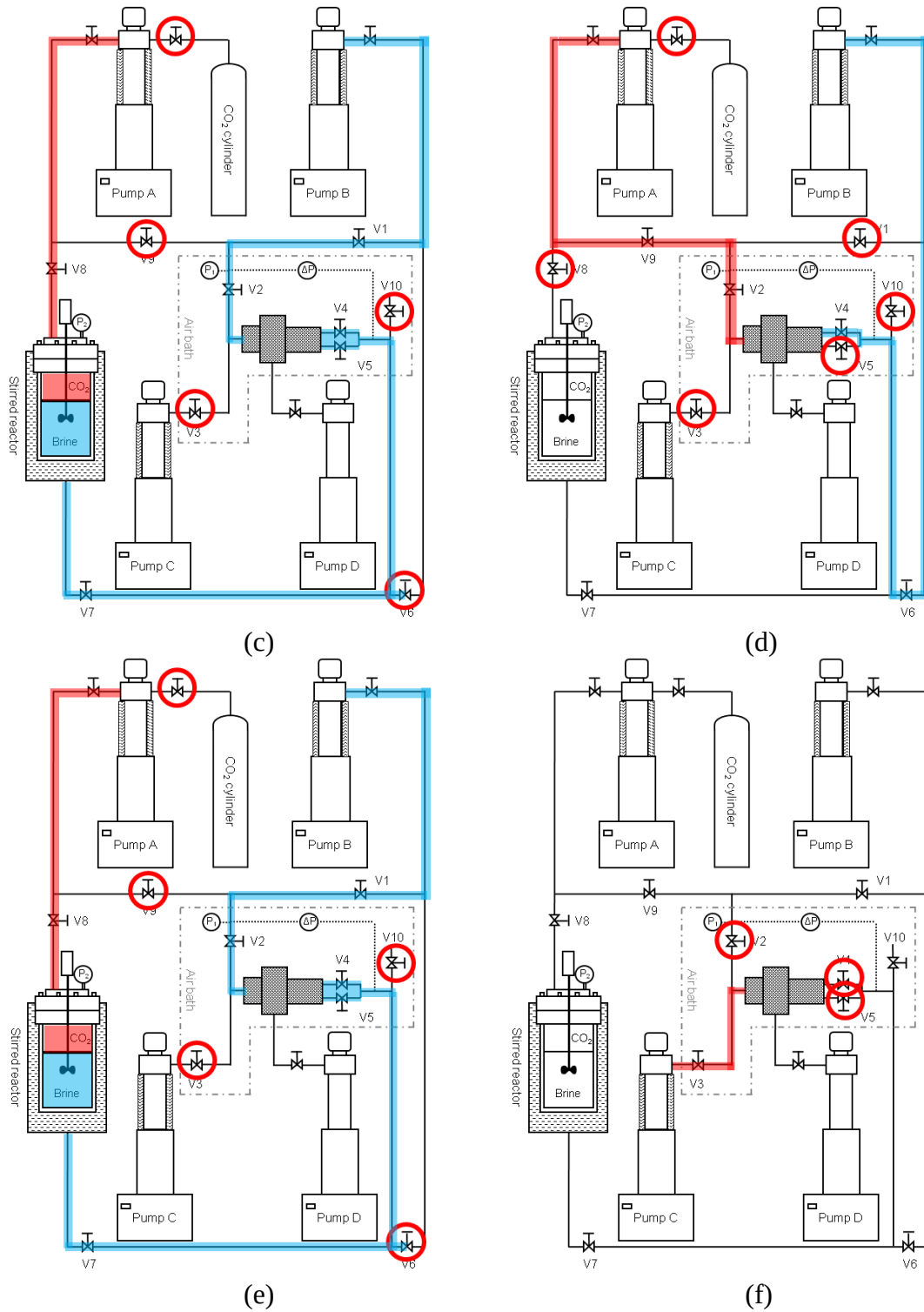


Figure A. 10: (a) ETP CO₂-brine coreflood apparatus. Pump A is charged with CO₂ and controls phase injection, pump B receives production from the core-plug and controls back-pressure, pump C is used for the isothermal expansion saturation measurement and pump D applies confining pressure. (b) **Mixing** – brine is introduced to the stirred reactor which is then connected to a CO₂ reservoir at constant pressure (pump A) Closed valves are marked with a red circle. CO₂ is injected into the reactor from the pump as it dissolves in the brine under agitation. (c) **Initial Saturation** – the core is initially vacuumed through pump B. Five pore volumes of fresh brine are then injected through V10. CO₂ from pump A is then used to displace five pore volumes of equilibrated brine through the core-plug (illustrated). (d) **Primary Drainage** – CO₂ from pump A is injected directly into the

