



Permeability and Relative Permeability Measurements at Reservoir Conditions for CO₂-Water Systems in Ultra Low Permeability Confining Caprocks

D. Brant Bennion, Hycal Energy Research Laboratories Ltd., Calgary, AB, Canada, and
Stefan Bachu, Alberta Energy and Utilities Board, Edmonton, AB, Canada

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This paper was prepared for presentation at the SPE Europec/EAGE Annual Conference and Exhibition held in London, United Kingdom, 11–14 June 2007.

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Abstract

Carbon dioxide has been successfully used in more than 80 enhanced oil recovery (EOR) operations in North America, and the number of such operations may increase significantly around the world if CO₂ becomes available at reasonable costs. On the other hand, geological storage in deep saline aquifers and hydrocarbon reservoirs of large amounts of CO₂, captured from large stationary sources is one method that is under consideration for reducing greenhouse gas emissions into the atmosphere on a worldwide basis. In both cases of CO₂-EOR and CO₂ capture and geological storage (CCGS), the containment of CO₂ within the injection unit and leakage avoidance are essential. Effective CO₂ containment is achieved by the overlying tight caprock that is initially highly saturated with formation brine, which prevents CO₂ migration into uphole intervals and potentially into shallow freshwater aquifers and ultimately to the atmosphere. The confining properties of the caprock are due to its very low permeability and to relative permeability and capillary pressure effects that prevent the penetration of CO₂ into, and significant flow through the caprock. Essential to the assessment of CO₂-EOR and CCGS operations, including numerical simulation, is knowledge about the caprock permeability to brine and CO₂. This paper presents results of detailed measurements at full reservoir conditions for permeability to water, primary drainage and secondary imbibition permeability, relative permeability and trapped saturation of supercritical, dense-phase CO₂ and brine for three different, regionally-extensive low permeability formations in the Alberta basin, Canada. These formations include Devonian and Cretaceous shales and a Devonian anhydrite whose measured relative permeabilities were found to be in the nano to pico Darcy range.

The methodology used in the test program and the results can be extended to the evaluation of other sealing caprocks for other prospective CO₂-EOR or CCGS operations around the world.

Introduction

Carbon dioxide from natural CO₂ reservoirs is used for enhanced oil recovery (CO₂-EOR) at more than 70 operations in the Permian Basin in west Texas in the United States¹. Other CO₂-EOR operations in the U.S. and around the world use CO₂ from anthropogenic sources such as gas plants and petrochemical and fertilizer plants. However, the number of these CO₂-EOR operations is much smaller due to the high cost of CO₂ capture from industrial sources. On the other hand, CO₂ capture and geological storage (CCGS) is considered to be a major component of climate change mitigation strategies², and, although deep saline aquifers have the largest storage capacity and widest distribution, oil reservoirs are the most likely to be used preferentially for CCGS because of the positive economic potential for increased oil production through CO₂-EOR schemes^{3,4}. Thus, the use of CO₂ in CO₂-EOR operations and the storage of CO₂ in deep saline aquifers are foreseen to increase in the next decades. In both cases it is essential that the caprock, which is saturated with formation water, does not allow the leakage of CO₂ from the injection reservoir or aquifer into overlying strata and possibly into shallow groundwater resources or even to the surface. If the caprock is not naturally fractured, then the necessary condition to avoid CO₂ leakage is to maintain the injection pressure below the capillary entry pressure or the rock fracturing pressure, whichever is lower. Even if the CO₂ pressure is higher than the capillary entry pressure (but lower than the rock fracturing pressure), if the absolute and relative permeabilities of the caprock are exceedingly low, then CO₂ may flow through the caprock on a geological time scale, in which case, from operational and CO₂-storage points of view it may not be significant. Thus, it is very important to know the CO₂-brine displacement characteristics of low permeability rocks, such as shale and anhydrite, which constitute the confining caprock of hydrocarbon reservoirs and deep saline aquifers. Yet very few data are available about the displacement behavior of CO₂-brine systems in such low permeability media, as most of the research effort to date has focused on CO₂-oil systems in higher quality reservoir rocks.