core-plug. Displaced brine passes through the porous plate – exiting the core holder via valve 4 – and is produced into pump B. (e) **Waterflooding** – Five pore volumes of equilibrated brine are displaced through the core-plug by CO₂ from pump A. (f) **Saturation Measurement** – The core-plug pore space is isolated from the remainder of the apparatus by closing valves 2, 4 and 5. Valve 3 is then opened connecting the pore space to the isothermal expansion pump – pump C. In figures b-f tubing highlighted in blue contains brine and tubing highlighted in red contains CO₂.

The procedure for equilibrating CO₂ and brine is described in Appendix 5. The procedures for the remaining steps are given below.

Core-plug Preparation. During the experiment the core-plug was housed within a core holder. A rubber (Viton®) sleeve separates the core-plug pore space from the confining liquid (de-ionized water). A layer of aluminium adhesive tape was placed in-between the core-plug and the rubber sleeve to prevent CO₂ dissolving in the rubber. The core-plug was first wrapped in a layer of PTFE tape to protect the aluminium from the rough rock surface. The adhesive aluminium tape was then wrapped around the core-plug. Finally the rubber sleeve was pulled on. These successive layers around the core-plug are shown in Figure A. 11.

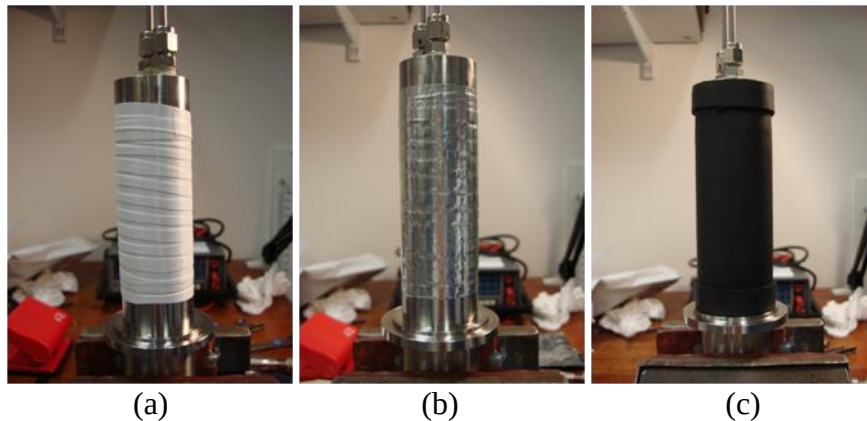


Figure A. 11: The preparation of the core-plug for use in a CO₂-brine ETP experiment. (a) The core-plug is initially wrapped with PTFE tape. This protects the aluminium from the rough rock surface. (b) Adhesive aluminium tape is wrapped around the sample. Using adhesive aluminium allows the rubber sleeve (c) to be slid onto the sample without damaging the aluminium. Additional rubber rings are placed over the rubber sleeve to affect a seal between rubber and metal end platens.

Initial Saturation. Once the equilibrated phases had been prepared the core-plug and process flowlines were saturated as follows:

1. A vacuum pump was connected to pump B and the valves between pump and core holder were opened. This volume (core-plug pore space plus flowlines) was vacuumed for 30 minutes.
2. Simultaneously pump C was filled with 200 mL of de-aired brine. The pump was connected to the system via valve 10 (note – valve 3 is closed throughout).
3. The vacuum pump was disconnected from pump B and brine introduced into the vacuumed volume from pump C by opening valve 10.
4. Once the volume was filled with brine the pressure was increased in steps to 9 MPa.
5. Five pore volumes of brine were pumped through the core-plug from pump C to pump B.
6. Five pore volumes of CO₂ saturated brine were pumped through the core-plug (Figure A. 10 c). Pump C was emptied of un-equilibrated brine and cleaned.

Primary Drainage. After the pore space and flowlines were evacuated CO₂ was injected from pump A into the core plug (Figure A. 10 d). The CO₂ displaced brine which passed through the porous plate and out of the core holder through valve 4. Equilibrium pressure – corresponding to P_c – was recorded when injection ceased and pressures stabilised. The maximum N_{cap} during primary drainage was 9.3×10^{-9} .

Waterflooding. The core-plug was waterflooded to S_r (Figure A. 10 e). Five pore volumes of CO₂ saturated brine were injected through the core-plug. The maximum N_{cap} during waterflooding was 3.7×10^{-7} .

Saturation Measurement. The residual saturation of the sample after waterflooding was measured as follows:

1. The core-plug was isolated from the rest of the apparatus by closing valves 2, 3, 4, and 5.
 2. Pump C – used for isothermal expansion – was vacuumed.
-

3. Valve 3 was opened slowly expanding the pore space phases into the pump volume. The pump piston could then be retracted – decreasing the phase pressure and increasing the pump volume. Volumes and pressures were measured allowing S_r to be calculated (Appendix 7).

Appendix 7 – ETP CO₂-brine Measurements

To characterise the trapping and capillary pressure curves for the CO₂-brine system six sets of P_c , S_i and S_r measurements were performed – each set relating to a separate coreflood experiment. This appendix contains additional details and data on these measurements.

Capillary Pressure

After a quantity of non-wetting phase is injected into a core-plug during a porous plate experiment a pressure differential – the capillary pressure – exists between the wetting and non-wetting phases at either face of the core-plug. This is measured once the injection and production rates are zero and the system is in equilibrium.

During primary drainage CO₂ was injected into the core-plug from a syringe pump. The displaced brine was produced through the porous plate into a second syringe pump. The CO₂ injection pump was operated in constant pressure mode. The brine production pump was operated in one of two modes: constant pressure or constant withdrawal rate. This is important as the method in which the experiment was controlled determined when P_c was measured.

Constant pressure mode primary drainage. At high initial saturations – higher P_c – both pumps were operated in constant pressure mode. The maximum flow rates possible in constant pressure mode were limited – the maximum N_{cap} was 4.3×10^{-10} . The CO₂ pump pressure was increased above 9 MPa and CO₂ entered the core-plug. Injection continued until no more brine could be forced from the core-plug for the given P_c . As this limit approached the rate of CO₂ injection and brine production decreased until – at equilibrium – the rates reached zero. At this point the sample was considered to be at initial CO₂ saturation. It was preferential to record brine production volumes instead of CO₂ injection volumes. CO₂ volumes were influenced by compressibility as the pressure was increased. Of the six ETP CO₂-brine corefloods three were performed with the pumps operating in constant pressure mode. The brine production data from these three corefloods is given in Figure A. 12.

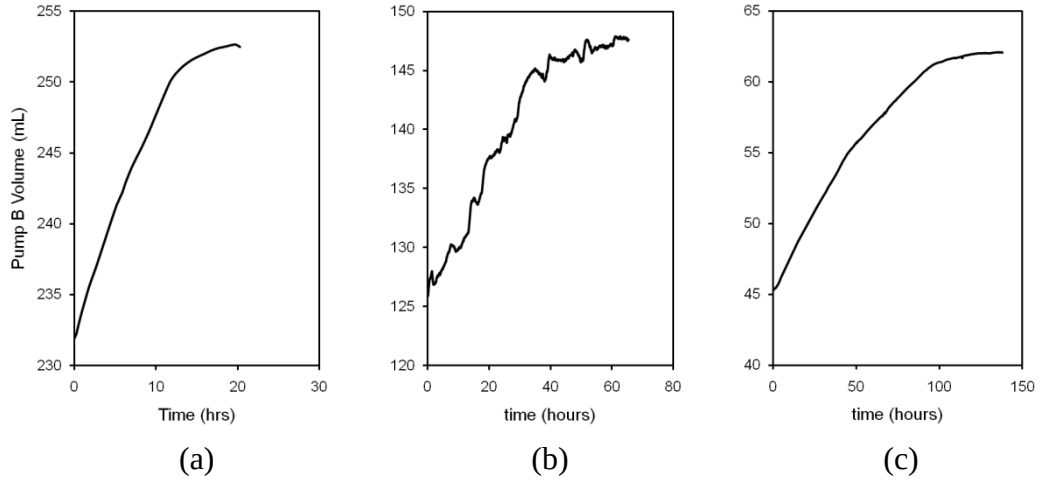


Figure A. 12: Brine production data during primary drainage. Graphs a-c correspond to data points 1-3 respectively in Table A. 10.