To cover this gap in data and knowledge, the authors commenced in 2004 an experimental program on core plugs taken from rocks at several locations in the Alberta basin, Canada. The rock samples were collected from oil reservoirs where oil producers started CO₂-EOR pilot operations using CO₂ or acid gas produced at nearby gas plants, and from deep saline aquifers that may be used in the future for CO₂ storage. Interfacial tension of CO₂-brine systems at reservoir conditions, capillary pressure and relative permeability to CO₂ and H₂S for carbonate and sandstone rocks were reported previously⁵⁻⁸. This paper presents the results of similar tests conducted on well-compacted, low-permeability shales and anhydrite that constitute the caprock at these locations, namely the Middle Devonian Muskeg Formation anhydrite in northwestern Alberta (well 5-2-116-6 W6M) and two shales/siltstones from central Alberta, the Upper Devonian Calmar Formation (well 7-3-52-27 W4M) and the Upper Cretaceous Colorado Group (well 7-11-48-9 W5M). The specific details of the equipment and procedures used to conduct the tests and measurements have been presented by the authors in previous papers^{5,6} and the interested reader is directed to these papers. Because pore-size and capillary pressure measurements are routine, only the procedure for the relative-permeability tests will be presented here briefly.

1. Mount test sample of core (3.81 cm OD core plug drilled using inert 10% KCl brine from vertical full diameter core sections in the vertical direction so that flow will be parallel to natural bedding planes).
2. Evacuate sample to remove all trapped gas.
3. Apply net reservoir overburden pressure.
4. Pressure-saturate sample 100% with formation brine.
5. Increase pore pressure to desired reservoir value while maintaining net overburden pressure.
6. Heat to reservoir temperature while maintaining pore pressure and net overburden pressure.
7. Pressure-saturate formation brine with CO₂ at operating temperature and pore pressure.
8. Saturate CO₂ with water vapor at operating temperature and pressure.
9. Displace degassed formation brine with live formation brine (saturated with CO₂ gas) and measure baseline absolute permeability to brine.
10. Conduct an unsteady-state displacement with supercritical-phase water-vapor saturated CO₂ (primary drainage test) in the water saturated core. The core is oriented vertically and this test is conducted in a base up fashion to simulate the flow direction that would be present in the reservoir with CO₂ invading from a sequestration zone below the caprock.
11. Measure final irreducible water saturation and maximum CO₂ saturation and endpoint permeability and relative permeability to CO₂.
12. Conduct a primary imbibition test by switching the injection fluid to CO₂-saturated formation brine (top down displacement). Displace the sample with brine to an immobile CO₂ saturation level and record endpoint permeability and relative permeability to

CO₂.

13. Using a computer history-matching method⁹, generate the CO₂ and brine relative permeability curves for the primary drainage and imbibition displacement tests for each sample.

Results specific to the work presented here include high-pressure air-mercury capillary pressure measurements, interfacial tension (IFT) measurements at reservoir conditions, and relative-permeability displacement characteristics for both drainage and imbibition cycles.

Results and Discussion

Core samples from the Upper Devonian Calmar Formation, Cretaceous Colorado Group and the Middle Devonian Muskeg Formation were obtained by drilling 3.81 cm OD plugs from parent sections of vertical full diameter core from the previous well locations. The relative permeability measurements for both the drainage and imbibition testing with CO₂ were conducted on the same core plug to eliminate possible effects of various pore distributions and rock characteristics on relative permeability and irreducible saturations. The offset end sections from each test plug (removed when the sample was drilled from the parent full diameter core to obtain a perfect right cylinder) were subjected to high pressure (60,000 psig) mercury injection capillary pressure testing. These end cut sections represented the best approximation to the actual test samples, being removed directly from the ends of the tested samples themselves. The plug samples were drilled in a vertical orientation from vertical full diameter core so that the permeability measurements would be along the vertical axis (perpendicular to natural bedding planes) to mimic the direction of potential fluid penetration in the reservoir caprock. The characteristics and in-situ conditions of the core plugs used in this work are presented in Table 1. This includes the test conditions of temperature and pressure, water composition and CO₂-brine interfacial tension. The test conditions presented were selected chosen as representative of the particular caprock from which they were sampled.