Constant rate mode primary drainage. At lower initial saturations it was not possible to operate both pumps in constant pressure mode because small fluctuations in pressure – due to changes in laboratory temperature – did not allow a low (< 13.8 kPa), stable P_c to be maintained. In these cases brine was withdrawn at a very low constant rate ($N_{cap} < 5.2 \times 10^{-11}$) from the core-plug. As brine was withdrawn CO_2 entered from the opposite face. This allowed a more stable dP to be maintained across the core-plug. The dP is not equal to P_c while phases are flowing as a component of the pressure difference is due to dynamic effects. As such P_c was measured after injection/production had been stopped and the pressure difference had stabilised. This is shown in Figure A. 13 for the three corefloods performed in constant withdrawal rate mode.

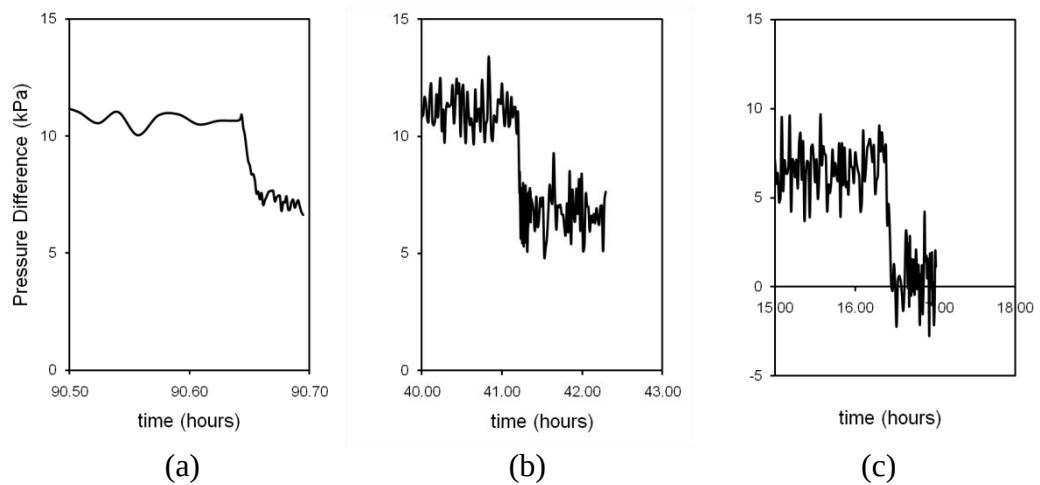


Figure A. 13: Pressure difference across the core holder versus time. Graphs a-c correspond to data points 4-6 respectively in Table A. 10. Each graph consists of two constant pressure intervals. The higher pressure interval represents the period

when brine is being withdrawn from the sample. When flow is stopped the pressure drops to the lower constant pressure interval. This lower pressure interval is taken to represent P_c for the constant rate coreflood experiments.

Initial Saturation

Once CO₂ injection stops and the system pressures stabilise the system is considered to be at S_i . The measurement of S_i is based on a volume balance calculation of the brine produced from the core-plug. The volume of brine produced is considered equal to the volume of CO₂ injected. When the brine production volume is measured care must be taken to take into account dead volume within the system. At the start of primary drainage CO₂ is injected by opening valve 9 (Figure 2.14; Figure A. 10). The CO₂ must initially pass through tubing from valve 9 to the core-plug, displacing brine as it goes. This volume of brine – the volume in the tubing in-between valve 9 and the core-plug – must be subtracted from the total brine production volume in order to determine the volume of CO₂ injected. It is therefore of key importance to measure this dead volume accurately. This was done by evacuating air from the dead volume and introducing water from a syringe pump. When the evacuated space had been filled with water the pump volume was recorded. There is considerable uncertainty in measuring this volume as ancillary flow lines (leading to pressure transducers) are connected to the dead volume. It is thought that once these ancillary tubes are saturated with brine CO₂ will not enter them. The tubes terminate at dead ends (pressure transducer diaphragms) and it is thought that the CO₂ will not enter these regions – preferring instead to advance to the core-plug in the direction of lower pressure.

The dead volume was measured as 4.5 mL but because of the uncertainty in the measurement it is considered to have an accuracy of ± 1 mL.