Figure 1 provides comparative plots of the generated pore size distributions of the tested Calmar Fm. and Colorado Gp. shale samples. The CO₂-brine capillary pressure curves at reservoir conditions (converted from the measured air-mercury capillary pressure data) for both the Calmar and Colorado shales are shown in Figure 2. The Colorado Gp. shale superficially appears to have slightly better quality on the pore size distribution curve than the Calmar Fm. shale, but this is due to artifacts associated with surface invasion of small dissolution pores on the surface of the Colorado Gp. shale sample matrix. If these effects are excluded, both samples consist of 100% microporosity. The Muskeg Fm. anhydrite porosity and permeability are extremely low: measured porosity on the matrix was less than 0.5% and unconfined absolute gas permeability was lower than the minimal detection limit of routine analytical equipment of 0.0001 mD. This didn't allow any accurate capillary pressure measurements to be conducted (virtually no measurable pore volume was available for any mercury intrusion to occur in), hence graphical capillary

pressure and pore size distribution data are not presented for this rock type. The capillary pressure curves and pore size data indicate ultra fine grained matrix with 100% microporosity and with average pore throat diameters in the <0.01 micron range. Table 2 presents the statistics of pore size distribution and capillary pressure data for the Colorado Gp. and Calmar Fm. shale samples.

Table 3 provides a summary of the permeability to brine, endpoint relative permeability and saturation data for the drainage and imbibition cycles for the three different low permeability displacement tests. Tables 4 to 6 provide the primary drainage and secondary imbibition relative permeability data for the three tests and these data have been plotted in Figures 3 to 5 (Calmar Fm. and Colorado Gp. shales and Muskeg Fm. anhydrite, respectively). The permeability to brine on the imbibition flood for the Muskeg Fm. anhydrite sample was below the measurement threshold of measurement (less than 1 picoDarcy, or 10^{-12} Darcy) so it was not possible to obtain a stabilized final endpoint permeability to gas and compute resulting relative permeability curves for this displacement cycle, hence only the primary drainage data are presented for this rock type.

Examination of the data indicates the following trends:

1. All of the samples tested exhibit initial permeability to brine of less than 1 microDarcy (10^{-6} Darcy).
2. All samples tested at high displacement pressures (in excess of 20,000 kPa) have finite permeability to CO₂ gas and ultimately indicated some displacement of the initial 100% water saturation level from the tight caprock matrix by the invading CO₂. However, endpoint permeability values to CO₂ were in the 1 to 100 picoDarcy range (10^{-12} to 10^{-10} Darcy) and indicate that, unless the caprock intervals are both very thin in vertical extent and exposed to extremely high overpressure in the gas injected zone in contrast to the pressure on the upper side of the caprock interval, any appreciable flow of CO₂ over a non-geological time scale would be minimal to non-existent.
3. The imbibition flood tests on the Colorado Gp. and Calmar Fm. shales indicated that the presence of even minor amounts of trapped gas saturation in the tight matrix has a very large reducing effect on the permeability to brine. This is not unexpected, given the extremely small pores present in the samples tested and the high level of interference that would be expected to be occurring between the CO₂ and brine phase, even at elevated temperature and pressure conditions, which have a moderate reducing effect on interfacial tension.
4. There does not appear to be a clear correlation between porosity and pore size distribution and the initial brine permeability and relative permeability properties of the samples that were evaluated. This is likely due to the fact that each sample represents a significantly different lithology and this fact is the main controlling variable in the determination of the

relative permeability character. Additional testing would be required for each specific facies type in order to quantify if there are any specific trends with permeability/porosity and pore system geometry.

5. In general it is expected that brine phase permeability will be greater during imbibition than during drainage, and conversely non-wetting (CO₂) phase permeability will be higher during drainage than during imbibition. This effect is indeed observed for the Calmar Fm. shale sample (except for very low K_{rw} values near the maximum saturation – this variance is attributed to numerical accuracy of the simulation model used to generate the relative permeability curves at the very low K_{rw} values in this region). For the Colorado Gp. shale sample, however, due to the extreme hysteresis in the brine phase relative permeability the observed value of the brine phase relative permeability is lower during imbibition than during drainage. This is attributed to severe relative permeability effects associated with the trapping of CO₂ in the very low permeability porous medium. Similar (even more pronounced) effects would have likely been present in the Muskeg Fm. anhydrite sample if full relative permeability curves could have been generated.
6. In contrast to similar studies conducted previously by the authors on ‘reservoir’ quality sandstone and carbonate formation samples⁵⁻⁸, these data indicate that the much finer grained, tortuous pore systems in these low-porosity and low-permeability shales and anhydrite have markedly different permeability and relative permeability characteristics, notably:
 - a. Much lower absolute permeability to brine
 - b. Much lower displacement efficiency of brine by the invading CO₂ phase, resulting in very high trapped water saturations.
 - c. Extreme relative permeability hysteresis effects on subsequent imbibition of water once trapped gas is present in the matrix.

Conclusions

Measured endpoint relative permeability values to CO₂ on primary drainage are in the 1 to 100 picoDarcy range, meeting acceptable caprock criteria for the low permeability rocks evaluated, and indicate that, unless the caprock intervals are both very thin in vertical extent and exposed to extremely high overpressure in the gas injected zone in contrast to the pressure on the upper side of the caprock interval, any appreciable losses of CO₂ over a non-geological time scale would be minimal to non-existent. This suggests that all three caprocks evaluated in this study would represent suitable long term sealing caprock for geological sequestration of CO₂. Relative permeability and permeability characteristics do not correlate strongly with observed pore size distribution, believed to be due to the high degree of variability in the lithology of the rock types that were evaluated. Comparison of these data to previous work by the authors on much higher permeability and porosity reservoir-rock samples (used to model the actual injection zones) indicates substantial

differences in the relative permeability characteristics, with significantly higher trapped water saturations to CO₂ displacement and very severe hysteresis effects between the drainage and imbibition displacements. These characteristics are undesirable for reservoir rocks, but for sealing caprock they are very favorable in that rocks of these grain sizes and morphologies will have the ability to provide long term sealing sources and containment of injected CO₂.

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Unit	Lithology	Depth (m)	Pressure (MPa)	Temperature (°C)	Salinity (mg/l)	IFT (mN/m)
Colorado Gp.	shale	1,618	20.00	43	27,100	19.8
Calmar Fm.	shale	1,566	12.25	43	129,700	27.6
Muskeg Fm.	anhydrite	1490.77	15.00	71	189,800	39.5

Table 1 - Lithology and in-situ conditions for the low-permeability rock samples from the Alberta Basin, Canada, tested for relative permeability and displacement characteristics of CO₂-brine systems.

Unit	% Micro Porosity	% Meso Porosity	% Macro Porosity	Median Pore Size (µm)	Porosity (%)	Threshold Capillary Pressure (kPa)
Colorado Gp.	95.5	1.9	2.6	0.011	4.4	172
Calmar Fm.	100.	0	0	0.006	3.9	72,827

Table 2 - Pore and permeability characteristics of low permeability rock samples from the Alberta Basin, Canada, used in the analysis of relative permeability and displacement characteristics of CO₂-brine systems. Micro pores are pore connected by pore throats of less the 1 micron in diameter, meso pores by throats of 1-3 microns in diameter and macro pores by pore throats of over 3 microns in diameter.