Residual Saturation

After primary drainage the core-plug was waterflooded to a residual CO₂ saturation. This S_r was then determined by measuring pressures and volumes during an isothermal expansion of the pore space. This was the procedure for all six of the ETP CO₂-brine coreflood experiments on the Berea 9 core-plug. This approach was

previously used by Suekane *et al.*, [49] – equations 18-20. Solving these equations for S_r (for a constant temperature) gives:

$$S_r = \frac{r'PV + r'V_{(DV)} + \rho_g'\Delta V - rPV - rV_{(DV)}}{PV(\rho_g - \rho_g' + r' - r)} \quad (47)$$

where PV is the core-plug pore volume, $V_{(DV)}$ is the cell dead volume, ΔV is the volume of expansion, r is the solubility of CO_2 in brine at the equilibrated system pressure prior to depressurisation, r' is the solubility of CO_2 in brine at a lower known pressure, ρ_g is the density of CO_2 at the equilibrated system pressure prior to depressurisation, and ρ_g' is the CO_2 density at a lower known pressure. $V_{(DV)}$ was measured to be 6.94 mL (± 0.5 mL). The volume of expansion comprised the volume due to the movement of the pump piston and also a dead volume at the head of the pump barrel. Using equation 47 S_r was calculated at a number of pressure steps below the equilibrated system pressure at the end of waterflooding. Figure A. 14 shows the relationship between pressure and volume and Figure A. 15 shows the calculated S_r at the depressurisation pressure steps.

During isothermal depressurisation the pressure is not dropped below 1.4 MPa because of concerns over water vaporisation at the elevated system temperature.

To understand how uncertainty of the measured parameters (T , P , $V_{(DV)}$, PV and the isothermal expansion pump dead volume) affects S_r uncertainty analysis was performed. Initially each of these measured values was varied by 5% – Figure A. 16 – to understand which parameters had the greatest impact on S_r . Next the parameter ranges were altered to better reflect the variation expected in the experiment. For example the temperature was recorded to vary by no more than ± 0.5 K. Table A. 9 summarises the parameter ranges used. The impact on S_r is shown in Figure A. 17. Based on this analysis an error of $\pm 6\%$ was used when reporting S_r values – with the exception of the final S_i/S_r measurement (#6) where the variation in the S_r isothermal expansion data was greater ($\pm 7\%$).

The calculated values of S_i and S_r , including error ranges, are summarised in Table A. 10.