Rock Sample	Initial Absolute Permeability to Brine (md)	K _{r CO2} @ Irreducible Brine Saturation	S _{CO2 - Max} fraction	K _{r Brine} @ Trapped Gas Saturation	S _{CO2-Trapped} - Fraction
Colorado Gp.	0.0000788	0.0148	0.395	0.0024	0.349
Calmar Fm.	0.00000294	0.1875	0.362	0.2823	0.256
Muskeg Fm.	0.000354	0.0000828	0.185	tstm	0.180

Table 3 - Relative permeability and displacement characteristics for the drainage cycle in CO₂-brine systems for low permeability rock samples from the Alberta Basin, Canada.

(a)

CO ₂ Saturation Fraction	K _{rg}	K _{rw}
0.395	0.0149	0.0000
0.375	0.0131	0.0005
0.356	0.0114	0.0010
0.336	0.0098	0.0015
0.316	0.0084	0.0020
0.296	0.0071	0.0026
0.277	0.0059	0.0034
0.257	0.0049	0.0045
0.237	0.0040	0.0065
0.217	0.0032	0.0100
0.198	0.0025	0.0159
0.178	0.0019	0.0258
0.158	0.0014	0.0417
0.138	0.0010	0.0666
0.119	0.0007	0.1044
0.099	0.0004	0.1600
0.079	0.0003	0.2401
0.059	0.0001	0.3527
0.040	0.0001	0.5081
0.020	0.0000	0.7188
0.000	0.0000	1.0000

(b)

CO ₂ Saturation Fraction	K _{rw}	K _{rg}
0.395	0.0000	0.0149
0.393	0.0000	0.0125
0.390	0.0000	0.0103
0.388	0.0000	0.0085
0.386	0.0000	0.0069
0.384	0.0000	0.0055
0.381	0.0000	0.0043
0.379	0.0000	0.0034
0.377	0.0000	0.0026
0.374	0.0000	0.0019
0.372	0.0000	0.0014
0.370	0.0000	0.0010
0.367	0.0000	0.0007
0.365	0.0000	0.0004
0.363	0.0000	0.0003
0.361	0.0001	0.0002
0.358	0.0001	0.0001
0.356	0.0001	0.0000
0.354	0.0001	0.0000
0.351	0.0002	0.0000
0.349	0.0002	0.0000

Table 4– CO₂-brine relative permeability data for Colorado Gp. shale: a) primary drainage, and b) imbibition.

(a)

CO ₂ Saturation Fraction	K _{rg}	K _{rw}
0.000	0.0000	1.0000
0.018	0.0039	0.8803
0.036	0.0095	0.7697
0.054	0.0160	0.6679
0.073	0.0232	0.5747
0.091	0.0310	0.4897
0.109	0.0393	0.4128
0.127	0.0480	0.3437
0.145	0.0570	0.2820
0.163	0.0664	0.2276
0.181	0.0762	0.1800
0.199	0.0862	0.1390
0.217	0.0965	0.1042
0.236	0.1070	0.0752
0.254	0.1178	0.0518
0.272	0.1288	0.0334
0.290	0.1401	0.0197
0.308	0.1515	0.0101
0.326	0.1632	0.0041
0.344	0.1751	0.0010
0.362	0.1871	0.0000

(b)

CO ₂ Saturation Fraction	K _{rw}	K _{rg}
0.362	0.0000	0.1871
0.357	0.0001	0.1672
0.352	0.0003	0.1486
0.346	0.0006	0.1311
0.341	0.0010	0.1149
0.336	0.0018	0.0998
0.330	0.0031	0.0858
0.325	0.0052	0.0730
0.320	0.0083	0.0613
0.315	0.0127	0.0507
0.309	0.0189	0.0412
0.304	0.0271	0.0328
0.299	0.0379	0.0254
0.293	0.0517	0.0190
0.288	0.0691	0.0137
0.283	0.0905	0.0092
0.277	0.1167	0.0057
0.272	0.1483	0.0031
0.267	0.1859	0.0014
0.261	0.2303	0.0003
0.256	0.2823	0.0000

Table 5 – CO₂-brine relative permeability data for Calmar Fm. shale: a) primary drainage, and b) imbibition.

CO ₂ Saturation Fraction	Krg	Krw
0.185	0.0000828	0.0000000
0.176	0.0000723	0.0004951
0.167	0.0000626	0.0009903
0.157	0.0000537	0.0014890
0.148	0.0000457	0.0020040
0.139	0.0000384	0.0025800
0.130	0.0000320	0.0033210
0.120	0.0000262	0.0044350
0.111	0.0000212	0.0063010
0.102	0.0000168	0.0095470
0.093	0.0000131	0.0151600
0.083	0.0000099	0.0245900
0.074	0.0000073	0.0399400
0.065	0.0000051	0.0641000
0.056	0.0000034	0.1010000
0.046	0.0000022	0.1557000
0.037	0.0000012	0.2349000
0.028	0.0000006	0.3471000
0.019	0.0000002	0.5028000
0.009	0.0000001	0.7152000
0.000	0.0000000	1.0000000

Table 6 – Primary drainage CO₂-brine relative permeability data for the Muskeg Fm. anhydrite (permeability is too low to generate imbibition data for this rock type).

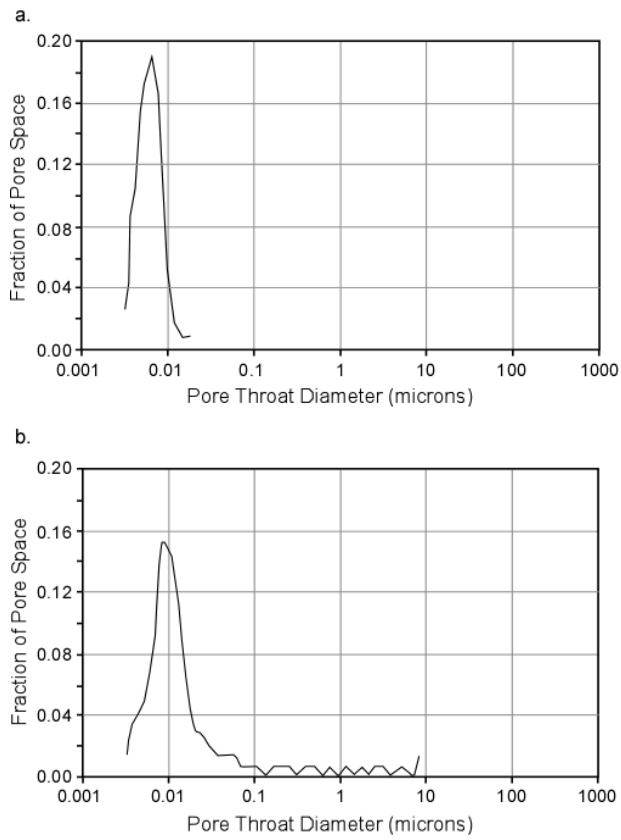


Figure 1 – Measured pore throat-size distribution for: a) Calmar Fm., and b) Colorado Gp. shale samples.