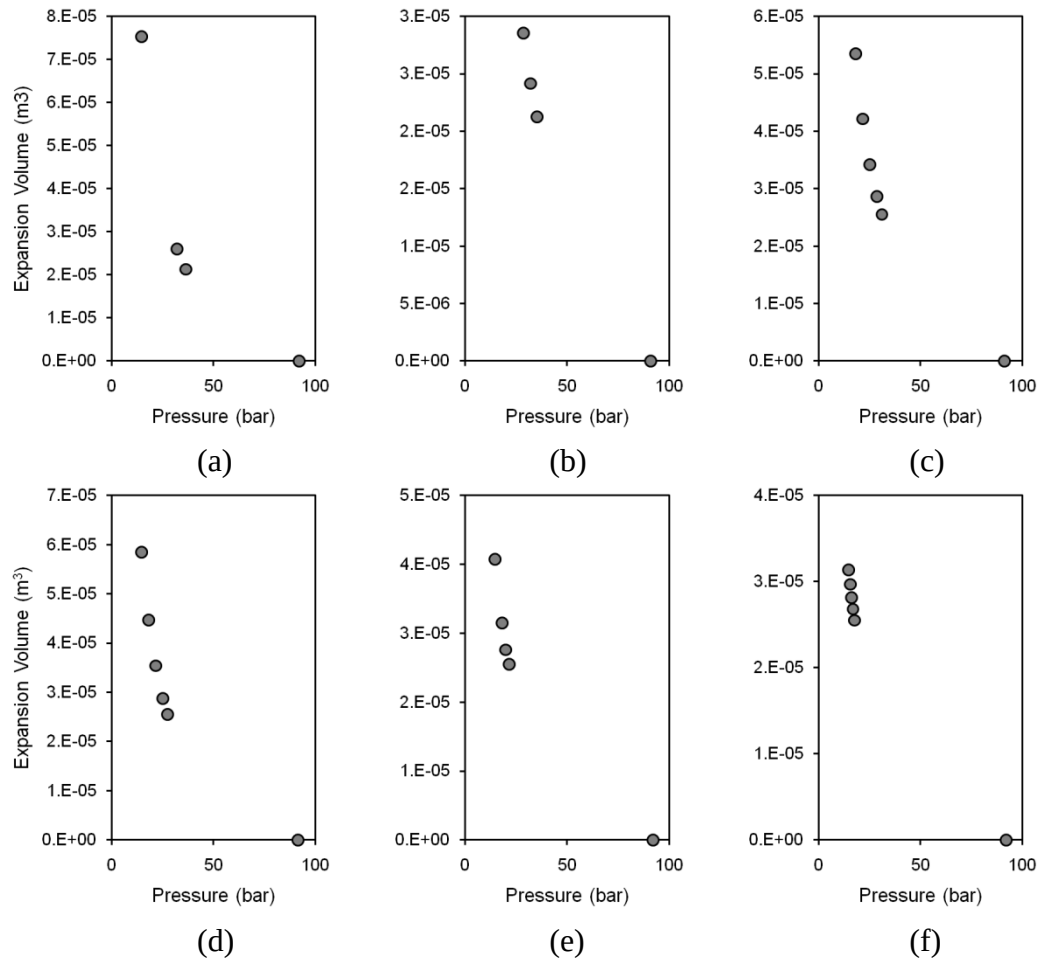
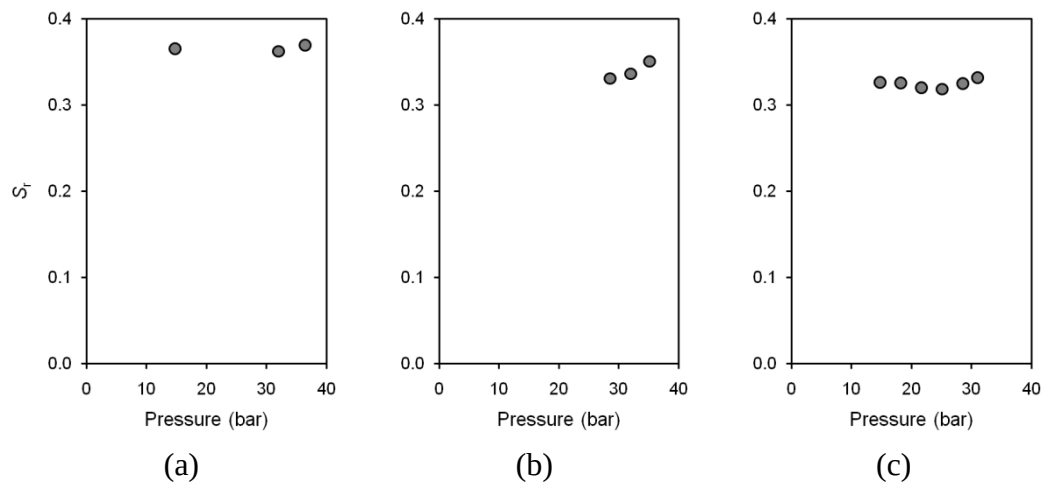


Figure A. 14: Relationship between expansion volume and pressure during S_r measurement. Graphs a-f correspond to corefloods 1-6 respectively.



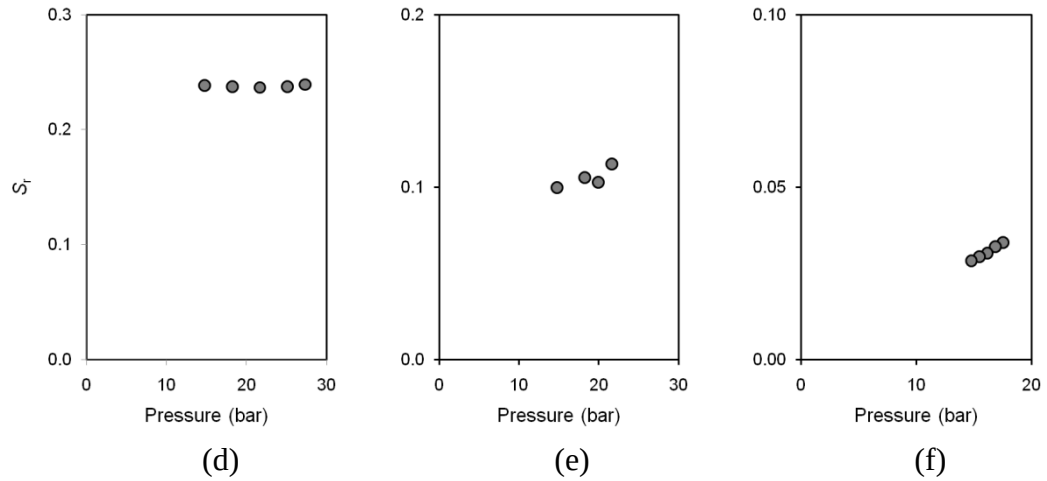


Figure A. 15: Relationship between pressure and S_r during isothermal depressurisation.