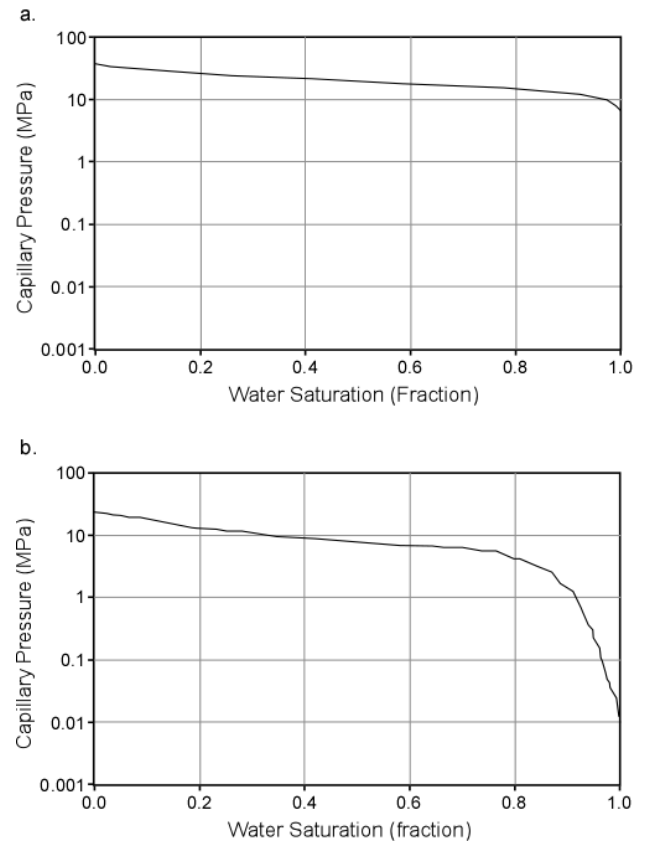


Figure 2 –CO₂-brine capillary pressure curves at reservoir conditions for a) Calmar Fm. and b) Colorado Gp. shales.