Table A. 9: Measurement error ranges for the parameters contributing to the calculation of S_r .

Parameter	Value Range
Pressure	± 103 kPa
Temperature	± 0.5 K
Dead volume (cell) - $V_{(DV)}$	± 0.5 mL
Dead volume (expansion pump + flowline)	± 1.5 mL
Pore Volume	± 0.5 mL

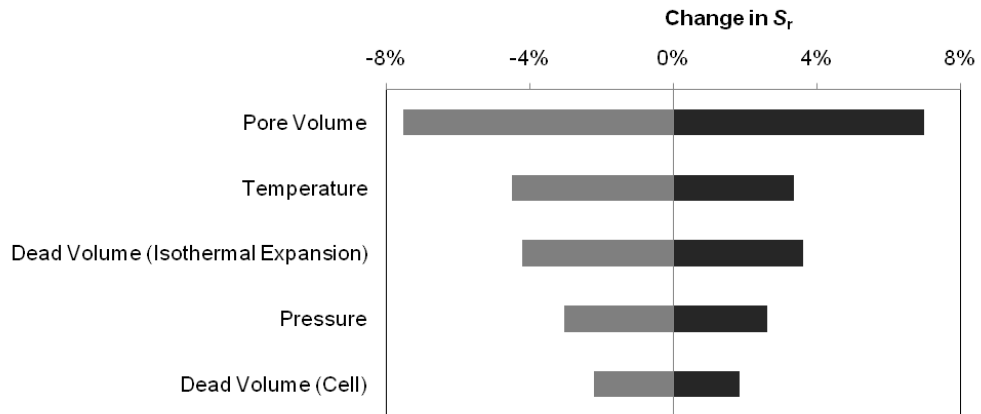


Figure A. 16: Impact on S_r when the measurement parameters were varied by $\pm 5\%$.

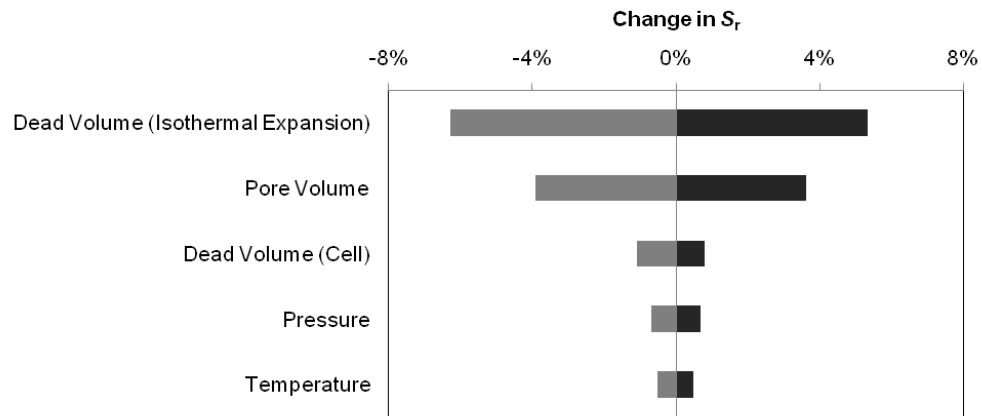


Figure A. 17: Impact on S_r when the measurement parameters were varied by realistic ranges based on an understanding of measurement accuracy – Table A. 9.

Table A. 10: ETP CO₂-brine coreflood saturation and capillary pressure results and associated error.

Coreflood	S_i	S_r	Error _i	Error _r	P_c (kPa)	Error _{P_c} (kPa)	Drainage time (hrs)
1	0.851	0.366	± 0.053	± 0.022	296.1	33.5	20.6
2	0.846	0.339	± 0.053	± 0.020	161.3	41.4	64.2
3	0.640	0.324	± 0.053	± 0.019	82.7	33.8	137.8
4	0.475	0.238	± 0.053	± 0.014	6.9	0.7	90.7
5	0.269	0.105	± 0.053	± 0.006	6.6	2.1	42.3
6	0.079	0.031	± 0.053	± 0.002	1.0	2.8	17.0

Appendix 8 – Wettability Indices

The capillary pressure results for a CO₂-water-sand system [130] have been analysed in terms of wettability indices. Three wettability indices were considered: the Amott index [120]; the Hammervold-Longeron index [121]; and the USBM index [119]. The Amott (water-drive) index (δ_w) is:

$$\delta_w = \frac{V_{sp}}{V_t} \quad (48)$$

where V_{sp} is the volume of oil displaced by spontaneous water imbibition and V_t is the total oil volume displaced by waterflooding (forced plus spontaneous displacement). The Hammervold-Longeron index I_{HL} is given by:

$$I_{HL} = I_w - I_o \quad (49)$$

and

$$I_w = \frac{B_1}{B_1 + A_2} \quad (50)$$

where B_1 is the area under the spontaneous imbibition curve and A_2 is the area under the forced imbibition curve. The USBM index (W) is given by:

$$W = \log\left(\frac{A_1}{A_2}\right) \quad (51)$$

where A_1 and A_2 are equivalent to B_1 and A_2 in the Hammervold-Longeron index.

In the case of the Plug and Bruining data subscript o was replaced with CO₂ to reflect the different two-phase system under consideration.

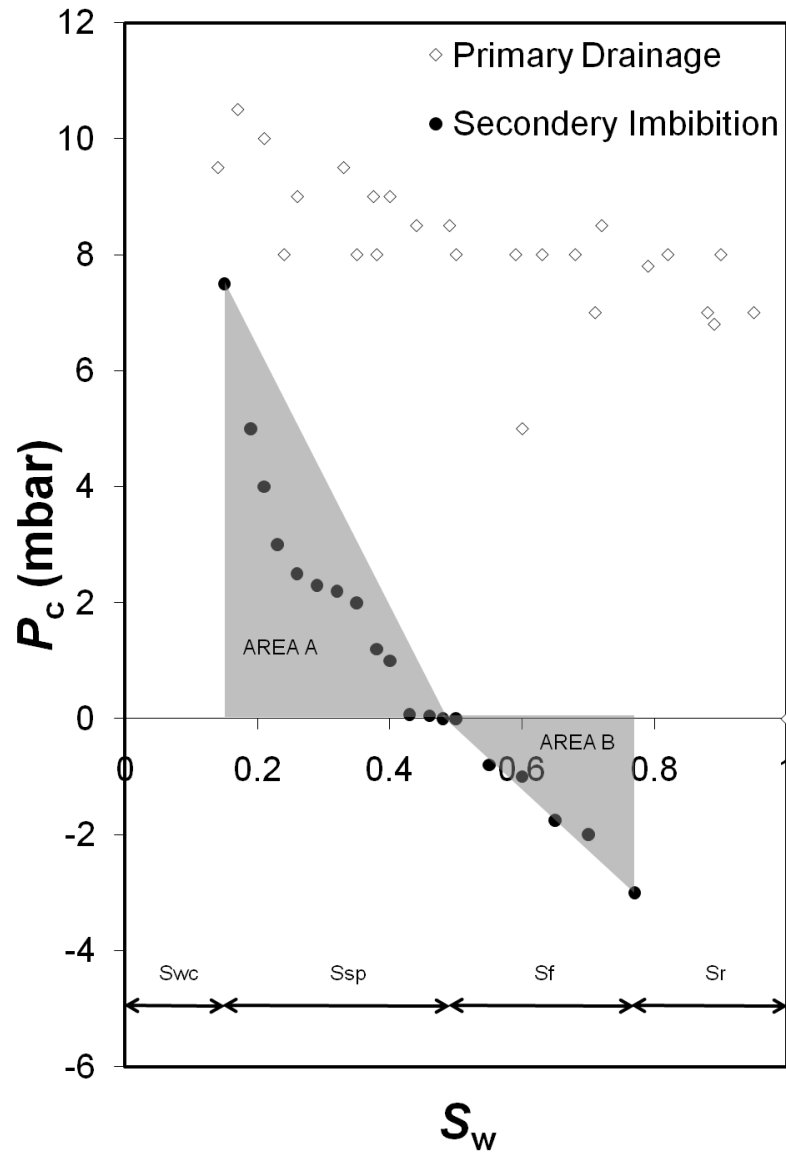


Figure A. 18: Drainage and imbibition capillary pressure data for a CO₂-water-sand system [130]. Area A is equivalent to B_1 and A_1 in the HL and USBM indices respectively. Area B is equivalent to area A_2 in the HL and USBM indices. The total CO₂ saturation change caused by waterflooding is equal to the spontaneous saturation change (S_{sp}) and the forced saturation change (S_f) combined. This is equivalent to V_t in the Amott index.