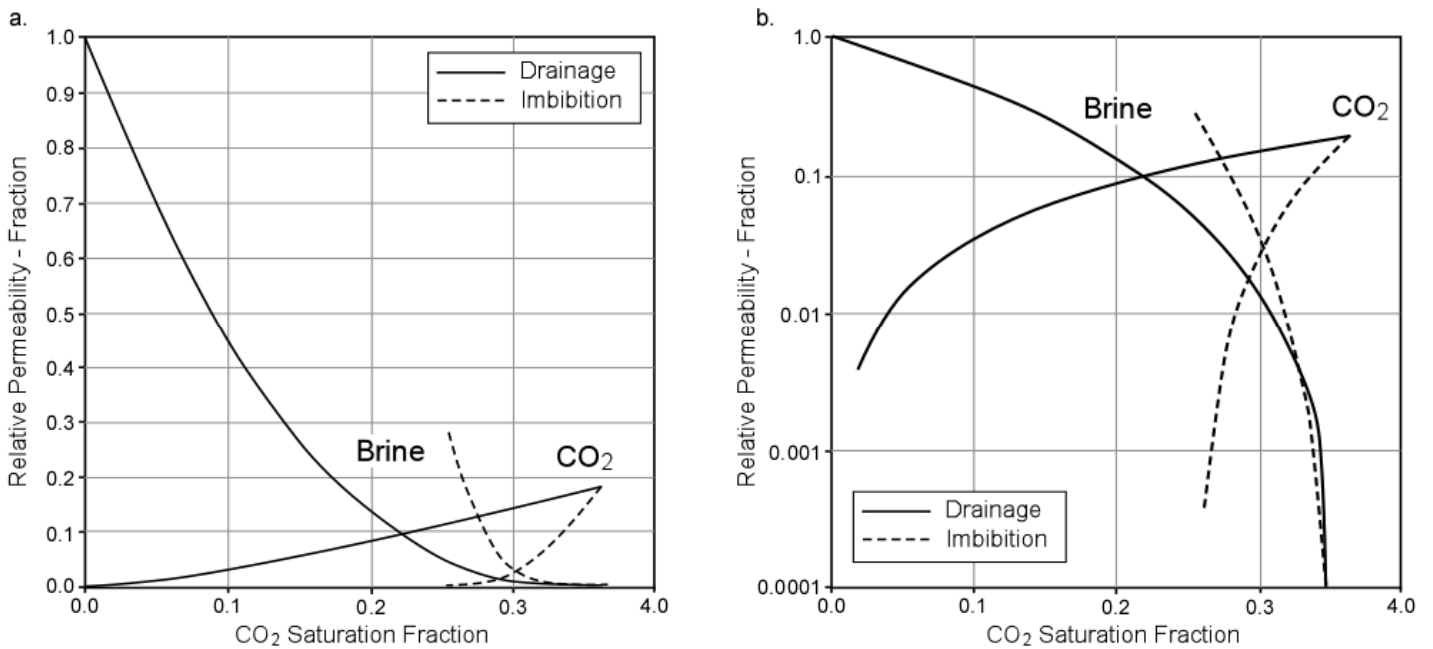


Figure 3 – Comparison of drainage and imbibition CO₂-brine relative permeability for Calmar Fm. shale in: a) Cartesian, and b), semi-log coordinates.

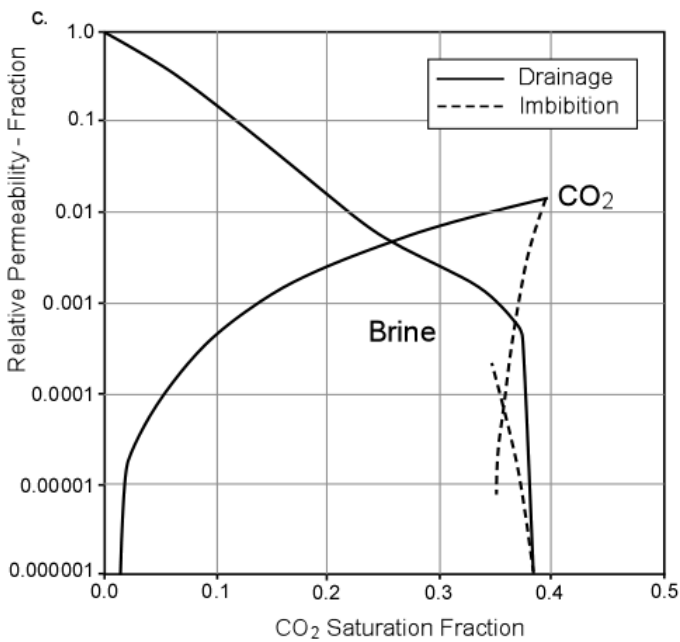


Figure 4 – Comparison of drainage and imbibition CO₂-brine relative permeability for Colorado Gp. shale, semi-log coordinates.

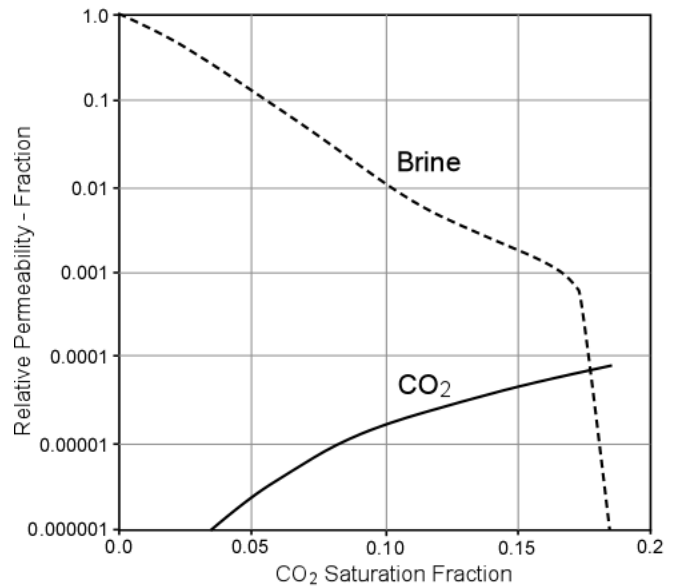


Figure 5 – Drainage CO₂-brine relative permeability for Muskeg Fm. anhydrite, semi-log coordinates.